



NMR Spectroscopic Investigations in Main Group Chemistry and In-Situ Illuminated Reaction Monitoring

Dissertation

Zur Erlangung des Doktorgrades der Naturwissenschaften

Dr. rer. nat.

an der Fakultät für Chemie und Pharmazie

der Universität Regensburg

vorgelegt von

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Februar 2025

Die vorliegende Dissertation beruht auf Arbeiten, die zwischen Mai 2021 und Februar 2025 am Arbeitskreis von Frau Professorin Dr. Ruth M. Gschwind am Institut für Organische Chemie der Universität Regensburg durchgeführt wurden.

Promotionsgesuch eingereicht am:	07. Februar 2025
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*Die Endlosigkeit des wissenschaftlichen Ringens sorgt unablässig dafür, dass dem
forschenden Menscheist seine beiden edelsten Antriebe erhalten bleiben und immer wieder
von neuem angefacht werden:
Die Begeisterung und die Ehrfurcht.*

Max Planck

Founder of Quantum Theory

NMR Spectroscopic Investigations in Main Group Chemistry and In-Situ Illuminated Reaction Monitoring

Franz F. Westermair

Table of Contents

1	Outline.....	1
2	Development of A High-Power, Laser Based Setup for in-situ Illuminated NMR-Spectroscopy.....	3
2.1	Abstract	4
2.2	Introduction	4
2.3	Results and Discussion.....	5
2.3.1	General Description.....	5
2.3.2	Design of the Setup	6
2.3.2.1	Diode Laser Housing, Collimation and Focusing to the Optical Fiber.....	6
2.3.2.2	Components Inside the Magnet: Illumination Head	7
2.3.2.3	Laser Controller to adjust Power Output and NMR-Spectrometer Control.....	9
2.3.3	NMR-Spectroscopic Investigations: Isomerization of 2,4-Dinitrobenzaldehyde with 450 nm in-situ illumination	10
2.4	Conclusion	11
2.5	Acknowledgements	12
2.6	Conflict of Interest	12
2.7	Supporting Information	12
2.7.1	NMR-Spectroscopic Investigations: Isomerization of 2,4-Dinitrobenzaldehyde with 450 nm in-situ illumination	12
2.7.1.1	NMR-Parameters	12
2.7.1.2	Determination of Illumination Intensity	12
2.7.2	Detailed Description of Illumination Setup.....	14
2.7.2.1	3D printing parameters	14
2.7.2.2	Preparation of NMRtorch Tubes.....	14
2.7.2.3	Laser module	15
2.7.2.4	Collimating Optics for Fiber Coupling (Part L)	15
2.7.2.5	Laser Housing.....	16
2.7.2.6	Illumination Head.....	17
2.7.2.7	Laser Controller.....	19
2.7.3	AVR-C code for the Laser Controller.....	21
2.8	References	23

3	Investigations on Diamino-Hydrido-cyclosilanes: Hydrogen Release Vs. N–Si Cleavage.....	27
3.1	Abstract	28
3.2	Introduction	29
3.3	Results and Discussion.....	31
3.3.1	Synthesis and Characterization of Diamino-hydrido-cyclosilanes 2 and 5	31
3.3.2	Reaction of 2 and 5 with HOSiPh ₃ in THF	32
3.3.3	Alternative Route to Si-chiral, Cyclic Diamino-Disiloxane 9.....	34
3.3.4	NMR Spectroscopic Investigations	35
3.3.4.1	¹ H and ²⁹ Si NMR Spectroscopic Investigation of 2 and HOSiPh ₃ at 180 K.....	35
3.3.4.2	Determination of the Activation Barrier for Pseudorotation between 10 and 11	37
3.3.4.3	Reaction Monitoring at 298 K	39
3.3.5	Quantum Chemical Investigations and Mechanistic Implications	42
3.4	Conclusions	43
3.5	Acknowledgements	43
3.6	Conflict of Interest	43
3.7	Supporting Information	44
3.7.1	General Considerations	44
3.7.2	Investigations by NMR-Spectroscopy.....	44
3.7.2.1	Activation Barriers from Chemical Exchange.....	44
3.7.3	Mechanistic Investigations with Density Functional Theory	44
3.7.3.1	Evaluation of the Method of Choice.....	45
3.7.3.2	DFT-Calculations of NMR Parameters for Starting Materials	47
3.7.3.3	DFT-Calculations of NMR Parameters of Pentacoordinate States	47
3.7.4	General Remarks for Syntheses	48
3.7.5	Synthetic Procedures	48
3.7.5.1	Synthesis of Compound 2.....	48
3.7.5.2	Synthesis of Compound 3.....	52
3.7.5.3	Synthesis of Compound 5.....	55
3.7.5.4	Synthesis of Compound 6.....	58
3.7.5.5	Synthesis of Compound 7.....	61
3.7.5.6	Synthesis of Compound 8.....	64
3.7.5.7	Synthesis of Compound 9.....	66

3.7.6	Single Crystal X-Ray Diffraction Analysis	69
3.7.6.1	XRD: Compound 1	72
3.7.6.2	XRD: Compound 2	73
3.7.6.3	XRD: Compound 3	74
3.7.6.4	XRD: Compound 6	75
3.7.6.5	XRD: Compound 7	76
3.7.6.6	XRD: Compound 9	77
3.7.7	Cartesian Coordinates of Optimized Structures	78
3.8	References	86
4	Unravelling White Phosphorus: Experimental and Computational Studies Reveal the Mechanisms of P ₄ Hydrostannylation	89
4.1	Abstract	90
4.2	Introduction	90
4.3	Results and Discussion	92
4.3.1	Computational Investigation	92
4.3.2	Experimental Study of Bulkier Hydrostannanes	99
4.3.3	Discussion and Analysis of Results	103
4.4	Conclusion	104
4.5	Acknowledgements	104
4.6	Conflict of Interest	104
4.7	References	104
4.8	Supporting Information	107
4.8.1	General experimental methods	107
4.8.2	Initial ³¹ P{ ¹ H}-NMR spectroscopic monitoring experiments	108
4.8.2.1	General methods for in situ measurements	108
4.8.2.2	AIBN-initiated hydrostannylation using Bu ₃ SnH	109
4.8.2.3	Light-initiated hydrostannylation using Bu ₃ SnH	111
4.8.2.4	Hydrostannylation using Ph ₃ SnH	113
4.8.3	Computational Investigations	114
4.8.3.1	General Methods	114
4.8.3.2	Radical hydrostannylation of P ₄	115
4.8.4	Investigation of bulkier Hydrostannanes	123

4.8.4.1	Synthesis and characterization of new hydrostannanes	123
4.8.4.2	$^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic monitoring experiments	131
4.8.4.3	Computational studies on NMR parameters of H/Sn substituted phosphines	154
4.8.5	Discussion of transition metal mediated P_4 functionalization	156
4.8.6	References for Supplementary Information	157
4.8.7	Cartesian Coordinates of Optimized Structures	159
4.8.7.1	Initiation	159
4.8.7.2	First P–P cleavage	160
4.8.7.3	Second P–P cleavage	163
4.8.7.4	Third P–P cleavage	167
4.8.7.5	Fourth P–P cleavage	173
4.8.7.6	Fifth P–P cleavage	175
4.8.7.7	Sixth P–P cleavage	178
4.8.7.8	Alternative P–P cleavage steps	178
4.8.7.9	Structures calculated for NMR prediction	181
5	Synthesis and Reactivity of an Iron–Tin Complex with Adjacent Stannylidene and Ferriostannylene Units	189
5.1	Abstract	190
5.2	Introduction	190
5.3	Results and Discussion	192
5.3.1	Synthesis and Characterization	192
5.3.2	Electronic Structure and Bonding	194
5.3.3	Reactivity Study	196
5.4	Conclusions	201
5.5	Acknowledgements	201
5.6	Conflict of Interest	201
5.7	Supporting Information	201
5.8	References	202
6	Transition-Metal-Stabilized Heavy Tetraphospholide Anions	207
6.1	Abstract	208
6.2	Introduction	208
6.3	Results and Discussion	209

6.4	Conclusion	216
6.5	Acknowledgements	217
6.6	Conflict of Interest	217
6.7	Supporting Information	217
6.7.1	General Considerations	217
6.7.2	[Co(η^4 -P ₂ C ₂ tBu ₂ SnAr')(η^4 -COD)] (2)	218
6.7.3	[Co(η^4 -P ₂ C ₂ tBu ₂ PbAr')(η^4 -COD)] (3)	221
6.8	References	223
7	[(K,Rb)@([2.2.2]crypt)] ₂ (K,Rb) ₄ [Si ₉ W(CO) ₄]·13.4 NH ₃ – The First Tungsten Functionalized Silicon Zintl Cluster	227
7.1	Abstract	228
7.2	Introduction	228
7.3	Results and Discussion	229
7.3.1	Crystal structure of [(K,Rb)@([2.2.2]crypt)] ₂ (K,Rb) ₄ [Si ₉ W(CO) ₄]·13.4 NH ₃	229
7.3.2	Chemical Bonding	231
7.3.3	NMR Spectroscopic Studies	233
7.4	Conclusions	233
7.5	Methods Section	233
7.6	Acknowledgements	235
7.7	Conflict of Interest	235
7.8	Supporting information	236
7.8.1	X-Ray Diffraction	236
7.8.2	Theoretical Calculations	239
7.8.3	NMR Investigations	242
7.9	References	245
8	Deeper Insight into Photopolymerization: The Synergy of Time-Resolved Nonuniform Sampling and Diffusion NMR	249
8.1	Abstract	250
8.2	Introduction	250
8.3	Experimental Section	252
8.3.1	UV Illumination Setup	252
8.3.2	Sample Synthesis and Preparation	252
8.3.3	NMR	253

8.3.3.1	Time-Resolved Diffusion NMR	253
8.3.4	Time-Resolved Nonuniform Sampling	253
8.3.5	Data Analysis	253
8.4	Results and Discussion.....	255
8.5	Conclusion	257
8.6	Acknowledgements	257
8.7	Supporting Information.....	258
8.8	References.....	258
9	Conclusion	261
10	Curriculum Vitae.....	265
11	Danksagung.....	267
12	Eidesstattliche Erklärung	269

1 OUTLINE

During the course of doctoral studies, valuable contributions to main group chemistry, involving the elements phosphorus, silicon, tin and lead, could be made via nuclear magnetic resonance (NMR) spectroscopy of the respective NMR-active nuclei. The findings could usually be corroborated by quantum chemical calculations of the NMR parameters of assumed species, compared with the experimental results. Furthermore, new promising approaches for in-situ illuminated NMR spectroscopy have been developed as well as methods for interpretation and data analysis of interleaved data acquisition. In this thesis, the current state of two unpublished proceedings (Chapter 2 and 3) are being presented, whereas the findings presented in Chapters 4–8 have been reported in peer-reviewed journals ($1 \times$ *Angew. Chem. Int. Ed.*, co-first authorship, $3 \times$ *J. Am. Chem. Soc. co-authorship*, $1 \times$ *Z. Anorg. Allg. Chem.* co-authorship). The results and discussion of each chapter are preceded by separate introductory sections to the respective topic in more detail, thus a short outline for each chapter is given here. Except of Chapter 2, all projects have been conducted in fruitful cooperations (see below).

Chapter 2 is a report on the current state of development of a low-cost fiber-based setup to perform in-situ illuminated NMR-spectroscopy. A high-power diode laser module is used instead of LEDs and the sample is illuminated via a sandblasted NMR tube rather than a sandblasted fiber end. The design, manufacturing and assembling processes of the setup for 450 nm illumination is fully described in this chapter, as well as promising initial performance tests to compare it with a currently used LED-NMR based setup.

In the next chapter (Chapter 3), I present and discuss the results of mechanistic investigations about the surprising, differing reactivity of two diamino-hydride-cyclosilanes via ^1H and ^{29}Si NMR spectroscopy and quantum chemical calculations. One silane reacts with triphenylsilanol in a formal substitution of Si–H by Si–OSiPh₃ under release of dihydrogen, while the other results in an addition product of the silanol with a cleaved Si–N bond. The results from ^1H and ^{29}Si VT-NMR and quantum chemical calculations conducted in the project suggest, that relative energies of anionic, pentacoordinate states are the key to explain these findings. The findings will soon be submitted to a peer-reviewed journal to become available to a broader audience.

In Chapter 4, the stepwise radical hydrostannylation of white phosphorus (P₄) has been investigated. Although it is a highly valuable reaction, a thorough mechanistic understanding of this transformation has remained elusive, hindering attempts to use this rare example of successful, direct P₄ functionalization as a model for further reaction development. Here, we were able to propose a deep and generalizable mechanistic picture for P₄ hydrostannylation by combining DFT (Density Functional Theory) calculations with in-situ ^{31}P NMR reaction monitoring and kinetic trapping of previously unobservable reaction intermediates using bulky tin hydrides. The results offer important insights into both how this reaction proceeds and why it is successful and provide implicit guidelines for future research in the field of P₄ activation.

In the next chapter, my contributions focused on the measurement and analysis of ^{119}Sn NMR parameters of iron–tin complexes, derived from $[\text{Fe}(\text{SnAr}')_2]$ ($\text{Ar}' = 2,6\text{-Dipp}_2\text{-C}_6\text{H}_3$, $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3$), which represents the first isolable neutral iron–stannylidyne complex featuring an Fe–Sn single– and Fe=Sn double bond. The multifaceted reactivity $[\text{Fe}(\text{SnAr}')_2]$ with main group nucleophiles, electrophiles, or transition metal complexes illustrates the behavior of the Fe and Sn sites in $[\text{Fe}(\text{SnAr}')_2]$, suggesting that complexes of this type are promising reagents for small molecule activation.

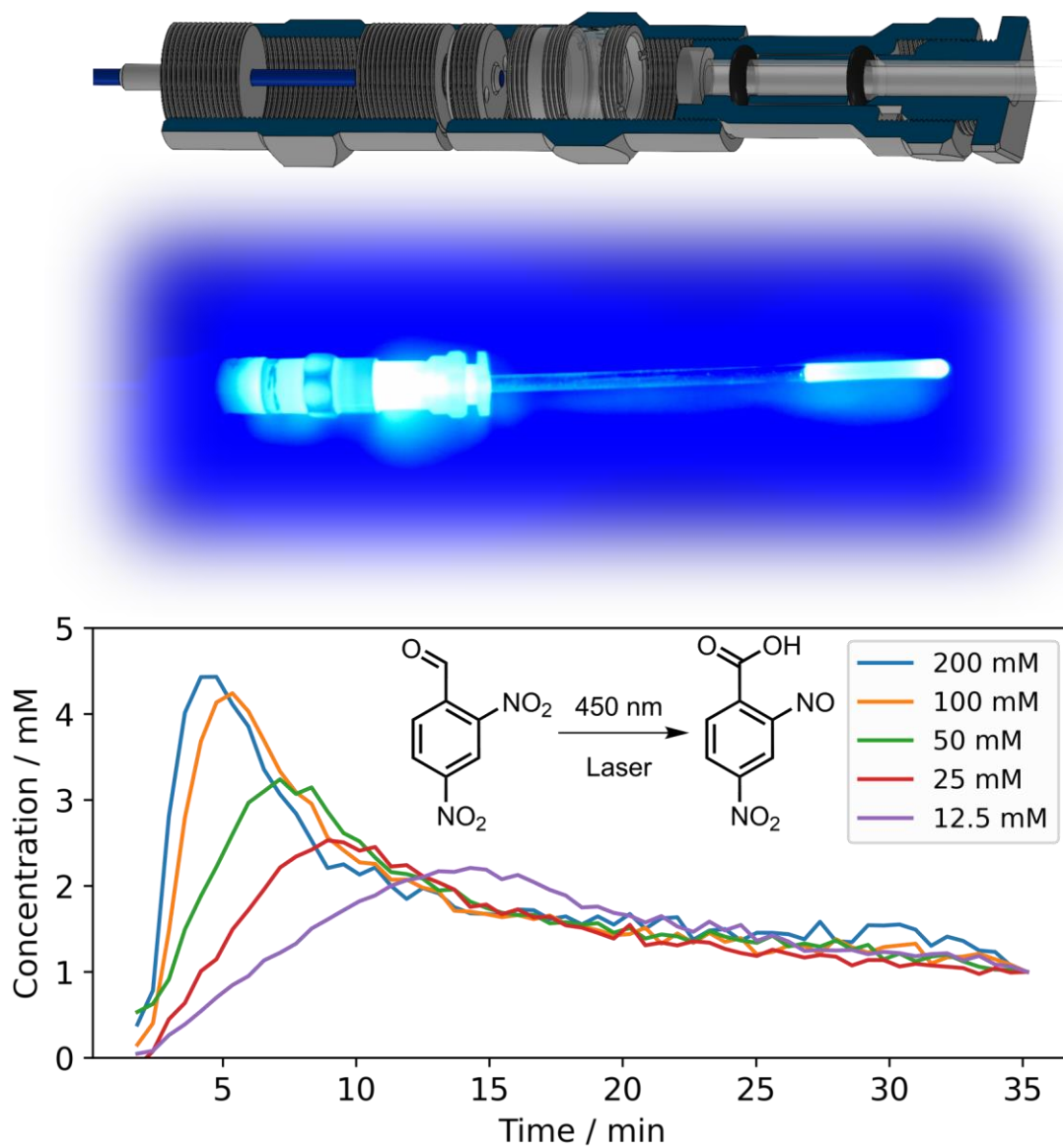
1 Outline

In the results presented in chapter 6, I could contribute to the rather tricky characterization of the two Co-centered complexes $[\text{Ar}'\text{TtCo}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)(\eta^4\text{-COD})]$ [$\text{Tt} = \text{Sn}, \text{Pb}$, $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-}\{\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2\}_2$, COD = cycloocta-1,5-diene], bearing a low-coordinate tin or lead ligand via measurement of ^{119}Sn and ^{207}Pb NMR spectra at -40° and room temperature.

Going back to silicon chemistry, I conducted ^1H and ^{29}Si NMR spectroscopic investigations in liquid ammonia (NH_3) to elucidate and characterize the solution behavior of the tungsten functionalized Zintl-anion $[\text{Si}_9\text{W}(\text{CO})_4]^-$ in chapter 7. The presence of this functionalized anion was suggested by the successful characterization of $[(\text{K,Rb})@([2.2.2]\text{crypt})]_2(\text{K,Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$, the first tungsten functionalized silicon Zintl cluster, via single crystal X-ray diffractometry. No ^{29}Si signal of the corresponding anion could be found so far, as the measurement conditions of such samples are highly challenging, solubilities are low and ^{29}Si is a rather insensitive nucleus for NMR. The investigations are ongoing and will eventually be rewarded with successful detection of the species.

Finally, the published results from a cooperation with Dr. Kristina Kristinaityte, group of Prof. Dr. Mateusz Urbańczyk (Polish Academy of Sciences, Warsaw, Poland) are presented. Here, the photopolymerization of *bis*(anthracen-9-ylmethyl)butane-1,4-diamine was investigated via in-situ illuminated NMR spectroscopy, employing time-resolved (TR) and interleaved NMR acquisition schemes. Following this project, the development of software tools for the analysis of TR acquired 2D and TR-DOSY (diffusion ordered spectroscopy) NMR data was the focus of a three-month research stay at the Polish Academy of Sciences, Warsaw, Poland, and will be published separately.

2 DEVELOPMENT OF A HIGH-POWER, LASER BASED SETUP FOR IN-SITU ILLUMINATED NMR-SPECTROSCOPY



Franz F. Westermair, Ruth M. Gschwind

Project ongoing

Franz Westermair designed, built, and evaluated the setup. Ruth Gschwind supervised the presented work.

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

2.1 Abstract

The current state of development of a low-cost fiber-based setup to perform in-situ illuminated NMR-spectroscopy is presented. A high-power diode laser module is used instead of LEDs and the sample is illuminated via a sandblasted NMR tube (NMRtorch tube) rather than a sandblasted fiber end. The design, manufacturing and assembling processes of the setup for 450 nm illumination is fully described herein, as well as promising initial performance tests to compare it with a currently used LED-NMR based setup.

2.2 Introduction

Photochemistry and photocatalysis are among the hot topics in current chemistry, because they enable otherwise very difficult reactions at mild and selective conditions.^[1,2] As the field is rapidly growing and gaining interest among a broader audience, the demand for explanatory tutorial reviews on understanding mechanisms of photochemistry and -catalysis is high, and has been satisfied.^[3,4] The current challenges in photocatalysis in a broader sense, as well as mechanistic investigations have been discussed recently in an excellent perspective article by Beil et al.^[5] One of the most valuable methods for mechanistic investigations in solution is nuclear magnetic resonance (NMR) spectroscopy, directly providing information about concentrations and structural information of dissolved species by routine techniques, but also about dynamic processes such as chemical exchange and aggregation. A comprehensive review on mechanistic investigations by NMR spectroscopy, including guides, general workflows and perspectives of emerging, modern methods has been published recently.^[6] In our endeavor to shine light on photochemical reaction mechanisms by NMR, we developed an easy-to-use LED-based setup for in-situ illuminated reaction monitoring of samples inside the magnet of the spectrometer in 2013.^[7] Methods for in-situ illumination have been reported before, but were usually highly sophisticated or tedious to use, thus difficult to rebuild by other researchers.^[8–11] Over the years, the term LED-NMR was established for the combination of in-situ sample illumination using LEDs and NMR spectroscopy, and many adaptations have been built by other researchers based on our concept.^[12–19] The topic of in-situ illuminated NMR spectroscopy has been reviewed by us in 2019.^[15] Since then, notable new practical approaches for in-situ illumination were reported. Paululat et al. modified an inverse probehead to directly include LEDs into the spectrometer, thus omitting optical fibers and the time-consuming sample preparation, with the tradeoff of removing the X-coil and gradient. This approach limits the functionality drastically, since only basic ¹H NMR pulse programs are available (Many 1D sequences use gradients for artefact suppression, but they are also the key to acquire DOSY, among many others).^[20] Following a similar concept, Bramham & Golovanov use LEDs directly in the NMR magnet, but instead of modifying the existing hardware, they developed a special illumination head which is connected to a sandblasted or etched heavy-walled NMR tube like a regular cap, again avoiding optical fibers and without requiring modifications to the spectrometer hardware. For their illumination device the authors coined the term “NMRtorch”.^[21,22] The LED-NMRtorch, as originally published, has meanwhile been successfully applied to organometallic photochemical reactivity studies of ruthenium complexes,^[23] assessment of the photostability of monoclonal antibodies,^[24] signal enhancement via photo-CIDNP (chemically induced dynamic nuclear polarization),^[25] reactivity studies on photocaged molecules^[26] and for EPR spectroscopy.^[27]

We report on the current state of a setup for in-situ illuminated NMR spectroscopy under development, using medium-walled, sandblasted NMRtorch tubes and a very low-cost, high-power laser as light source. To the best of our knowledge this work represents the first approach to combine all advantages of optical fibers for delivering

Laser Setup for in-situ Illuminated NMR Spectroscopy 2

light into the magnet and sandblasted NMR tubes. We are confident, that the ease of use, low-cost and detailed descriptions of the setup will serve as a valuable guide for other chemists interested in in-situ illuminated NMR spectroscopy.

2.3 Results and Discussion

2.3.1 General Description

The aim of the project was to investigate, whether the LED-NMRtorch setup reported by Bramham & Golovanov in 2022 with LEDs mounted directly on top of an ‘etched’ NMR tube inside the magnet for illumination, ^[22] would also be feasible using optical fibers and external light sources instead. All necessary components are either 3D printable (see Section 2.7.2.1) or commercially available.



Figure 2.1: Overview of the components of this illumination setup. a) Components outside the magnet: Arduino based control unit, power supply unit, laser module with additional fan and optics. b) Illumination head under operation: Sandblasted medium-walled, NMR-tube and optics on polished fiber end.

In the setup, sandblasted medium-walled NMR tubes were used for in-situ illumination. The sample tube is connected via a threaded sample holder to the flat polished end of a 1.5 mm optical fiber. Between sample and fiber end is a pair of lenses (see Sections 2.3.2.2 and 2.7.2.6) to transform the beam into a ring-shape for optimal coupling into the NMR tube.

As light source, a very affordable 10 W 450 nm (blue) diode laser is used in combination with a collimator package to facilitate optimal coupling of the laser beam into the glass fiber.

Finally, a simple and open-source controller was built to enable automatic control of the laser from the NMR spectrometer hardware in addition with allowing to adjust and monitor the output power. All components of the setup are depicted in Figure 2.1 for overview.

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

2.3.2 Design of the Setup

2.3.2.1 Diode Laser Housing, Collimation and Focusing to the Optical Fiber

For this setup, very low-cost fixed-focus 450 nm diode lasers with 10 W continuous optical output power were acquired from eBay (See also Section 2.7.2.3), prices range typically from 70 to 130 EUR (incl. VAT). These modules are frequently used for CNC-laser cutting or engraving of wood, metals, etc., and are already equipped with a cooling fan and electronics for PWM control (Pulse Width Modulation, 5 V) from external sources. Since the high power of the laser beam can cause severe damage (Class IV!), a housing for the module was designed and 3D-printed from white PETG (glycol-modified polyethylene terephthalate). This housing was found to withstand any stray light from the laser without degradation and prevent accidental exposure to the beam (Section 2.7.2.5). In addition, to enable efficient coupling into an optical fiber with SMA-connectorized end, a ready-bought collimation package was mounted in front of the module via optomechanical components of the Thorlabs, Inc. 30 mm cage system (see Section 2.7.2.4). Finally, an auxiliary 80 mm fan was included for better cooling of the laser module device during elongated illumination periods. Connectors for power supply for the laser module and control unit (black / red 4 mm laboratory connector) as well as for the 80 mm fan are included at the backside of the housing. The closed unit is depicted in Figure 2.1a, right side. a sectional view of a 3D model of the assembled unit is shown in Figure 2.2.

As 24 V power supply, a variable lab power supply unit (Korad KAP-3005) was used. This comes with the advantage of being able to monitor the current at all times.

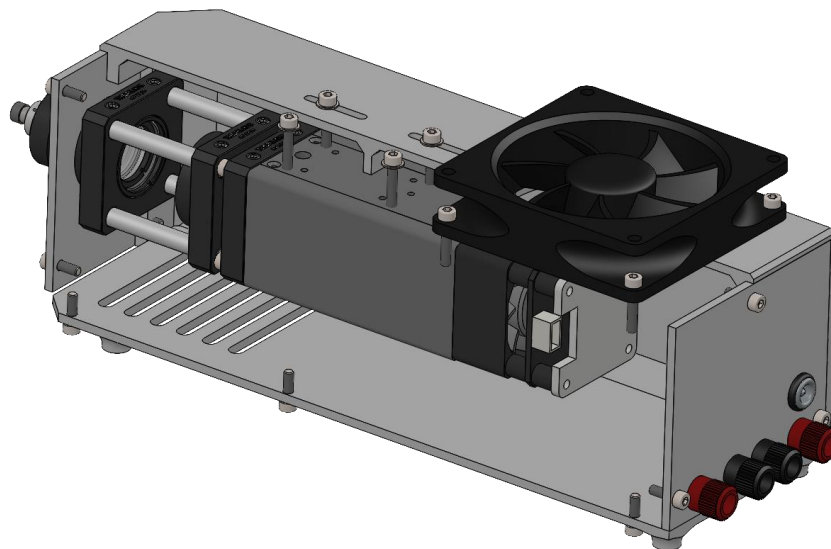


Figure 2.2: Sectional view of the CAD-construction of the laser housing Further details are given in Section 2.7.

2.3.2.2 Components Inside the Magnet: Illumination Head



Figure 2.3: Laser setup in use: the sample is connected to the end of the optical fiber with a specially designed, threaded sample cap (“illumination head”), then lowered into the magnet by hand as with other established in-situ illumination methods.

A key difference of this setup, in contrast to our previously reported one is, that sandblasted NMR tubes are used for sample illumination instead of the sandblasted end of an optical fiber.^[22] The light is guided from the end of a polished fiber end via multiple, modular components into the NMR tube (Figure 2.3). Bramham & Golovanov coined the term “NMRtorch tube” in their original work for hand-etched heavy-wall tubes, so we will also use it to highlight their invention.^[21,22] Likewise they call the LED assembly on top of the sample “illumination head”, thus we will use the same term for our assembly. It must be noted, that heavy-walled tubes were used in the original publication, but we use medium-walled tubes which result in approximate doubling of the active volume (360 μL vs 170 μL). Since such tubes are not commercially available, it was initially tried to manufacture them by grinding medium-walled NMR tubes with diamond files (dt. Feile) or sandpaper while rotating the tube via lathe or power drill. This simple and fast method does not yield good results and much higher quality tubes were obtained by professional sandblasting with corundum (Figure 2.4, see Section 2.7.2.2).

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

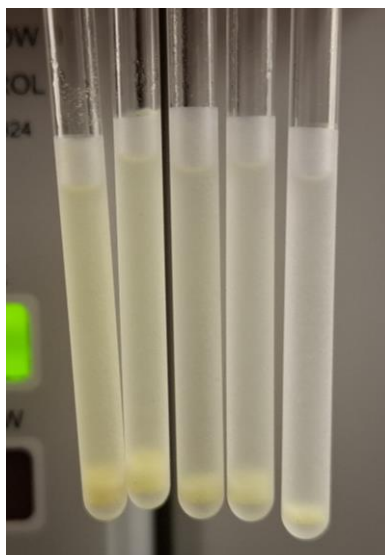


Figure 2.4: Medium-walled NMRtorch tubes used in the photochemical isomerization of DNBA, 2 days later. The etching of the glass is highly uniform across sample tubes, ensuring reproducible results.

The end of the fiber is polished as flat and clear as possible as in most classical applications of optical fibers to provide a clean output beam from the large diameter fiber. The divergent beam is collimated using a 3 mm plano convex lens and brought to a ring shape using an axicon with 20 ° deflection angle (Figure 2.5). Axicons are special lenses, which are planar on one side, and cone shaped on the other side. The transformation of a beam to a sharp ring requires good incident beam quality and exact concentric alignment of all optical components.

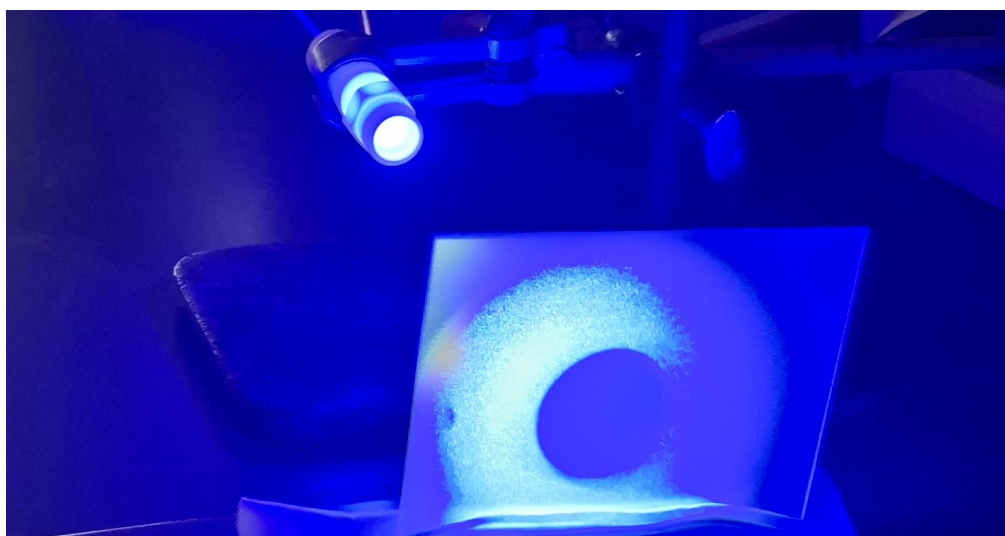


Figure 2.5: Ring of 450 nm light generated by optical elements between fiber end and NMRtorch tube, visualized by a diffuser at a distance of 30 cm. The unsymmetric intensity across the ring originates from very small axial misalignment of the axicon with the beam. Difficulties with alignment are addressed in Section 2.7.2.6.

The ring beam is then coupled into the NMRtorch tube, which itself is mounted to the assembly via a threaded connector. Since the presence of any metallic objects inside the magnet should be avoided, all parts of the assembly have been designed and 3D printed from either PLA (polylactic acid) when no chemical resistance was necessary or PP (polypropylene) for the sample tube holder as it may come into contact with chemical vapors. Indeed, after few iterations and redesigns the presented setup emerged. It was decided to use fine threads, compatible to the

Laser Setup for in-situ Illuminated NMR Spectroscopy 2

SM05 thread used encountered in optical devices. While 3D printing such fine threads (dt. Gewinde) comes with challenges in the manufacturing process, the compatibility enabled us to faster integrate and evaluate the feasibility of the design (Full Description see Section 2.7).

2.3.2.3 Laser Controller to adjust Power Output and NMR-Spectrometer Control

To properly operate the laser device, allow control from the NMR-spectrometer via pulse programs and add necessary safety features, a laser controller was designed and built. An Arduino Nano was chosen as suitable basis for the controller (see Section 2.7.2.7). While the predominant task of the controller is to generate the 5 V PWM-signal in order to enable the laser via a BNC-connector, it further allows to adjust the power in a range from 0–100% of the max output via a potentiometer. In accordance with laser safety requirements, the controller features a key-switch to prevent operation by unauthorized personnel. The status of the device is displayed by an LCD and by the backlit color of the power adjust knob, which will be blue when the laser is off, and red when on. A case for all components was designed and 3D-printed to yield a handy device that could be placed next to the spectrometer computer for convenient control by the user. (for a more detailed description see Section 2.7.2.7)

Except for the key switch, which is in series with the power input, all other components are controlled by software. The firmware for the controller was written in the AVR-C programming language and can be found in Section 2.7.3. Many publicly available projects based on Arduino use a heavily modified and abstracted version of C and a conscious decision was made to omit this and write the code in “pure” C. The implementation of the Arduino-style programming language comes with uncertainties and pitfalls when timing is critical as in our case.



Figure 2.6: Controller of the laser setup: left switch: enable /disable illumination; right switch: select source Spectrometer / manual, knob: adjust illumination power. The current state is written on an LCD.

While for manual switching of the laser, the exact timing is not critical, the opposite is the case if the light source is controlled via input of the NMR-spectrometer, where temporal precise illumination pulses are usually demanded (Note: The shortest possible pulse to be generated by our Avance III / Neo spectrometers is 2 cycles at 80 MHz / 25 ns). In our previously described LED-based setup,^[7] a simple transistor was used to switch illumination based on the voltage from the spectrometer output. In the NMR-controlled mode, the spectrometer output is being evaluated by the microcontroller and the illumination switched accordingly. The state of the input from the NMR

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

spectrometer is being read approximately every 500 ns (8 clock cycles at a clock frequency of 16 MHz) and as such more than sufficiently fast to switch regular LEDs or laser diodes. On the other hand the exact real delay in the built device has not been determined yet.

2.3.3 NMR-Spectroscopic Investigations: Isomerization of 2,4-Dinitrobenzaldehyde with 450 nm in-situ illumination



Figure 2.7: Photochemical intramolecular isomerization of 2,4-dinitrobenzaldehyde (DNBA) to 2-nitroso-4-nitrobenzoic acid.

For an initial test of the newly built setup, the photochemical intramolecular isomerization of 2,4-dinitrobenzaldehyde (DNBA) to 2-nitroso-4-nitrobenzoic acid in dichloromethane- d_2 at room temperature (Figure 2.7) was selected. The feasibility of this reaction to serve as NMR-actinometer was first described in detail by Reibarkh and coworkers in 2018.^[18] The advantage of DNBA instead of earlier reported actinometry with *ortho*-nitrobenzaldehyde is, that it can be used with wavelengths of 450 nm, thus serving a suitable model system for evaluation (see Section 2.7.1).^[28] While the original publication was focused on determining the quantum yield Φ_λ of a photoreaction, it can be likewise used to derive experimental illumination intensities from measured initial rate constants since all other parameters are predetermined (see Section 2.7.1.2). Samples with varying concentrations from 12.5 mM to 200 mM were monitored either with illumination via the new laser setup with NMRtorch tubes (Figure 2.8) or the familiar LED-based setup with a sandblasted fiber and coaxial insert under otherwise identical conditions (Figure 2.9). With the laser setup, a small initial temperature increase of 1 K was noted by the flow gas thermometer, which was regulated quickly down again to stable 298 K.

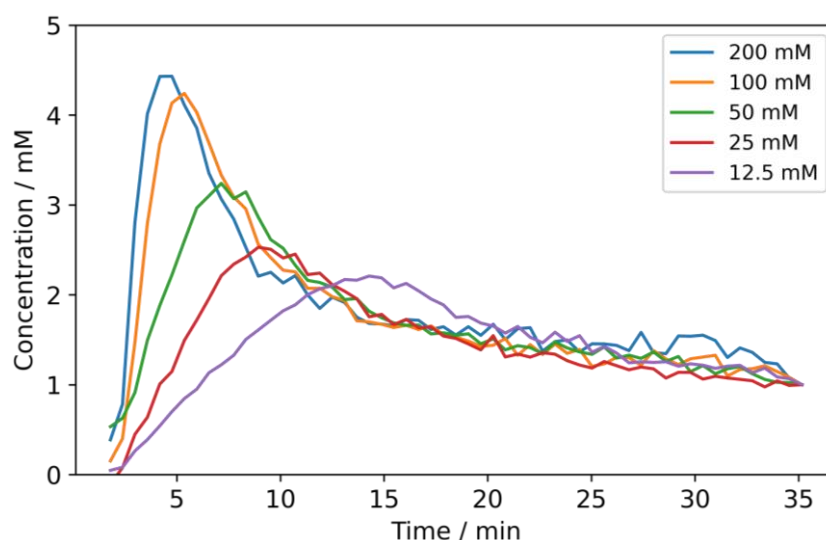


Figure 2.8: In-situ illuminated ^1H -NMR reaction monitoring of DNBA isomerization using the new 450 nm laser setup with NMRtorch tubes at varying initial DNBA concentrations. The sample was illuminated during all used datapoints with 100% power. The product concentration reaches a maximum before precipitating out of solution.

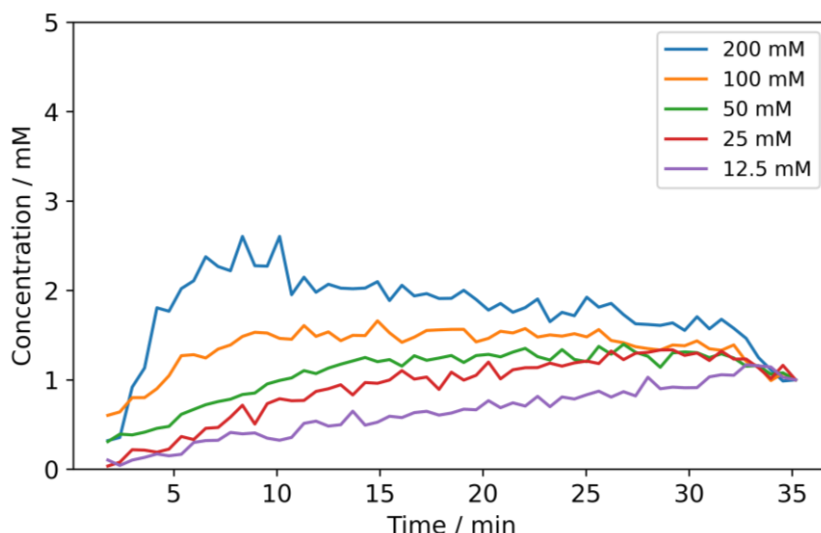


Figure 2.9: In-situ illuminated ^1H -NMR reaction monitoring of DNBA isomerization using a 1.5 mm sandblasted fiber with coaxial insert with 450 nm LED at varying initial DNBA concentrations. The sample was illuminated during all used datapoints. The product concentration reaches a maximum before precipitating out of solution.

The illumination intensity I_0 was calculated for each reaction monitoring from the initial, pseudo-zeroth order rate k_0 using an established scheme and previously reported values for the absorption coefficient ϵ and quantum yield Φ (see Section 2.7.1.2, Equation 3 and Table 2.1).^[18] A value of $(530 \pm 120) \mu\text{Einstein L}^{-1}\text{s}^{-1}$ was obtained for the reactions with the laser setup (Einstein is the common unit for a number of photons, simply 1 Einstein = 1 mol photons). In contrast, reactions with LED resulted in an average illumination intensity of only $(80 \pm 30) \mu\text{Einstein L}^{-1}\text{s}^{-1}$. More data and refinement are needed to determine I_0 with less deviations, but a six- to sevenfold increase of illumination intensity of the laser setup in comparison with our LED-NMR setup was on average achieved in this series of reaction monitorings (further discussion see Section 2.7.1.2). With their LED-NMR setup, Ji et al. reported an illumination intensity of $57 \mu\text{Einstein L}^{-1}\text{s}^{-1}$ for the same reaction.^[18] Bramham & Golovanov report an I_0 of $(438 \pm 21) \mu\text{Einstein L}^{-1}\text{s}^{-1}$ at 550 nm using a novel approach with the reversible diarylethene-based actinometer DAE (1,2,-bis(2,4-dimethyl-5-phenyl-3-thienyl) perfluorocyclopentene), thus only needing a single sample to determine the full curve.^[27,29–31]

As is discussed, more data is necessary to obtain reliable values, but the results of these initial series of measurements are highly promising, since a six- to sevenfold increase in illumination intensity I_0 was achieved by the herein presented setup in comparison to the established LED-NMR setup. Furthermore, the new setup is far from being fully optimized, thus a further increase by a factor of two or three should be achievable.

2.4 Conclusion

In conclusion, the current state of development of a new, low-cost laser-based setup for in-situ illuminated NMR spectroscopy is presented. The overall cost for all parts in the assembly is approximately 1000 EUR. On average, six- to sevenfold higher illumination intensities were observed in the photoisomerization of DNBA in dichloromethane, a known chemical actinometer, when compared to the established LED-based setup. As this project is not finished yet, it must be emphasized that more measurements are necessary. The focus will be put on optimizing the setup further and obtaining better data. We hope the device will prove to be valuable to the photo-NMR community, as its high illumination intensity should make previously not considered reactions feasible for

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

in-situ NMR-monitoring and mechanistic investigations. With the increasing availability of 3D printing, it should be easy for persons skilled in the art to rebuild our setup and use it for their own research or further improve it.

2.5 Acknowledgements

Franz F. Westermair gratefully acknowledges Thorlabs, Inc., for permission to use 3D-models of their parts for visualization, Dr. Willibald Stockerl for introduction to the topic and Markus Lindner, Head of the Glass-Blowing Workshop of the University of Regensburg for excellent preparation of sandblasted NMR tubes. Franz F. Westermair and Ruth M. Gschwind would like to thank the Deutsche Forschungsgemeinschaft for funding (DFG, RTG 2620 IonPairs in Reaction Project 426795949).

2.6 Conflict of Interest

The authors declare no conflict of interest.

2.7 Supporting Information

2.7.1 NMR-Spectroscopic Investigations: Isomerization of 2,4-Dinitrobenzaldehyde with 450 nm in-situ illumination

2.7.1.1 NMR-Parameters

¹H-NMR reaction monitoring with in-situ illumination has been carried out on a Bruker Avance III 400 MHz NMR spectrometer with a room temperature broadband observe probehead with z-gradient (X, ¹H) at 298 K at 298 K. Parameters were set in accordance with Ji et al.^[18] to: Pulse program zg0, flip angle $\pi/4$, relaxation delay d1 2.743 s, acquisition time aq 1.000 s, sweep width sw 20.025 ppm, center shift 6.175 ppm, number of complex FID points td 16024, number of transients ns 8; resulting in theoretical exactly 30 seconds per spectrum in the reaction monitoring. The real values from the measured raw data were used for analysis which show a time difference of 35–37 seconds. This extra inactive time is needed by the spectrometer to save a finished experiment and initiate the next measurement. Using the theoretical value will lead to overestimation errors of up to 20%, since the time axis will be squeezed, yielding higher rates k_0 . For the LED-NMR measurement, an OSRAM Oslon SSL 80 royal blue LED was used as light source, driven at 1000 mA in combination with a sandblasted 1500 μ m fiber and coaxial insert. 2,4-Dinitrobenzaldehyde (97%, Sigma Aldrich, used without further purification) and dichloromethane-d₂ (99.5 atom% D, Sigma Aldrich) from a fresh bottle were used to prepare the solutions for reaction monitoring in 1 mL volumetric flasks. The amount was exactly enough to prepare one sample for the laser setup measurement and a sample with LED-NMR illumination per flask.

2.7.1.2 Determination of Illumination Intensity

The light intensity I_0 of a light source, which is the number of photons absorbed by a sample, can be determined by measurement of initial rate constants k of a suitable photocatalyzed reaction using equation

$$-\frac{d[\text{Act}]}{dt} = I_0 \Phi_{\lambda} (1 - 10^{-\epsilon b [\text{Act}]}) \quad (1)$$

whereas $\frac{d}{dx}[\text{Act}]$ is the change of concentration of the actinometer with time, I_0 the light intensity, Φ_{λ} the quantum yield, ϵ the decadic molar absorption coefficient and b the path length of incident light.

Laser Setup for in-situ Illuminated NMR Spectroscopy 2

$\frac{d}{dx}[\text{Act}]$ can be substituted with the zeroth-order approximated initial rates k_0 at the beginning of reaction monitoring, thus:

$$k_0 = I_0 \Phi_\lambda (1 - 10^{-\epsilon b [\text{Act}]}) \quad (2)$$

Rearranging to solve for I_0 yields equation

$$I_0 = \frac{k_0}{\Phi_\lambda (1 - 10^{-\epsilon b [\text{Act}]})} \quad (3)$$

Ji et al. determined $\Phi_{440 \text{ nm}} = 0.077$ and $\epsilon_{440 \text{ nm}} = 2340 \text{ M}^{-1} \text{ m}^{-1}$, the same values were assumed for 450 nm in our calculations of I_0 , as UV-Vis measurements of 2,4-DNBA indicate an almost identical absorption coefficient.^[18] I_0 reflects the number of photons delivered to a sample per time unit and volume, thus is a suitable parameter to compare different approaches for in-situ illumination without the direct need of further assumptions on geometry or other factors. Higher I_0 reflect a generally brighter illumination of a sample and it is desired to achieve as high as possible I_0 values, i.e. to accelerate rates in in-situ NMR reaction monitoring, thus saving spectrometer time and better approximating “bench” conditions.

Initial rate constants k_0 were determined from the initial linear region of the reaction monitoring. In accordance with Bramham & Golovanov, the inner radius of the NMRtorch tube was used as the distance parameter b , 1.7 mm for the laser setup and 1.1 mm for the coaxial setup with LED (Discussion of choice for b , see below).^[18,22] All measured k_0 and derived I_0 are listed in Table 2.1. As noted in Section 2.3.3, more measurements and refinements are necessary in order to obtain reliable data, thus these measurements are termed “preliminary”.

Table 2.1: Initial rates k_0 , calculated intensities I_0 and deviations obtained at different concentrations of DNBA with either 450 nm laser setup or 450 nm LED-NMR.

Setup	[DNBA] / mM	k_0 / mM min ⁻¹	I_0 (eq. 3) / $\mu\text{mol L}^{-1} \text{s}^{-1}$	$\emptyset I_0$ / $\mu\text{mol L}^{-1} \text{s}^{-1}$	σI_0 / $\mu\text{mol L}^{-1} \text{s}^{-1}$
Laser setup	200	2.692	693.8		
	100	1.822	657.4		
	50	0.653	384.7		
	25	0.448	473.8		
	12.5	0.229	458.2	533.6	120.4
LED-NMR	200	0.489	126.0		
	100	0.147	53.2		
	50	0.073	43.0		
	25	0.081	85.8		
	12.5	0.044	87.0	79.2	29.3

For example, it is logical in the LED-NMR setup to assume the path length b as the liquid sample thickness (inner radius of the NMR tube minus outer radius of coaxial insert), since irradiation is going from the center of the sample towards outside, similar to a regular lamp and back reflection can be ignored. In NMRtorch tubes, the effective pathlength b_{eff} may be larger, since photons can in principle travel through the whole sample diameter, then be reflected back into the sample again and the geometry is not linear (as in a cuvette or similar). The

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

consequence would be a larger amount of photons being absorbed by the sample at equal illumination intensity and an equal value b , when NMRtorch tubes are used than with the NMR-LED approach. Experimentally, the exact values of ϵ and b are not important at the high concentrations limit, since the exponential Lambert-Beer term in Equation 3 will approach zero. Ji et al. and Bramham & Golovanov determined the extinction coefficient ϵ by fitting their data to Equation 2 with a set value for b . Mathematically, only the exponent ($\epsilon \cdot b$) is being obtained from the fit and ϵ is calculated by division with b . Bramham & Golovanov determined a value for ϵ in dichloromethane- d_2 by NMR actinometry (using the inner radius as b) which is circa 50% higher than the ϵ determined by UV-Vis in n -hexane / EtOH.^[22] If the correct ϵ would be assumed to be the same value for both measurements, it would mean that the effective pathlength b_{eff} is, in the NMRtorch case, also circa 50% larger than just the inner radius of the tube:

$$b_{eff} = \frac{p_{fit}}{\epsilon_{UV-Vis}} \quad (4)$$

Whereas p_{fit} resembles ($\epsilon \cdot b$) in the fit of Equation 2, ϵ_{UV-Vis} the accurately determined extinction coefficient and b_{eff} the effective illumination path. Again, for the determination of I_0 in the high concentration limit b and ϵ are not important. In our case, with the values for b and ϵ as stated above, the Lambert-Beer term in Equation 3 is 0.84 for the reaction at 200 mM, thus deviations of the obtained values for I_0 may be explained by this factor. Appropriate measurements at higher concentrations will resolve this uncertainty.

2.7.2 Detailed Description of Illumination Setup

2.7.2.1 3D printing parameters

All 3D printed parts have been manufactured on a Bambu Lab X1C printer, equipped with a 0.4 mm nozzle. The filaments used in the project were Geeetech PETG (polyethylene terephthalate with glycol modifier) Black / White for the laser housing and controller, BASF Ultrafuse PP (polypropylene) natural for parts potentially exposed to chemicals or Bambu Lab PLA (polylactic acid) Basic White for all other parts. High detail was achieved by adjusting the layer height to 80 μm and reducing printing speeds to 40 mm s^{-1} . All files and settings to reproduce the setup are available on the included CD.

CAD-models of parts were created using Dassault Systems SolidWorks 2022.

Permission for the use of 3D models for figures of parts from Thorlabs, Inc. was granted by Thorlabs, Inc. under a CC-BY license.

2.7.2.2 Preparation of NMRtorch Tubes

Medium-walled 7" borosilicate NMR tubes (Norell S-5-500-MW-7, wall thickness 0.8 mm) were covered with crepe tape except on the bottom 4 cm of the tube. Multiple tubes at once were then sandblasted in a sandblasting cabin using fine corundum. The open end of the NMR tubes was cut flat and polished with fine grit sandpaper on a rotary polishing machine. With this process it is possible to manufacture multiple NMRtorch tubes of reproducible quality very fast. The process can also be used to safely prepare medium-walled quartz tubes, which are much more expensive and more prone to breaking. To the best of our knowledge, no process of manufacturing NMRtorch tubes has been reported before.



Figure 2.10: In-house manufactured medium-walled NMRtorch tube.

2.7.2.3 Laser module

High power 450 nm diode laser modules for CNC-cutting or engraving are available from multiple vendors off eBay and usually shipped directly from China. The laser module used in this setup was advertised as “48 W Doppel-Lasermodul mit ultrafeinem komprimiertem Punkt 10W optische Leistung” by seller “creality-3d-flagship-store”, which is not active anymore as of writing this manuscript. The same or similar, compatible modules can be sourced from other vendors at a price of approximately 100 EUR.

The optical output power was determined to be 9.86 W at full power with a Thorlabs, Inc. PM100D optical power meter and Thorlabs, Inc. S425C thermopile power sensor.

2.7.2.4 Collimating Optics for Fiber Coupling (Part L)

In order to achieve efficient coupling of the laser beam (L.1) into our optical fibers (Thorlabs, Inc. FP1500URT 1500 μm with SMA connector) without need of tedious alignment procedures, a ready built 1" fiber collimation package with SMA connector (L.5, Thorlabs, Inc. F810SMA-405) was placed coaxial in front of the module using parts of the Thorlabs 30 mm cage system (see Figure 2.11). Fortunately, the laser module features 4 M3 taps in a square around the laser beam, which are close to the correct distance to fit the 30 mm cage system. Thus, one internally SM1-threaded cage plate (L.2, Thorlabs, Inc. CP33/M) was mounted to the module using DIN912 M3 $\times$ 16 screws and washers. Another cage plate was then connected via an externally SM1-threaded adapter (SM1T3), making the laser module fully compatible with the cage system. The correct distance between laser module and collimator was determined by setting the laser power to 10% and searching for the maximum output power through a short piece of connected 1500 μm fiber with the power sensor (see above).

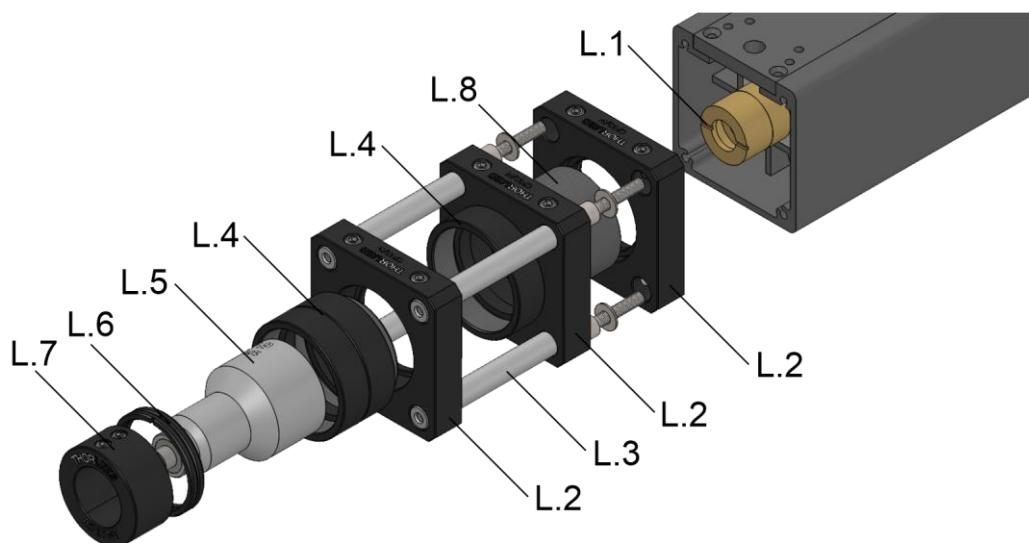


Figure 2.11: Part L, Collimating Optics. L.1: Fixed focus 450 nm diode laser module; L.2: SM1-threaded 30 mm cage plate, 0.35" thick (Thorlabs, Inc. CP33/M); L.3: cage assembly rod, 2" long, $\varnothing$ 6 mm (Thorlabs, Inc. ER2);

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

L.4: stackable SM1 lens tube, 0.30" thread depth (Thorlabs, Inc. SM1L03); L.5: 405 nm SMA collimation package, NA = 0.27, $f=33.9$ mm (Thorlabs, Inc. F810FC-405); L.6: SM1 retaining ring (Thorlabs, Inc. SM1RR); L.7: Ø1" unthreaded adapter for Ø15 m cylindrical components (Thorlabs, Inc. AD15NT); L.8: SM1 coupler, external threads, 0.25" long (Thorlabs, Inc. SM1T3).



Figure 2.12: Assembled collimation package mounted to a diode laser module.

2.7.2.5 Laser Housing

A fitting housing was designed for the laser module and connected optics to facilitate ease of use and prevent accidental exposure to the laser beam. For this, a model of the module was created in CAD from the physical part. The housing consists of four individual components, being a frontplate (Figure 2.13, H.4), backplate with connectors (H.2), bottom lid (H.3) and the main housing (H.1). The parts are assembled with DIN912 M3×10 screws, while the laser module with optics is connected to the main housing with four DIN912 M3×16 screws in slotted holes, thus allowing to fit laser modules of varying lengths into this housing. M3 threads were directly cut into the plastic, the use of brass inserts is advised for enhanced longevity. Four 4 mm lab cable connectors are included in the backplate for +24 V / GND power supply and +5 V / GND PWM input. An auxiliary 80 mm fan (H.5), mounted on top of the main housing part is powered via an additional 12 V power supply (5.5×2.1 mm plug, 12 V).

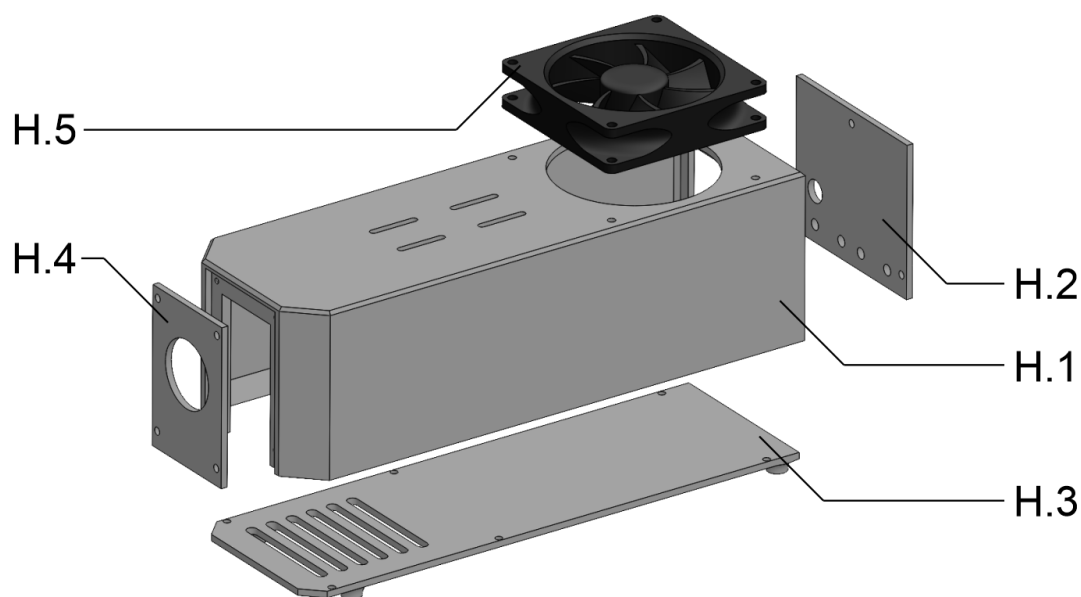


Figure 2.13: Part H, Laser Housing. H.1: main body; H.2: backplate with holes for connectors, H.3: bottom lid with air vents and feet; H.4: frontplate with 31 mm hole; H.5: 80 mm 12 V fan.



Figure 2.14: Assembled light source, consisting of the laser module, the fiber coupling optics, and connectors for power supply. Components L.2 were 3D printed in this case.

2.7.2.6 Illumination Head

The illumination head was completely 3D printed with a hardened steel nozzle to avoid incorporation of metals. All threads are compatible to the SM05-thread (0.535"-40 TPI) primarily used by Thorlabs, Inc., except for the connection of the fiber end to the optics, which are SMA-threads (1/4"-36 TPI).

Part A. Fiber Connector

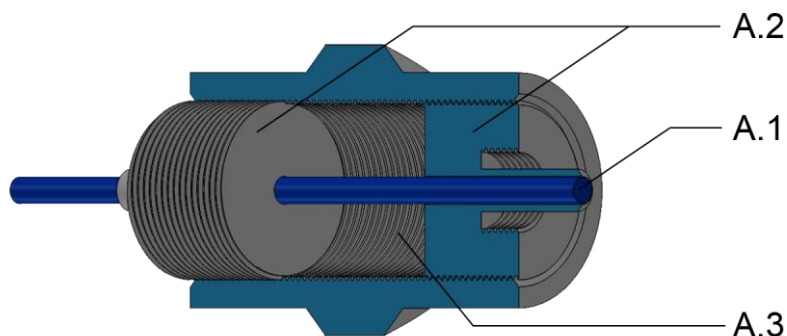


Figure 2.15: Sectional view of part A, Fiber Connector. A.1: 1500 μm high-OH fiber with coating; A.2: external SM05, internal SMA adapter; A.3: internally SM05 threaded tube, length 35 mm.

First, the externally SM-05 threaded connector parts (Figure 2.15, A.2) are to be screwed into the housing tube A.3. The 1500 μm fiber (A.1) is friction-locked to be kept in place as follows: As PP is a rather soft polymer, the fiber can be fit through part A.2 when it is heated in a glass drying oven (80 °C) for a few minutes or heat gun. When cooling down, the part will shrink, and the fiber end will be connected very tightly and strongly.

After the connection is made, the fiber end is cut to length with a ruby fiber scribe (Thorlabs, Inc. S90R) and polished flat by screwing A.2 into a polishing puck (Thorlabs, Inc. D50-SMA) with the internal SMA thread, using successively finer grained 600 grit sandpaper, 5 μm silicon carbide, 3 μm aluminium oxide, 1 μm silicon oxide and 0.3 μm calcined alumina sheets (Thorlabs, Inc. LF5P, LF3P, LF1P, LF03P) on a glass plate. The quality of the polish was finally inspected with a fiber scope (Thorlabs, Inc. FS201). It is critical, that a properly polished fiber end is used. To the best of our knowledge, fully metal-free 1500 μm optical fiber connectors with SMA thread are not commercially available, although the metals incorporated are generally not ferromagnetic. An objective

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

advantage to commercially available fiber connectors is, though, that mating the fiber with the connector is achieved without the need of sometimes difficult to handle epoxy glue.

Part B. Optics for Ring Generation

The internally SM05-threaded optics tube (Figure 2.16, B.1) houses a 3 mm plano-convex lens ($f = 9$ mm, B.3/B.4, Thorlabs, Inc. LA4039) for collimation of the outgoing laser beam and a 0.5" axicon (deflection angle = 20° , B.2, Thorlabs, Inc. AX1220) to convert the beam into a ring shape. The optics are kept in place by compatible threaded retaining rings (B.6, either Thorlabs SM05PRR, or compatible, thicker, 3D printed rings). A drawback of the closed system is, that it is difficult to adjust the distances of the optics and many trials had to be made to achieve acceptable results. Thus, in the next iteration the optics housing tube will be made of two halves for easy and fast adjustment. Part B is connected to part A via B.5, a threaded adapter with SMA as well as SM05 external thread.

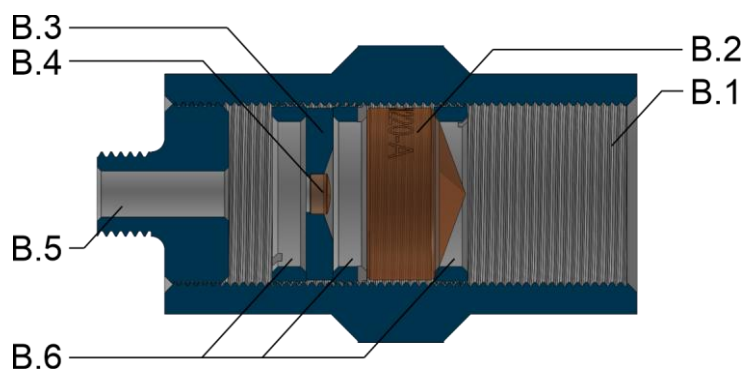


Figure 2.16: Sectional view of part B, Optics for Ring Generation. B.1: internally SM05 threaded tube; B.2: 20° 0.5" Axicon (Thorlabs, Inc. AX1220); B.3: 0.5" disc to hold lens B.4; B.4: 3 mm plano convex lens, $f = 9.0$ mm (Thorlabs, Inc. LA4039); B.5: Thread adapter, external SM05, external SMA; B.6: retaining rings with external SM05 thread.

Part C. Sample Holder / Cap

The main sample holder part (Figure 2.17, C.2) is again fitted with an external SM05-thread, which is screwed into the bottom part of the optics housing (B.1). NMRtorch tubes (C.4) are inserted from the bottom of the sample holder and locked by screwing the bottom screw (C.1) tightly. By rotation of the bottom screw, two silicone O-gaskets (C.6) are getting compressed by the screw (C.1) and a short cylinder (C.3), reversibly around the NMRtorch tube, thus holding it concentrically in place. Together with a tight-fit, epoxied glass window (C.5) on top of the sample holder, it should be gastight and allow to prepare samples under an inert atmosphere e.g. via glovebox techniques. Initial tests with DCM revealed, that the sample holder printed from PP is not very air-tight directly. A feature of many 3D prints that are microporous, inherently by the printing process. Thus, it may be advised to traditionally machine the sample holder from the full material by means of a lathe or consider other resistant materials which are easier to print than PP, such as PA (polyamide), PET (polyethylene terephthalate) with or without carbon fiber reinforcement. Alternatively one could try to seal the surface by sealant coatings, such as Dichtol AM.

Laser Setup for in-situ Illuminated NMR Spectroscopy 2

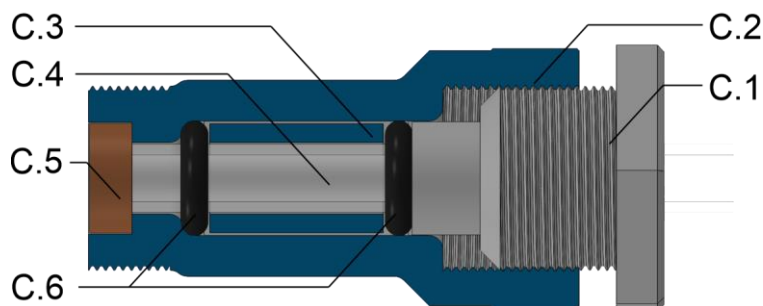


Figure 2.17: Sectional View of part C, Sample Holder. C.1: locking screw, external SM05 ; C.2: main sample holder body, internal and external SM05; C.3: barrel / cylinder; C.4: NMRtorch tube; C.5: glass window; C.6: silicone O-ring gaskets.

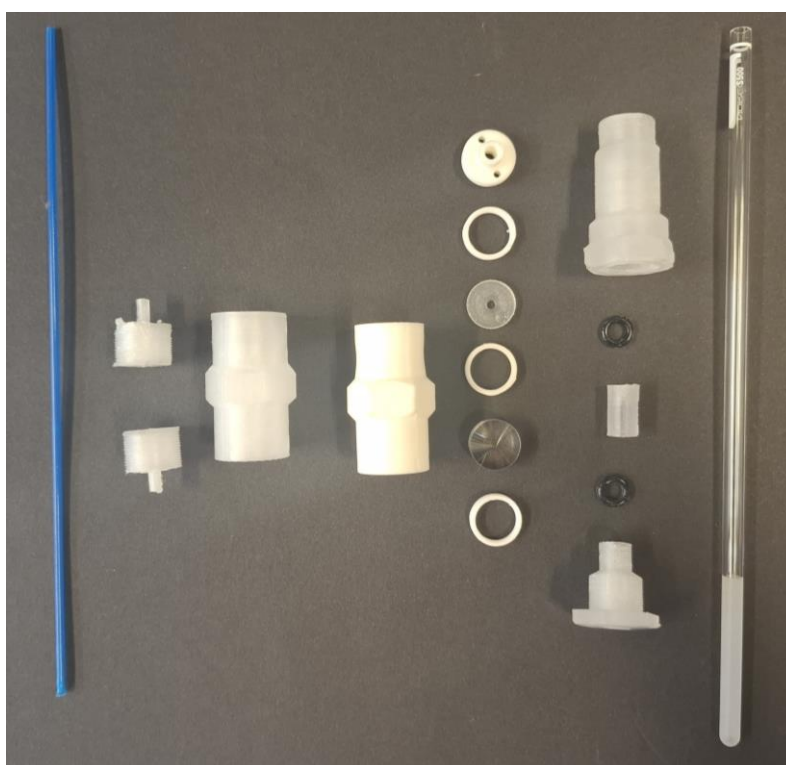


Figure 2.18: All required parts required to build an illumination head for the new laser setup.

2.7.2.7 Laser Controller

The PWM signal to switch the laser module was generated by a self-designed and programmed controller, which can be rebuilt from provided schematics for less than 100 EUR.

It is based on an Arduino Nano v3 microcontroller board (with Microchip Technology ATmega 328P microcontroller, formerly Atmel), a platform which is extensively used in all sciences for fast development of sensors, data logging, prototyping, teaching, and many more.^[32–36] Even in NMR-spectroscopy, the use of Arduino controlled devices is reported in literature, from small uses up to being the basis for complete spectrometers:

An accurate and low-cost automatic tune-and-match system termed “ArduiTam” was reported by Korvink and coworkers.^[37] The low-cost NMRduino project is aimed at open-source low-field NMR applications to make NMR accessible to a broader audience and inspire users towards new applications of nuclear magnetic

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

resonance.^[38] A full NMR-console, controlled by an Arduino Due was reported by Yubonmhat et al.^[39] and other means of low-cost NMR applications, often relying on Arduino or other open-source hardware have been discussed.^[16]

The controller can be powered either by an external 12 V power supply or via USB. The external power supply is in series with a key-switch to prevent operation of the laser module by untrained persons. Another safety measure included in the software is, that the controller checks if the power output would be on when powered up and prompts the user to switch the output off first, thus preventing accidental exposure when setting up experiments. Having the USB port accessible in the assembled state allows to quickly update the software, e.g., adding a functionality to control the laser via the spectrometer software directly (not via the console). PWM is generated by hardware using the integrated 16-bit timer in fast-PWM mode operating at ~2 kHz and available on a BNC-connector. When the output is disabled, the output power percentage can be adjusted with the central knob precisely between 0 and 100%. In contrast, the value can not be adjusted when in the “on” state, to prevent accidental change during an experiment. The light source can be switched either by hand or from the NMR spectrometer console. An LCD (HD44780 1602 with I2C interface controller) is used to accurately display the currently set output power and operating mode of the controller.

A schematic drawing of the laser controller is shown in Figure 2.19.

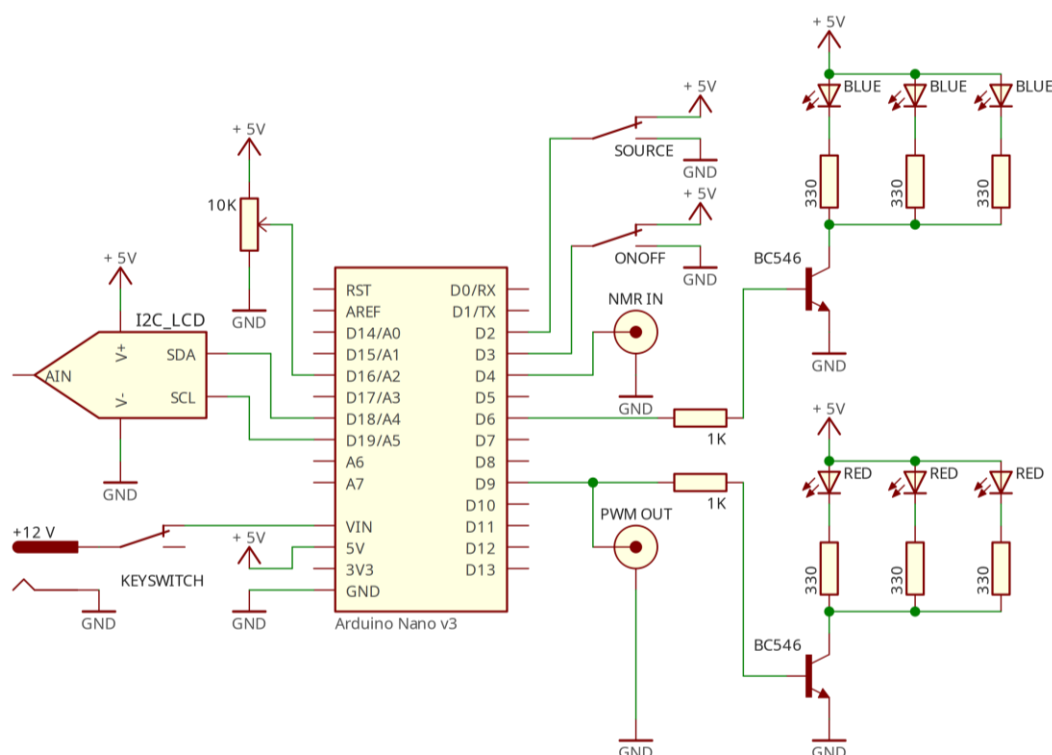


Figure 2.19: Schematic of the circuit for the laser controller with Arduino Nano v3. The schematic was made with LibrePCB 1.2.0.

A simple housing for all electrical components was printed from black PETG (Figure 2.20). All screws are DIN912 M3×16.

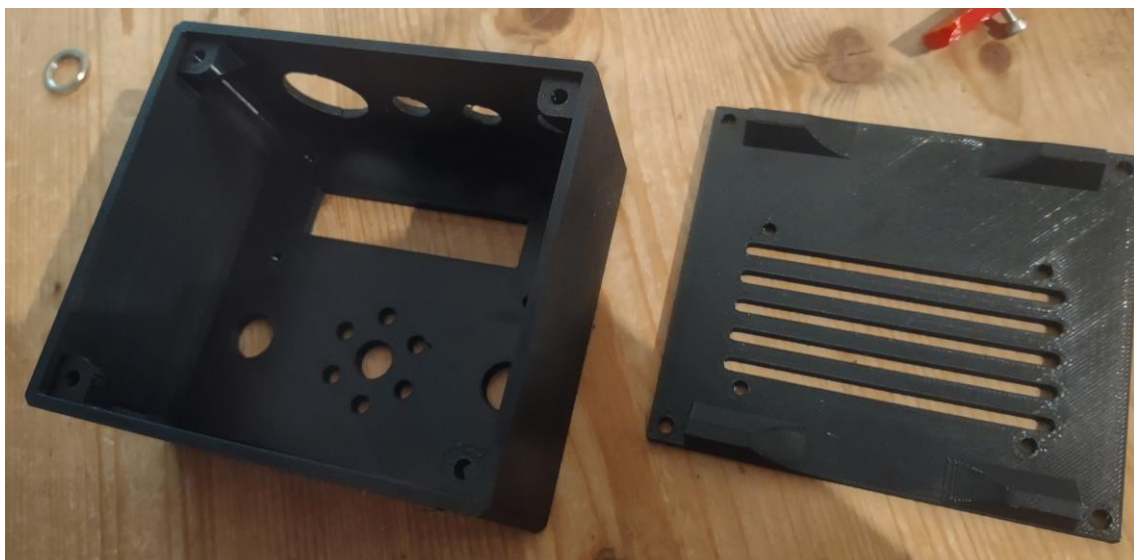


Figure 2.20: Case for the laser controller before assembly.

2.7.3 AVR-C code for the Laser Controller

The firmware was written using Microchip Technology, Inc. Microchip Studio 7.0.2594 for 5 V Arduino Nano v3 boards. It should be directly compatible to all other 5 V Arduino boards with a Microchip Technology 8-bit ATmega328(p) microcontroller (e. g. Arduino Uno rev3).

The firmware was flashed with AVRDUDE 5.10. Many Arduino Nano clones still use an older version of the bootloader, running at 57600 baud instead of 115200 baud. This is often the origin why flashing would not work on first try .The program uses modified libraries based on Peter Fleury's i2cmaster.h, lcd.h and uart.h AVR-C libraries for control of the I2C-LCD.

```

/*
FWest  AVR-C (ATMEGA 328P)    24.09.2024
laser_controller_final

A device which generates 5V PWM signals to control a high power laser
for in-situ illuminated NMR-Spectroscopy

The laser can be switched on and off manually,
or controlled automatically via a TTL signal from the spectrometer
that is ACTIVE LOW (0V = Laser On)

An I2C LCD Display is used to provide Infos about the power setting.
*/

// Defines

#define SOURCE PIND2    // Pin of Source switch / Input Pullup
#define ONOFF  PIND3    // Pin of On/Off Switch      0 = Manual      1= Spectrometer (ACTIVE LOW) //Input Pullup
#define NMRIN  PIND4    // Pin for BNC Connector from spectrometer / Input
#define LEDOUT PIND6    // Pin for LEDS / Output for visuals
#define TTLOUT PINB1    // Pin for BNC Connector to Laser / Output
#define POTI   PINC2    // Pin for Potentiometer / Analog Input

#define PWM_OFF DDRB &= ~(1<<TTLOUT) // Turn On Laser Output
#define PWM_ON  DDRB |= (1<<TTLOUT)   // Turn Off Laser Output

#define LED_OFF DDRD &= ~(1<<LEDOUT)  // Turn On Visual LEDS (Blue)
#define LED_ON  DDRD |= (1<<LEDOUT)   // Turn Off Visual LEDS

#define F_CPU 16000000 // CPU clock in Hz
// Includes
#include <stdio.h>
#include <stdlib.h>
#include <stdint.h>
#include <stdbool.h>
#include <avr/io.h>
#include <avr/interrupt.h>
#include <avr/pgmspace.h>

```

2 Laser Setup for in-situ Illuminated NMR Spectroscopy

```
#include <util/delay.h>

#include "uartATM328.h"
#include "i2cmaster.h"
#include "i2clcd.h"

// Global variables
uint8_t u8_current_state;
uint8_t u8_locked;
uint16_t u16_poti;
char buffer[16];

/*
ISR (TIMER0_COMPA_vect)
{
    u8Timer0TickCounter++;
}*/

void timer0_init()          // Timer0: Used for decorative blue LEDs when Light is Off 244 Hz
{
    //TIMSK0 = (1<<OCIE0A);
    OCR0A = 0;
    TCCR0A = (1<<COM0A1) | (1<<WGM01) | (1<<WGM00);    // Fast PWM Mode
    TCCR0B = (1<<CS02); // Prescaler 256                //
}

void timer1_init()          // Timer1: Fast PWM with 2 kHz for Laser PWM.
{
    ICR1 = 1000;
    OCR1A = 0;
    TCCR1A = (1 << COM1A1) | (1<<WGM11) | (0<<WGM10);
    TCCR1B = (1<<WGM13) | (1<<WGM12) | (0<<CS12) | (1<<CS11) | (0<<CS10); // 100=prescaler 256 011=prescaler 64
    //010=prescaler 8
}

void adc_init()
{
    ADMUX = (1 << REFS0) | (1<<ADLAR);
    ADCSRA = (1<<ADEN) | (1 << ADPS2) | (1 << ADPS1) | (1 << ADPS0);
}

uint8_t read_adc(uint8_t pin) // ADC read function, accepts Pins C0 to C3 (C4 and C5 are for I2C)
{
    switch(pin)
    {
        case 0: ADMUX = (1 << REFS0) | (1<<ADLAR); break;
        case 1: ADMUX = (1 << REFS0) | (1<<ADLAR) | (1<<MUX0); break;
        case 2: ADMUX = (1 << REFS0) | (1<<ADLAR) | (1<<MUX1); break;
        case 3: ADMUX = (1 << REFS0) | (1<<ADLAR) | (1<<MUX1) | (1<<MUX0); break;
    }
    ADCSRA |= (1<<ADSC);
    while(ADCSRA & (1<<ADSC))
    {
    }
    return ADCH;
}

int main(void)
{
    // Initiation sequence
    i2c_init();
    lcd_init();
    adc_init();
    timer1_init();
    timer0_init();

    // Printing some "bootup" message
    LED_ON;
    lcd_command(LCD_DISPLAYON | LCD_CURSOROFF | LCD_BLINKINGOFF);
    lcd_light(1);
    lcd_command(LCD_CLEAR);
    _delay_ms(2);
    lcd_printlc_P(1,1, PSTR("FWest 2024"));
    lcd_printlc_P(2,1, PSTR("AK Gschwind"));
    _delay_ms(1000);
    lcd_command(LCD_CLEAR);
    _delay_ms(2);
    lcd_printlc_P(1,1, PSTR("High Power 24V"));
    lcd_printlc_P(2,1, PSTR("Laser-Controller"));
    _delay_ms(1000);
    lcd_command(LCD_CLEAR);
    _delay_ms(20);

    // Initializing Ports
```



```

PORTD |= (1 << SOURCE) | (1 << ONOFF); // Activating Pullups
sei();

//Safety Check If Laser is switched on, switch off before continuing
do
{
    lcd_printlc_P(1,1, PSTR("Set to OFF!"));
    _delay_ms(100);
    //Lcd_command(LCD_CLEAR);
    //_delay_ms(2);
} while (PIND & (1 << ONOFF));
lcd_command(LCD_CLEAR);
_delay_ms(2);

while (1)
{
    u8_current_state = u8_locked;
    if (!(PIND & (1 << ONOFF))) // Power is Off Source does not Matter
    {
        if ((DDRB & (1 << TTL0UT))) {PWM_OFF;} // If power is on, switch it off
        u16_poti = (((uint16_t)read_adc(POTI))*4)/10; // Check poti value, we use C2 pin because C0 is broken on
this board
        if (u16_poti > 100) {u16_poti = 100;} // Happens sometimes to be above 100
        OCR1A = u16_poti*10; // Set the Laser output timer (shown in % but internally is
1/1000 increment.
        OCR0A = (uint8_t)(u16_poti*10 / 4); // Set the decorative blue LED timer value
        LED_ON;
        u8_locked = 0;

        // Display printing etc.
        lcd_printlc_P(1,1, PSTR("POWER: "));
        itoa(u16_poti, buffer, 10);
        lcd_gotohc(1,8);
        if (u16_poti < 10)
        {
            lcd_print_P(PSTR(" "));
        }
        else if (u16_poti<100)
        {
            lcd_print_P(PSTR(" "));
        }
        lcd_print(buffer);
        lcd_print_P(PSTR("%"));
        if ((u8_locked != u8_current_state) && (u8_locked==0))
        {
            lcd_printlc_P(1,13, PSTR(" "));
        }
        lcd_printlc_P(2,1, PSTR("SOURCE: "));
        if (!(PIND & (1 << SOURCE))) {lcd_print_P(PSTR("MANUAL"));}
        else {lcd_print_P(PSTR("NMR "));}
    }
    else if ((PIND & (1 << SOURCE))) // NMR Spectrometer Control On and Power On
    {
        LED_OFF;
        if (!(PIND & (1 << NMRIN))) {PWM_ON;} //Spectrometer is LOW (Active Low)
        else {PWM_OFF;} //Spectrometer is 5V
        u8_locked = 1;
    }
    else if (!(PIND & (1 << SOURCE))) // Manual Control and Power On
    {
        PWM_ON;
        LED_OFF;
        u8_locked = 1;
    }
    if ((u8_locked != u8_current_state) && (u8_locked==1))
    {
        lcd_printlc_P(1,13, PSTR("LOCK"));
        _delay_ms(2);
    }
}
}

```

2.8 References

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2 Laser Setup for in-situ Illuminated NMR Spectroscopy

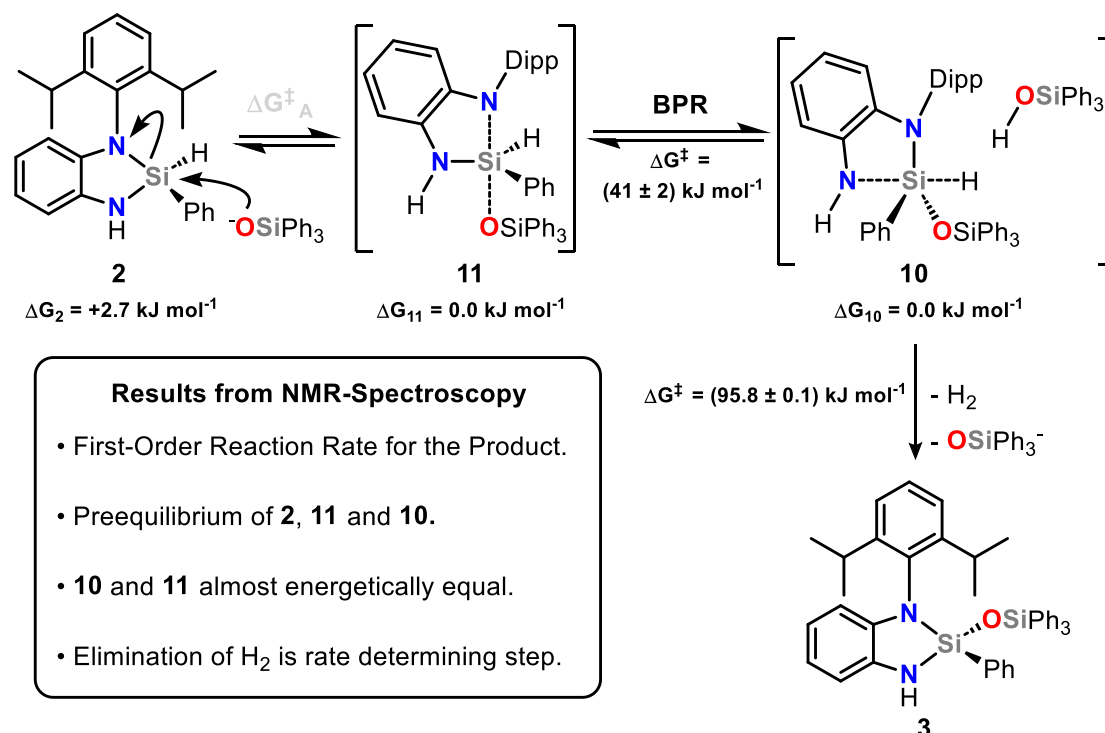
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Laser Setup for in-situ Illuminated NMR Spectroscopy 2

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2 Laser Setup for in-situ Illuminated NMR Spectroscopy

3 INVESTIGATIONS ON DIAMINO-HYDRIDO-CYCLOSILANES: HYDROGEN RELEASE VS. N–SI CLEAVAGE



Franz F. Westermair, Manuel Kümper, Tobias Götz, Ruth M. Gschwind,* Jonathan O. Bauer*

Manuscript in preparation

Franz F. Westermair performed VT-NMR and reaction monitorings, conducted and interpreted quantum chemical calculations to investigate and propose a mechanism for the reactivity of the compounds described herein. Manuel Kümper and Tobias Götz carried out synthesis and characterization of all compounds. This chapter was written by Franz F. Westermair with XRD data and experimental procedures provided by Manuel Kümper and Tobias Götz. The project was overseen by Jonathan O. Bauer and Ruth M. Gschwind.

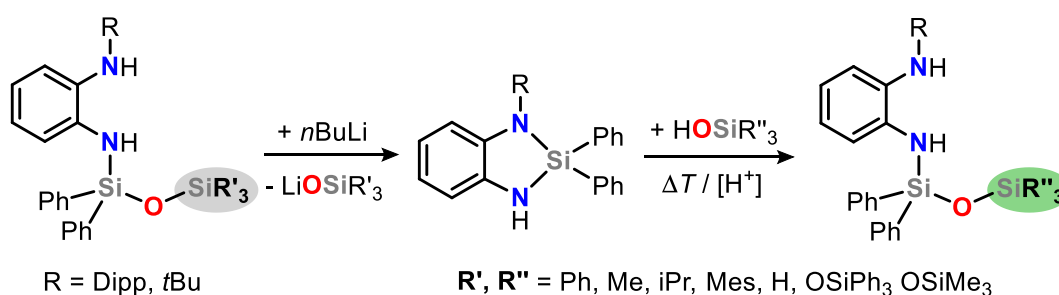
3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.1 Abstract

Two Si-chiral diamino-hydrido-cyclosilanes with either *N*-Dipp-*N'*-H (**2**, Dipp = 2,6-di-*iso*-propylphenyl) or *N*-*t*Bu-*N'*-H (**5**, *t*Bu = *tert*-butyl) substituents have been synthesized and characterized. In the reaction of **2** with triphenylsilanol (HOSiPh₃) in tetrahydrofuran (THF), another diamino-hydridocyclosilane (**3**) with formal substitution of Si-H by Si-OSiPh₃ and evolution of dihydrogen (H₂) are observed as only products without catalyst above -10 °C. **3** was obtained with 73% yield by this method.

In contrast, under the same conditions with silane **5**, no spontaneous H₂ evolution is observed. Instead, the symmetric heptaphenyl-trisiloxane **6** (SiHPh(OSiPh₃)₂, 20%) was isolated along with the free diaminoligand **4**. Mechanistic investigations by ¹H and ²⁹Si VT-NMR and quantum chemical calculations conducted in this work suggest, that relative energies of anionic, pentacoordinate states are the key to explain these findings.

b) Bauer, 2022



a) This Work

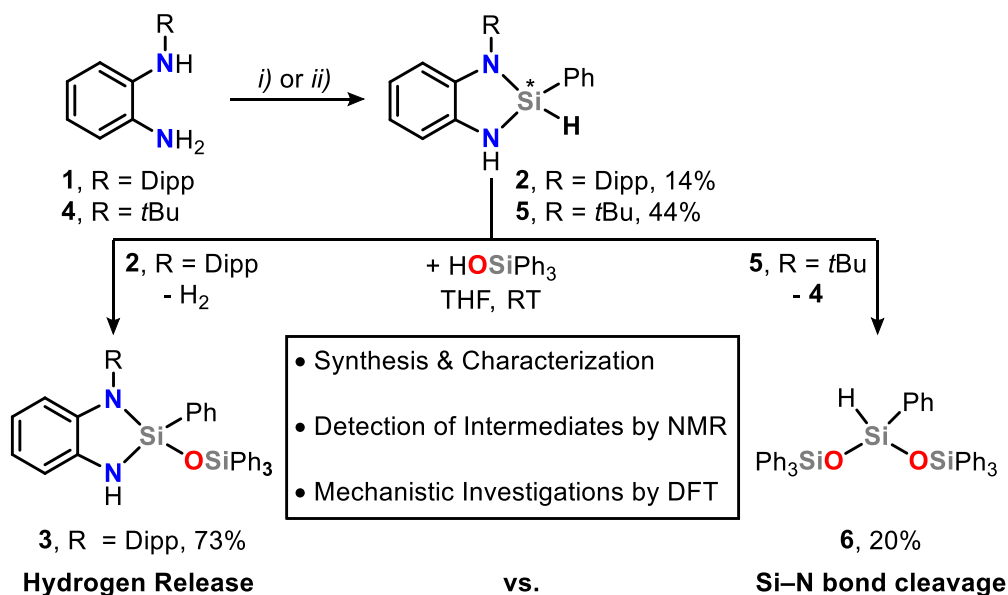


Figure 3.1: Graphical summary of the work presented herein. The synthesis of new diamino-hydrido-cyclosilanes (**2**, **5**) is described, as well as detailed investigations on their different reaction outcome with HOSiPh₃. Previous work (b) was focused on the synthesis and reactivity of cyclic diamino-diphenylsilanes.^[1] Synthetic conditions: *i*) R = Dipp, 1.) *n*BuLi (2.1 eq.), 2.) Cl₂SiPhH (1.0 eq.), THF, -80 °C→RT, 16 h. *ii*) R = *t*Bu, Cl₂SiPhH (1.0 eq.), Et₃N (2.1 eq.), THF, 0 °C→RT, 16 h.

3.2 Introduction

Recently, we reported about the synthesis and characterization of achiral, cyclic diamino-diphenylsilanes (Figure 3.1b).^[1] Investigations on the reactivity of these silanes with tertiary silanols allowed us to develop a powerful method to synthesize tailored amino-disiloxanes and disiloxanols by refluxing the starting materials for 15–120 hours either without additives in THF, or with catalytic amounts of *para*-toluenesulfonic acid (*p*-TsOH) in toluene. Under these conditions, the substituted (R)N–Si bond (R = *t*Bu, Dipp) is selectively cleaved and amino-diphenylsiloxanes were obtained as formal addition products of the respective silanol and diamino-diphenylsilane (Figure 3.1b).^[1]

In order to expand the class of cyclic-diaminosilanes further and investigate their unique reactivity, we developed (racemic) synthetic procedures for two new Si-chiral diamino-hydrido-phenylsilanes, **2** and **5** (Figure 3.1 and Section 3.3.). While both silanes react already at room temperature with triphenylsilanol (HOSiPh₃), only *N*-*t*Bu substituted silane **5** yields N–Si bond cleaved products (**6**, **7**, see below) similar to the ones reported before by us for diamino-diphenylsilanes.^[1] Stirring the *N*-Dipp substituted silane **2** with HOSiPh₃, in contrast, resulted in the formal substitution product of Si–H by Si–OSiPh₃, **3** and evolution of dihydrogen without catalyst.

Many organosilanes similarly react with alcohols under base catalysis in a dehydrogenative coupling (DHC) and mechanistic investigations on this topic have been carried out at least since 1947.^[2]

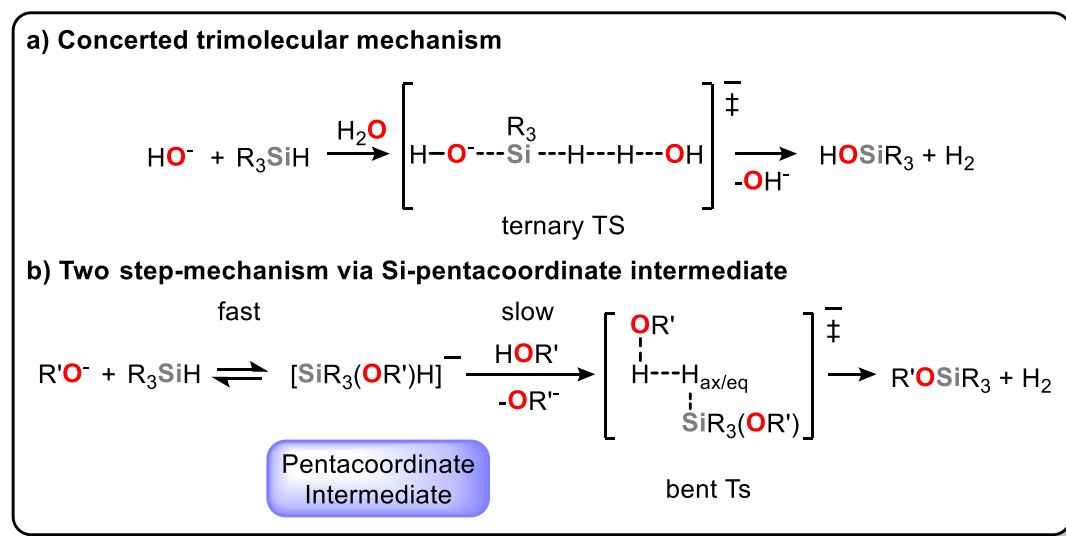


Figure 3.2: Earlier proposed mechanisms for base catalyzed dehydrogenative coupling of alcohols and silanes. a) Initially advocated, single step mechanism by Kaplan & Wilzbach via a ternary TS.^[3] b) Refined, two-step mechanistic proposal from Eaborn & Jenkins via initial, reversible formation of pentacoordinate ionic intermediates and subsequent expulsion of H₂ via a bent TS.^[4]

A concerted mechanism for the hydroxide catalyzed alcoholysis of Si–H in aqueous media has been proposed by Kaplan & Wilzbach (1955), in which nucleophilic attack of OH[−] towards Si simultaneously occurs with protonation / H₂ evolution from the solvent (Figure 3.2a).^[3] Later, a refined overall two-step mechanism was proposed from better data by Schowen and coworkers,^[5] and in more detail by Eaborn & Jenkins in 1974,^[4] where reversible addition of base to the silane is the first, and kinetically fast step, resulting in a trigonal-bipyramidal pentacoordinate, anionic intermediate (Figure 3.2b) with, at the time, unspecified axial / equatorial stereochemistry. The second step, formation of H₂ from concerted Si–H and H–OR' bond cleavage, is slow and irreversible, ultimately driving the reaction to full conversion (Figure 3.2b).

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

Note that, in contrast to a still somewhat popular misconception, pentacoordinate silicon species are not hypervalent, i.e. apparently bearing more than eight valence electrons via inclusion of d-orbitals to hybridization.^[6,7] The correct bonding is best described by molecular-orbital (MO) theory using symmetry adapted linear combinations (SALCs).

Works by Corriu et al. arrived at the conclusion, that nucleophiles generally attack at Si, such that they would initially take an axial position and preferably anti to another electronegative substituent.^[8] This concept is now widely accepted as the first step of the nucleophilic substitution reaction at silicon (Si-S_N2, Figure 3.3).^[9]

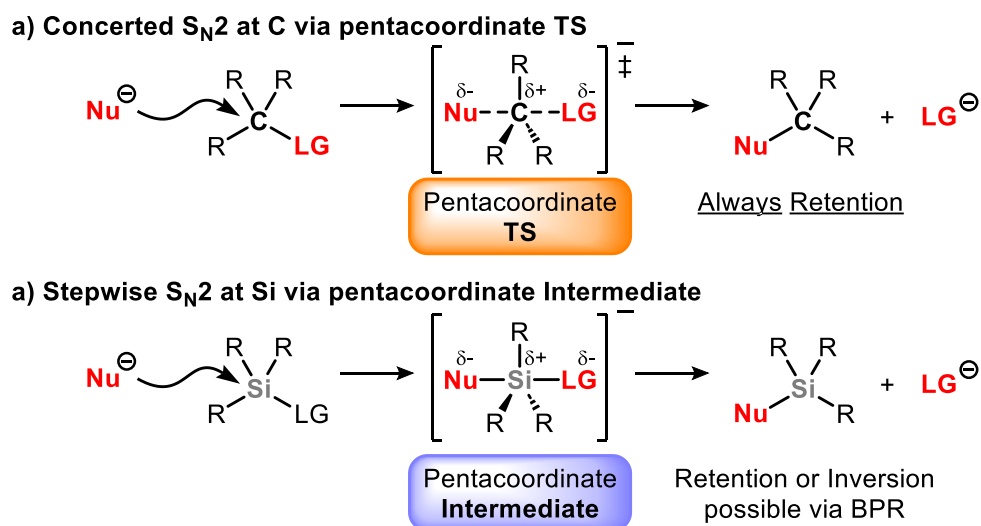


Figure 3.3: Comparison of nucleophilic substitution mechanisms (S_N2) at carbon and silicon.

The general implication of this concept is, that the leaving group and nucleophile must be axial in order to be exchanged.^[10] Pentacoordinate silicon anions are, like their undoubtedly more minded, neutral phosphorus equivalents, stereochemically flexible and undergo exchange of substituents by Berry-pseudorotation (BPR) with comparable energy barriers.^[10–14] With these implications, it is logical to propose, that the ability of a silane to function as hydride donor in the DHC reaction is governed by the population of pentacoordinate, anionic isomers with hydride in the axial position, which are generated by attack of a nucleophile to this silane. H_{axial} isomers may be formed as downstream species after initial addition of the nucleophile, while the populations would be determined by the relative energies of pentacoordinate anionic intermediates.

Herein we report on mechanistic investigations and key aspects of the successful dehydrogenative coupling of triphenylsilanol with the *N*-Dipp substituted diamino-hydrido-phenylsilane **2**, and discuss why no DHC is occurring with the *N*-*t*Bu silane **5** under otherwise equal conditions. Our conclusions are based on the observation of transient species by ¹H- and ²⁹Si VT-NMR, NMR reaction monitoring, and quantum chemical calculations. We are convinced, that these insights are invaluable for understanding reactions involving pentacoordinate silicon species and can generally be transferred to rationalize the reactivity of other systems.

3.3 Results and Discussion

3.3.1 Synthesis and Characterization of Diamino-hydrido-cyclosilanes 2 and 5

The synthesis of *N*-substituted diamino-hydrido-cyclosilanes was achieved by adaptation of a synthetic route we previously developed to access diamino-diphenyl-cyclosilanes (see Section 3.7.5).^[1]

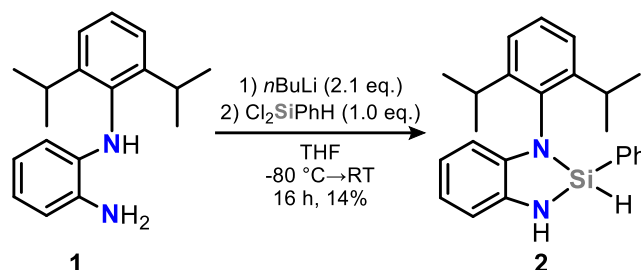


Figure 3.4: Synthesis of *N*-Dipp-diamino-hydridocyclosilane **2**. See also Section 3.7.5.1.

Dilithiation of *N*-(2,6-di-*iso*-propylphenyl)-1,2-diaminobenzene (**1**) and subsequent addition of dichlorophenylsilane (Cl₂SiPhH) led to the formation **2**, which could be isolated as pure compound after recrystallization from *n*-pentane in 14% yield (Figure 3.4, Section 3.7.5.1). Experiments to improve the yield of the synthesis are ongoing. The structure was additionally confirmed by single-crystal X-ray diffraction (XRD, Figure 3.5). Si–N1 (1.7381(9) Å) and Si–N2 (1.724(1) Å) are in accordance with similar Si–N bond lengths reported in literature.^[1,15] However, the $\angle$ (N1–Si–N2), 91.19(5)°, is slightly smaller than reported ones, which appears to have an effect on Si–H1 (1.45(2) Å), which is elongated in comparison to other reported Si–H bonds in diamino-cyclosilanes, e.g. 1.382(15) Å in a compound reported by Avent et al.^[16] This would be consistent with an assumption, that the Si–H bond in **2** is weaker than in comparable systems.

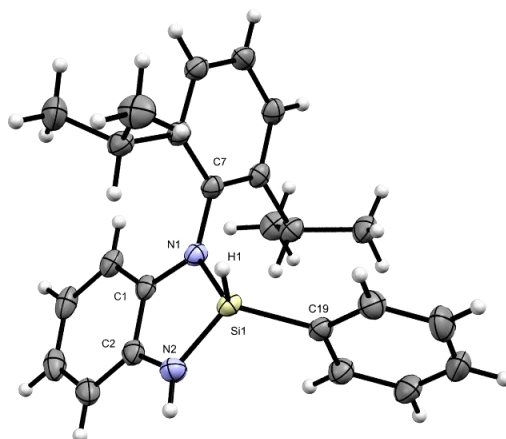


Figure 3.5: Molecular structure of **2** determined by XRD (displacement ellipsoids set at the 50% probability level). Selected bond lengths / Å and angles / ° (at 123 K): Si1–N1: 1.7381(9), Si1–N2: 1.724(1), Si1–H1: 1.45(2), N1–Si1–N2: 91.19(5), N1–Si1–H1: 109.8(6), N2–Si1–H1: 119.1(6). See also Section 3.7.6.2.

The *N*-*t*Bu substituted diamino-hydrido-cyclosilane **5** was obtained in a similar approach as described above, although at milder conditions. Adding Cl₂SiPhH to a solution of *N*-(*tert*-butyl)-1,2-diaminobenzene (**4**) and excess triethylamine in THF at 0 °C, followed by stirring at room temperature for 16 hours and purification resulted in **5** with 44% isolated yield (Figure 3.6, see also Section 3.7.5.3).

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

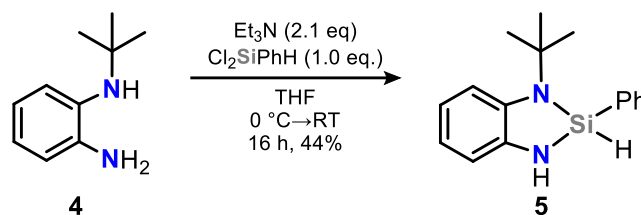


Figure 3.6: Synthesis of *N-t*Bu-diamino-hydridocyclosilane **5**. See also Section 3.7.5.3.

Crystals suitable for single crystal XRD of **5** could unfortunately not be obtained yet.

3.3.2 Reaction of **2** and **5** with HOSiPh_3 in THF

In order to explore the reactivity and stability of the new silanes, **2** and **5** were initially mixed with stoichiometric amounts of HOSiPh_3 , respectively at room temperature in THF and the mixture analyzed after 16 hours.

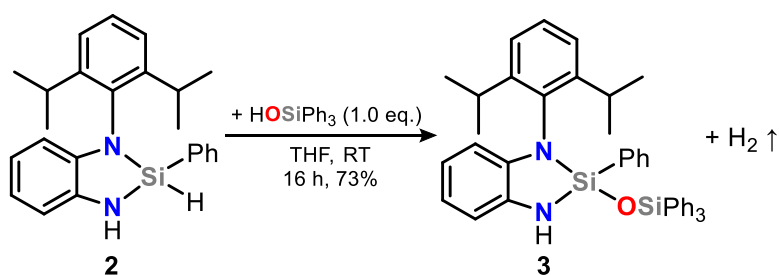


Figure 3.7: Reaction conditions for the formation of **3** from **2** and HOSiPh_3 with evolution of H_2 .

From the reaction mixture with *N*-Dipp substituted diaminosilane **2**, another Si-chiral, cyclic diaminosilane (**3**) with formal substitution of Si–H by Si–OSiPh₃ could be isolated in 73% yield (Figure 3.7). This pathway is in stark contrast to the corresponding, previously reported reaction of the *N*-Dipp substituted diamino-diphenylsilane with HOSiPh_3 , which resulted in a ring-opened amino-disiloxane (42% isolated yield) only after refluxing in THF for 120 hours (see Figure 3.1b).^[1] Further experiments revealed, that the formation of **3** from **2** and HOSiPh_3 with evolution of H_2 still occurred at temperatures as low as $-10\text{ }^\circ\text{C}$. Recrystallization of **3** from *n*-pentane resulted in suitable material for single crystal XRD and confirmed the assumed structure with a still intact five-membered heterocycle (Figure 3.8). An analysis of the structure revealed only little differences in the Si–N1 (1.733(1) Å) and Si–N2 (1.724(1) Å) bond lengths if compared to **2** and also little deviation in the $\angle(\text{N1–Si–N2})$ angle (91.81(6)°). For more data from XRD see Section 3.7.6.3.

While the driving force of the reaction can intuitively be rationalized by the certainly energetically favored formation of a stable Si–O bond and irreversible loss of H_2 via comproportionation of hydridic Si–H and protic silanol H–O, it is still somewhat surprising as it is occurring at such mild conditions, i. e. activation barriers in each step of the reaction mechanism must be rather low or at least energetically accessible. On the other hand, the equivalent reaction pathway with previously reported diamino diphenylsilanes (see Figure 3.1b), which lack Si–H, would have to proceed via elimination of a formal phenyl anion to generate benzene, which is not observed even at higher temperatures.^[1] Mechanistic insights are discussed below.

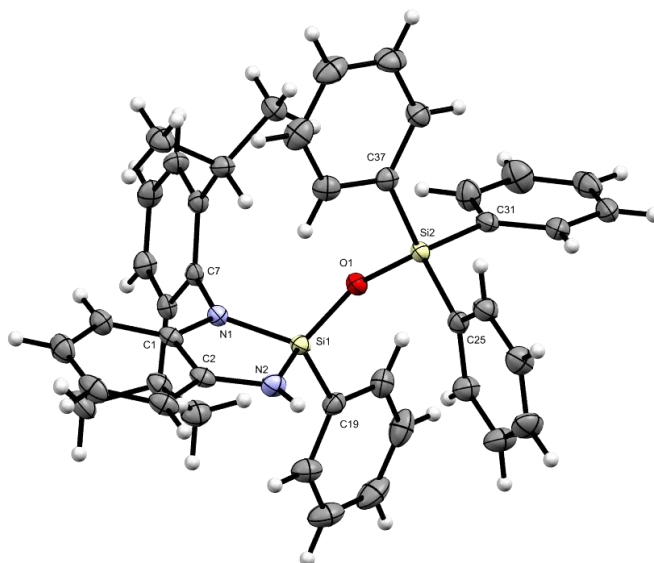


Figure 3.8: Molecular structure of **3** determined by XRD (displacement ellipsoids set at the 50% probability level). Selected bond lengths / Å and angles / ° (at 123 K): Si1–N1: 1.733(1), Si1–N2: 1.724(1), Si1–O1: 1.618(1), N1–Si1–N2: 91.81(6), N1–Si1–O1: 114.13(5), N2–Si1–O1: 115.86(6). See also Section 3.7.6.3.

The reaction outcome of stirring *N*-*t*Bu substituted diaminosilane **5** with HOSiPh₃ in THF at room temperature for 16 hours differ not only from the above discussed case for **2**, but also from the diamino-diphenylsilanes reported previously (Figure 3.1b).^[1] A symmetric trisiloxane (**6**) was isolated in 20% yield as downstream product from the cleavage of both Si–N bonds by two molecules of silanol (Figure 3.9, left side). The structure of **6** was confirmed by single crystal XRD; as it is a known compound the parameters are not discussed here but important bond lengths and angles are given in Section 3.7.6.4.

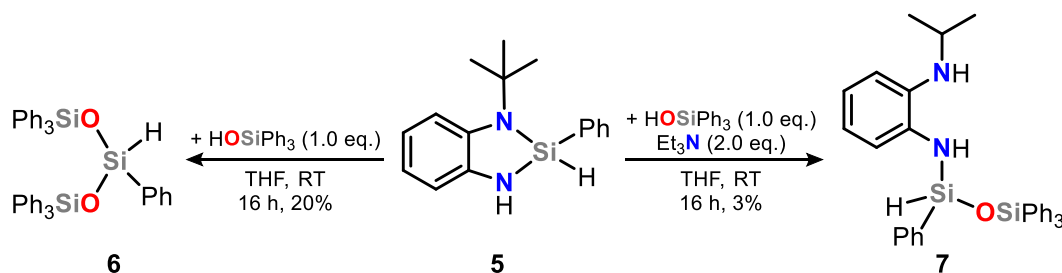


Figure 3.9: Reaction outcomes of stirring **5** and HOSiPh₃ in THF, either without additives (left side) and with added excess of triethylamine to suppress cleavage of the second Si–N bond. Yields are isolated yields.

In an attempt to prevent the full Si–N silanolysis and observe, or even isolate the expected transient amino-disiloxane **7**, the reaction was carried out with two equivalents of triethylamine as base. Indeed, an aliquot taken from the crude reaction mixture after 16 hours revealed a conversion of 86% from **5** to **7**, but only minute amounts of **7** (8 mg, 3%, see 3.7.5.5) could be isolated. Fortunately, these were in the form of crystals suitable for single crystal XRD (Figure 3.10).

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

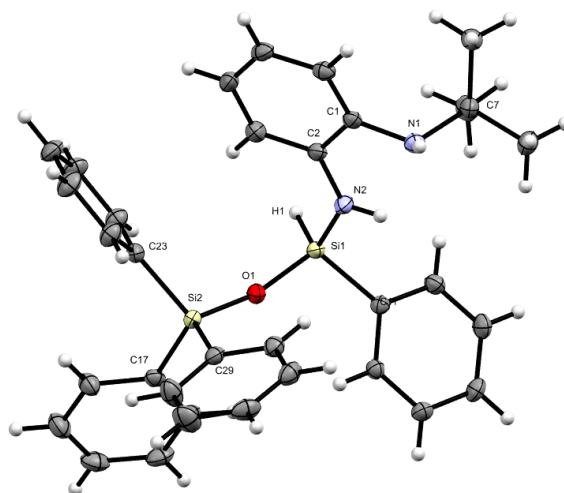


Figure 3.10: Molecular structure of compounds **7** in the crystal (displacement ellipsoids set at the 50% probability level). Selected bond lengths / Å and angles / ° of compound **7** (at 293 K): Si1–N1: 1.709(1), Si1–H1: 1.37(2), N2–Si1–O1: 113.60(5), N2–Si1–H1: 110.2(7).

A significantly shorter Si1–N2 bond (1.709(1) Å) compared to **2** or **3** is present in **7**, which could be explained by a less strained environment in the open chain. On the other hand, this value is still less than the ones found in related amino-disiloxanes we investigated previously (1.7149(15) Å – 1.7215(13) Å).^[1] This could be rationalized with the decreased steric demand from substituents at Si1 (H, Ph, OSiPh₃) in **7** if compared to diamino-diphenyl derived amino-disiloxanes (2 × Ph, OSiPh₃).^[1]

3.3.3 Alternative Route to Si-chiral, Cyclic Diamino-Disiloxane **9**

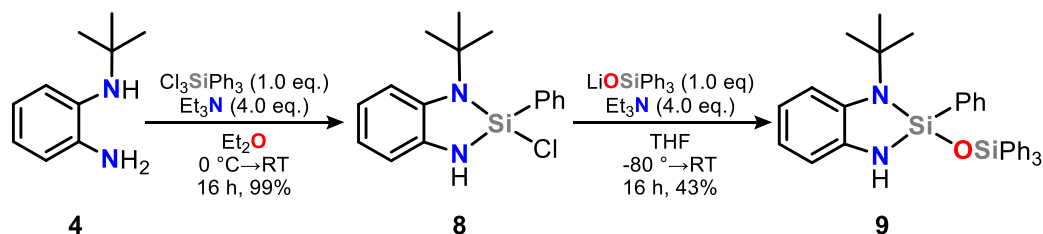


Figure 3.11: Alternative synthetic route towards *N*-*t*Bu substituted disiloxane **9** from **4** via silyl chloride **8**. Given yields are isolated yields.

The *N*-*t*Bu analog of **3**, cyclic diamino-siloxane **9** was accessible by an alternative synthetic route (Figure 3.11, Section 3.7.5.6 and 3.7.5.7) via silyl chloride **8** as a stable compound. The Si1–N1 (1.7342(9) Å) and Si1–N2 (1.719(1) Å) bond lengths, as well as the $\angle$ (N1–Si1–N2) angle are similar to the values found for **3** (Figure 3.12). An assumption on the mechanism that could be inferred from these findings is, that the difference in observed reactivities of **2** and **5** do not rely on the stability of their siloxane products **3** and **9**, respectively. Instead, the differences must originate from relative energies in earlier transient species in the mechanism, being decisive if either hydrogen release or Si–N cleavage occurs.

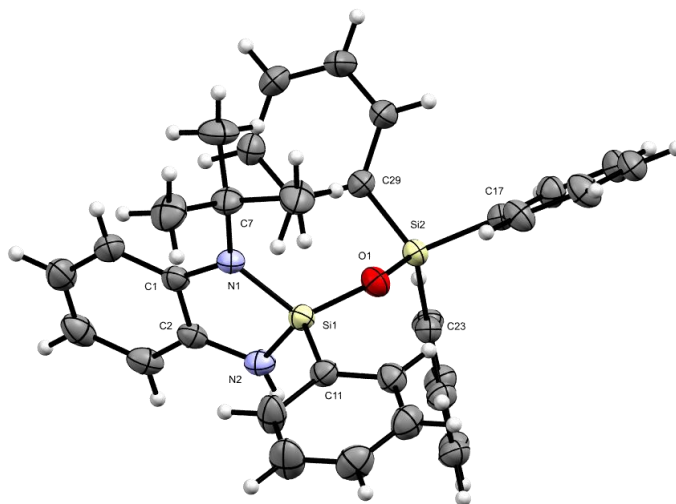


Figure 3.12: Molecular structure of **9** in the crystal (displacement ellipsoids set at the 50% probability level). Selected bond lengths / Å and angles / ° (at 123 K): Si1–N1: 1.734(2), Si1–N2: 1.719(1), Si1–O1: 1.625(1), N1–Si1–N2: 92.55(7), N1–Si1–O1: 116.67(7), N2–Si1–O1: 113.78(7).

3.3.4 NMR Spectroscopic Investigations

3.3.4.1 ^1H and ^{29}Si NMR Spectroscopic Investigation of **2** and HOSiPh_3 at 180 K

^1H and ^{29}Si NMR-spectroscopic investigations have been carried out at temperatures between 180 K and 298 K for samples of *N*-Dipp-substituted diaminosilane **2** and HOSiPh_3 in THF-d_8 . It was presumed that pentacoordinate intermediates could be observed below -10 °C while the energy barrier for elimination of H_2 would be too high to noticeably occur. Although experimentally it was challenging to prepare proper samples, it was possible to observe two sets of signals at 180 K in the ^{29}Si NMR spectrum (Figure 3.13) and corresponding signals could further be assigned in the ^1H NMR spectrum via their ^{29}Si -satellites (Figure 3.14).

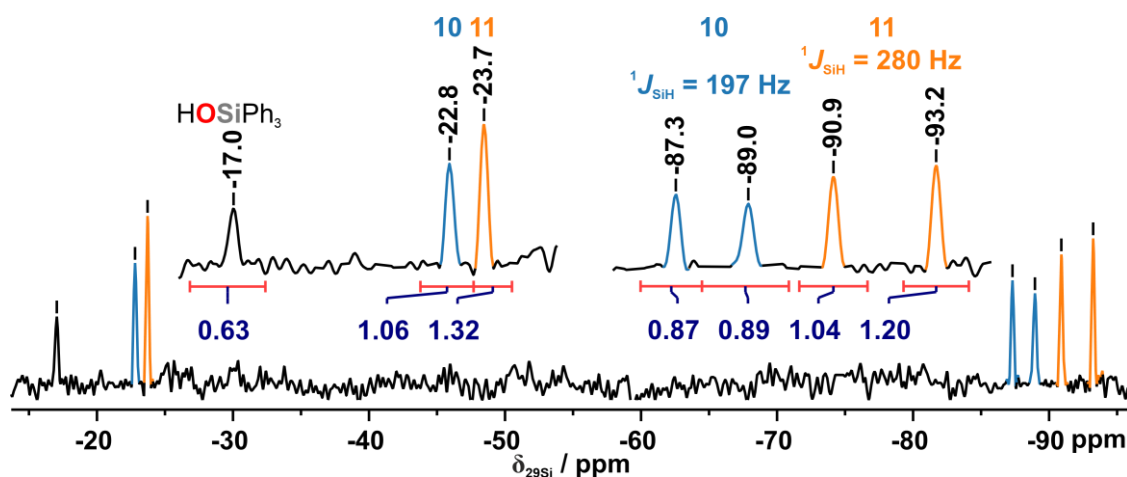


Figure 3.13: ^{29}Si NMR spectrum of a freshly prepared mixture of *N*-Dipp-substituted diaminosilane **2** and HOSiPh_3 (1.0 eq) in THF at 180 K. The new signals have been assigned to numbers **10** and **11**. The integrals should be interpreted as estimates only, since advanced baseline correction was necessary, and relaxation delays have not been determined.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

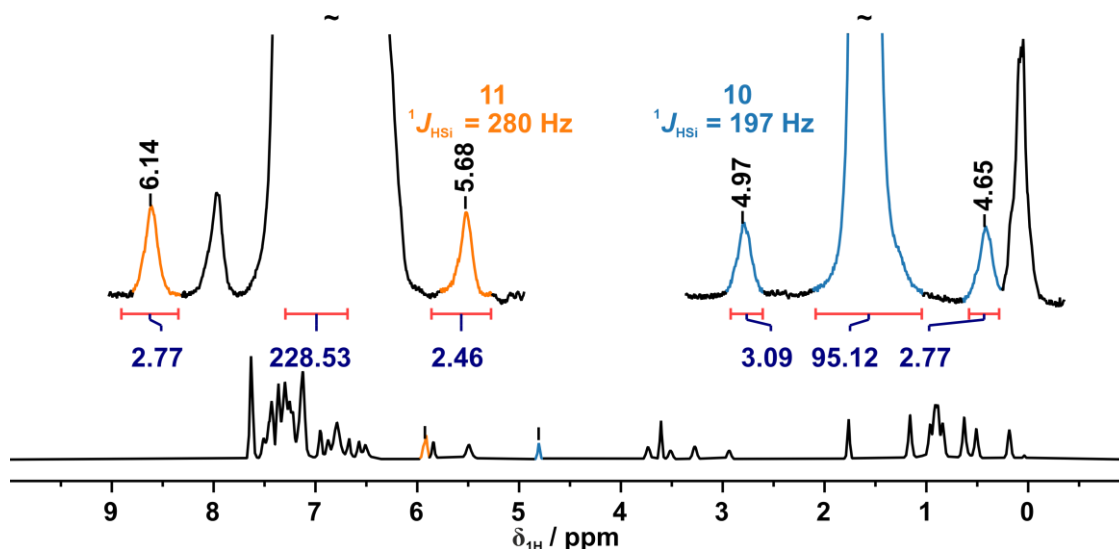


Figure 3.14: ^1H NMR spectrum of a freshly prepared mixture of *N*-Dipp-substituted diaminosilane **2** and HOSiPh (1.0 eq) in THF at 180 K. The new signals have been assigned to numbers **10** and **11**, in accordance with Figure 3.13. The central signal of **11** is overlapping with other species. Expected integral ratios for a ^1H - ^{29}Si would be 2.35 : 95.3 : 2.35 (^{29}Si has a natural abundance of 4.7 and is a spin $\frac{1}{2}$ nucleus).

Based on the chemical shifts and integrals, both species were preliminary assigned to two different pentacoordinate silicon intermediates, **10** (δ_{H} 4.81 ppm, $\delta_{^{29}\text{Si}}$ -22.8 (-OSiPh₃), -87.8 (Si-H, $^1J_{\text{HSi}} = 197$ Hz) ppm) and **11** (δ_{H} 5.91 ppm, $\delta_{^{29}\text{Si}}$ -23.7 (-OSiPh₃), -92.1 (Si-H, $^1J_{\text{HSi}} = 280$ Hz) ppm) in an approximate ratio of 1:1 (based on integrals of ^{29}Si satellites of ^1H signals), arising from coordination of the silanolate to starting material **2** (δ_{H} 6.14 ppm, $\delta_{^{29}\text{Si}}$ -13.8 ($^1J_{\text{HSi}} = 233$ Hz) ppm).

The observed ^{29}Si chemical shifts for **10** and **11** would suggest anionic, pentacoordinate silicon species, in accordance with literature, e. g. alkali tetraalkoxy-hydridosilicates, $\text{M}[\text{HSi}(\text{OR})_4]^-$ ($\text{M} = \text{K}, \text{Na}, [\text{K}(18\text{-crown-6})]$, $\text{R} = \text{Et}, i\text{Pr}, n\text{Bu}$) reported by Corriu and coworkers, with a range of ^{29}Si chemical shifts from -82.5 – -92.0 ppm.^[17] Likewise, the observed upfield shifts of the ^1H NMR signals from 6.14 ppm (**2**) to 4.81 ppm (**10**) and 5.91 ppm (**11**), respectively are consistent with more polarized Si-H bonds, towards a more hydridic character which would be expected in hypercoordinate compounds of third row main group elements. Intuitively, as the valency of the central atom cannot exceed 4, the average bond order in pentacoordinate compounds would be reduced to 4/5, thus increasing ionic contributions. This simplification can qualitatively describe the weakening, although for a comprehensive discussion on the subject of hypercoordination, we shall refer to literature.^[6]

While both species **10** and **11** follow the same trends in their chemical shifts, they strongly differ from each other in their observed $^1J_{\text{HSi}}$ scalar coupling constants. For **11**, a coupling constant of 280 Hz was observed and the chemical shift difference from **2** is less pronounced as for **10**, which has a decreased $^1J_{\text{HSi}}$ of only 197 Hz. Thus, for **11** a Si-H bonding motif with higher Si-s orbital character than **2** is assumed, in contrast to **10** where the Si-s orbital character of the bond is lowered.

All findings would be consistent with assignment of **10** to a pentacoordinate silicon species with Si-H in the equatorial position, and **11** with an axial H. In addition, the measured trends for chemical shifts and coupling constants are directly reflected in the MO energy level diagram of trigonal bipyramidal compounds and an evidence, that hypervalency in the flavor of sp^3d hybrid orbitals cannot be present in our case.^[6]

Further, in trigonal-bipyramidal geometries where a bidentate ligand and the central atom are forming a five membered ring, one of the chelating atoms prefers to reside in an equatorial position, while the other one would then occupy an axial position for steric reasons.^[8,18] From the general and specific rules, and the findings described, only few candidates for **10** and **11** remain, and are depicted in Figure 3.15.

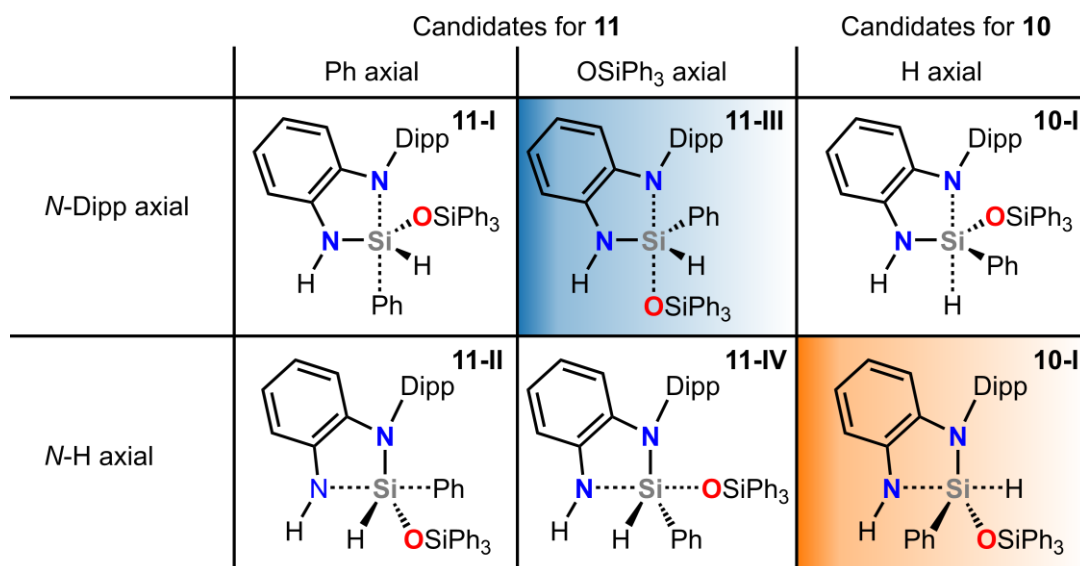


Figure 3.15: Reasonable anionic pentacoordinate silicon species. The negative charge of the compounds was omitted for clarity). In agreement with later herein presented findings, **11** is assigned to **11-III** and **10** to **10-II**. All structures are Si-chiral; the absolute stereochemistry is not subject of this discussion as all compounds were used as racemates.

Since Ph is not a very electronegative ligand, the structures **11-I** and **11-II** are assumed to be rather unstable compared to structures **11-III** and **11-IV**, in which the electronegative silanolate would occupy the axial position. Further, in **11-II** the two sterically demanding Dipp and OSiPh₃ would be as far apart as possible. For **10**, the effects appear to be more subtle and no decisive choice could be made from the first measurements.

From the further results presented herein, we assign the structure of intermediate **10** to **10-II** and **11** to **11-III** (Figure 3.15).

3.3.4.2 Determination of the Activation Barrier for Pseudorotation between **10** and **11**

In agreement with the widely accepted aspects of the S_N mechanism at Si, discussed in Section 3.2, it was rationalized, that pentacoordinate **11** would be the first formed intermediate, being the product of nucleophilic attack of triphenylsilanolate ([OSiPh₃]⁻) to diamino-hydrido-cyclosilane **2**, opposite to the *N*-Dipp nitrogen, as the large Dipp and OSiPh₃ would stay furthest apart. Furthermore, the N(Dipp)–Si bond is assumed to be already weaker than N(H)–Si, which is reflected in the significantly longer bond length of N(Dipp)–Si, determined by single-crystal XRD (see Sections 3.3.1 and 3.7.6.2) and similar cases for the preference of the sterically demanding –N(*i*Pr)₂ to reside in the axial position in contrast to the small amido ligand (–NH₂) in phosphorus species have been reported previously.^[19] The H_{ax} intermediate as the proposed reactive species **10** would then be accessible through a single Berry pseudorotation from **11**, with Si–Ph being the stereochemically inert substituent.

In order to observe this proposed dynamic behavior, ¹H NMR spectra at variable temperatures (VT-NMR) of the same sample as described above were carried out, ranging from 180 K to 263 K (Figure 3.16).

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

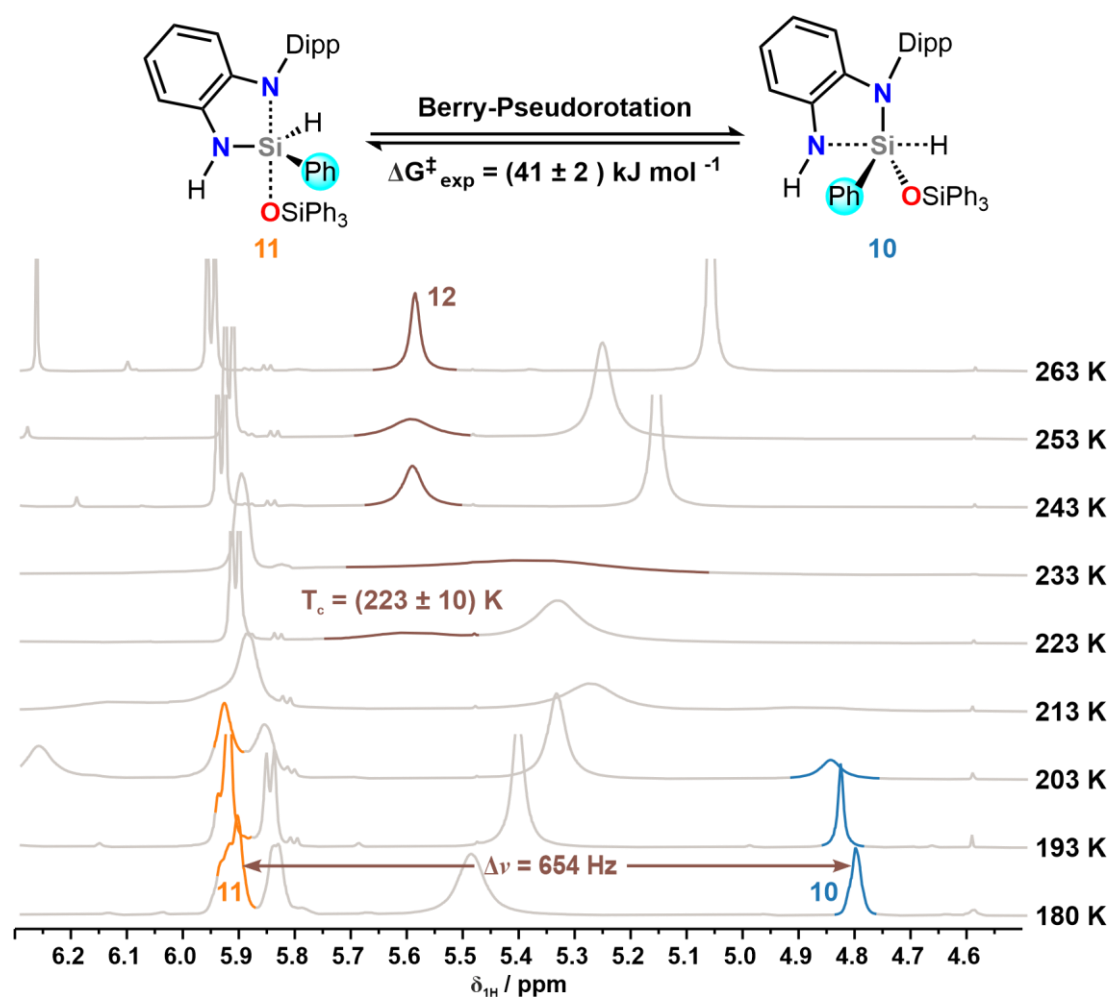


Figure 3.16: ^1H VT-NMR spectra of a the same sample discussed above (mixture of *N*-Dipp-substituted diaminosilane **2** and HOSiPh (1.0 eq) in THF) at temperatures from 180 K–263 K. From the coalescence temperature T_c and $\Delta\nu$, the energy barrier for $\Delta G^\ddagger$ was determined to $(41 \pm 2) \text{ kJ mol}^{-1}$ (see Section 3.7.2.1). The ^1H NMR assignment to **10**, **11** and averaged signal **12** is based off observed ^{29}Si -satellites. It is assumed, that the Ph–Si bond (highlighted by azure circle) remains in the equatorial position, while N(H) and H assume axial positions in exchange with OSiPh₃ and N(Dipp).

At 180 K, the ^1H NMR signals **10** and **11** appeared broad already (the apparently sharper signals at 193 K can be attributed to the high viscosity of THF at 180 K), and could not be detected anymore at 213 K. At further increased temperatures, a new signal (**12**) appeared which was very broad at 223 K, then became more narrow when approaching 263 K. In a first approximation, the energy barrier for the Berry-pseudorotation $\Delta G^\ddagger_{\text{BPR}} = (41 \pm 2) \text{ kJ mol}^{-1}$, could be derived from the observed coalescence temperature T_c of $(223 \pm 10) \text{ K}$ and the difference of Larmor frequencies $\Delta\nu$ of both exchanging partners in the slow exchange regime (654 Hz). Thus, **12** should be interpreted as the averaged signal of intermediates for the sake of readability.

3.3.4.3 Reaction Monitoring at 298 K

In a separate sample with **2**, but five equivalents HOSiPh₃ in THF-d₈, it was possible to observe transient ¹H and ²⁹Si NMR signals of presumed pentacoordinate mixtures (**12**, Figure 3.17) at room temperature. The sample was monitored by ¹H and ²⁹Si NMR spectroscopy for 12 hours.

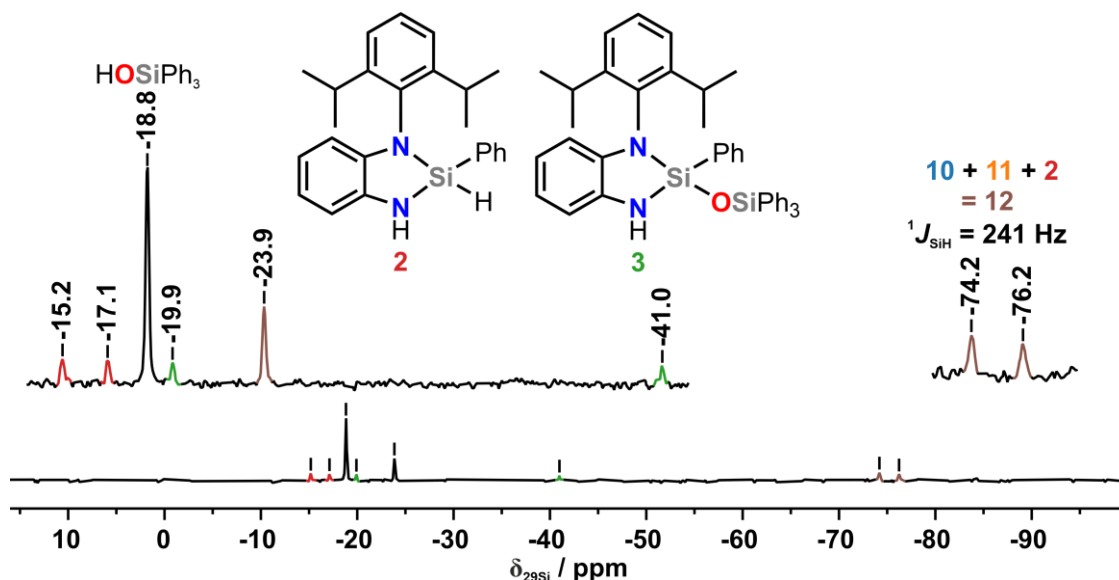


Figure 3.17: ²⁹Si NMR spectrum of a mixture of *N*-Dipp-substituted diaminosilane **2** and HOSiPh₃ (marked with *, 1.0 eq) in THF after warming from 180 K to 298 K (duration 80 minutes). The doublet around -75 ppm is proposed to originate from fast exchange of **10** and **11**, while **2** must also participate as exchanging partner based on the chemical shift (see below). For the sake of readability, this mix of isomers is defined as **12**.

In the first ¹H NMR spectrum, sharp signals corresponding to the starting material **2**, intermediates **12** and the product **3** in a ratio of 1 : 3 : 1.3 were observed (Figure 3.18). Likewise, only a single set of signals was observed for a mixture of intermediates **10** and **11** at fast exchange (**12**) in the ²⁹Si NMR spectrum, in the presence of starting material **2** and product **3** (Figure 3.17).

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

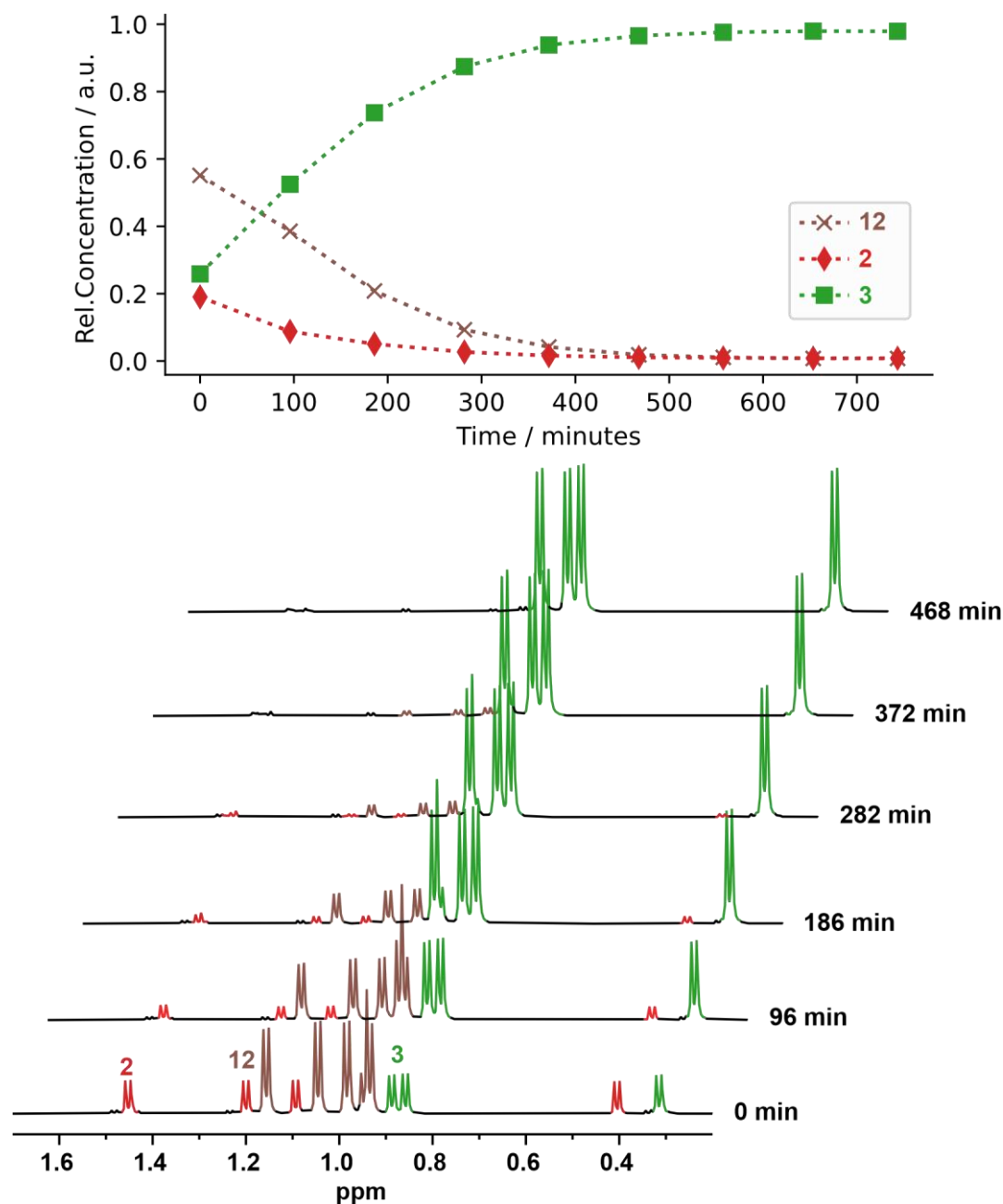


Figure 3.18: Methyl region of the ^1H NMR reaction monitoring of a mixture of *N*-Dipp-substituted diaminosilane **2** and HOSiPh in THF at 298 K. **2** and **12** are consumed over time, with simultaneous formation of the product **3**. A first order rate constant could be determined by fitting to the data, $k = (101 \pm 4) \cdot 10^{-6} \text{ s}^{-1}$.

Extended monitoring of the sample revealed, that the time dependent concentrations of **2**, **12** and **3** each follow a monoexponential function, resulting in full conversion to the final product **3** after 12 hours. With an almost similar ratio of 1 : 3 for **2** and **12**. It can be inferred, that the constant ratio of both species would originate from reversible exchange between **2** and **12** which is slow on the ^1H NMR time scale (two sets of sharp signals), but still much faster than the following irreversible elimination of H_2 . From the ratios, the relative Gibbs free energy ΔG of **2** vs. **12** was determined to be $+2.7 \text{ kJ mol}^{-1}$ (according to a Boltzmann distribution model). A quantitative value for $\Delta G^\ddagger$ for this reversible process cannot be given from the available data, it is estimated to be in the range of

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

60–90 kJ mol⁻¹, as it must be larger than the value obtained for Berry pseudorotation, but also not be rate determining. More data would be needed to determine this parameter.

The sum over the integrals of **2**, **12** and **3** remained constant over the full monitoring and no other intermediates could be observed in the spectra. Since HOSiPh₃ was used in large excess, a pseudo-first order reaction model was assumed, and absolute concentrations are not necessary.

The relationship of normalized concentrations C_i of each reactant was found accordingly to be:

$$(1 - C_2(t) + C_{12}(t)) = C_3(t) \quad (1)$$

or in differential form:

$$\frac{d}{dt} C_2(t) + \frac{d}{dt} C_{12}(t) = -C_3(t) \quad (2)$$

where $C_i(t)$ are of the form

$$C_i(t) = f_i e^{-kt} \quad (3)$$

f_i are prefactors and k the first order rate constant. Following from Equations 1 and 3, f_3 must be equal to unity. As **2** and **12** are assumed to be in a preequilibrium and the relative Gibbs energies $\Delta G_2 / \Delta G_{12}$ have been determined (see above). f_2 and f_{12} are equal to the weighted factors of a Boltzmann distribution, or the normalized integral ratios of **2** and **12** in the ¹H NMR spectra (Figure 3.18). The activation barrier for irreversible H₂ elimination and formation of the product **3** could be determined by fitting the data to a function according to Equation 3 and first obtain the (pseudo) first-order rate constant $k = (101 \pm 4) \cdot 10^{-6} \text{ s}^{-1}$. From this value, $\Delta G^\ddagger$ for the dehydrogenative coupling can be derived with the Eyring-Polanyi equation,

$$\Delta G^\ddagger = RT \ln\left(\frac{k_B T}{h k}\right) \quad (4)$$

where R is the universal gas constant, k_B is Boltzmann's constant and h is Planck's constant. A value for $\Delta G^\ddagger = (95.8 \pm 0.1) \text{ kJ mol}^{-1}$ was obtained. In accordance with the mechanism proposed by Eaborn & Jenkins 50 years ago, the H₂ evolution is the rate determining step, with a preequilibrium of the tetracoordinate starting material and pentacoordinate intermediates.^[4] Note that these calculations are all based on a single reaction monitoring and more data is still needed to verify the full reaction kinetics of this system.

The overall proposed reaction mechanism for the formal nucleophilic substitution of Si–H (**2**) by Si–OSiPh₃ (**3**) with elimination of H₂ along with all determined energies and energy barriers is summarized in Figure 3.19.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

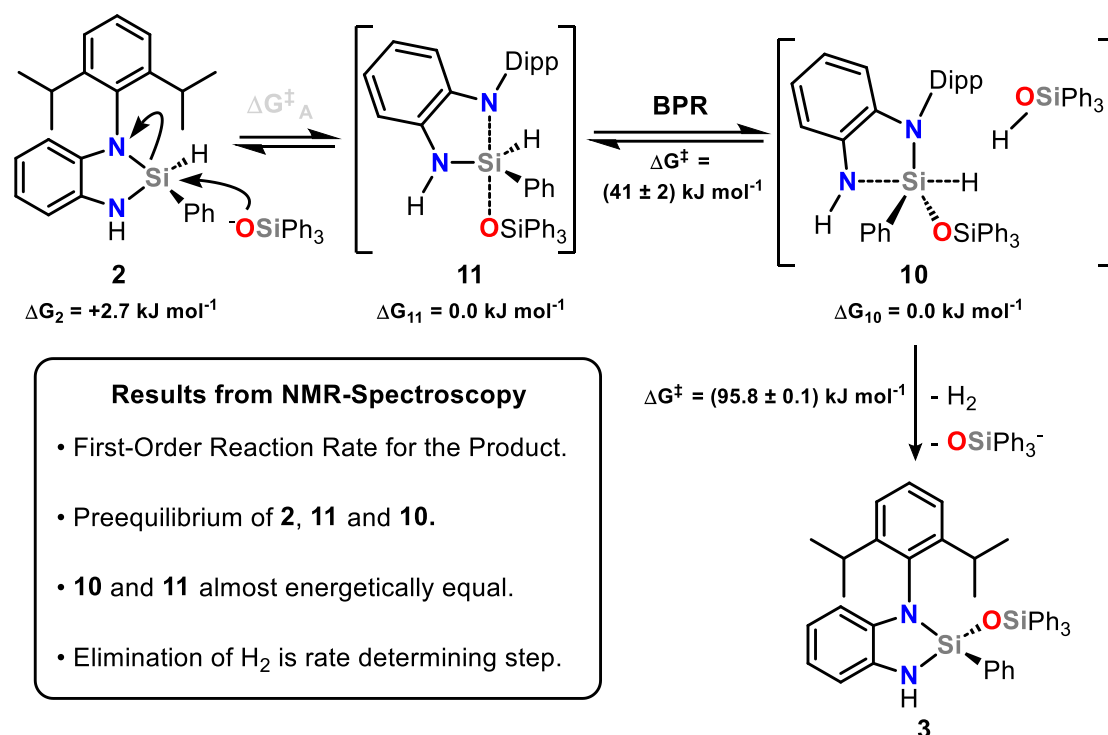


Figure 3.19: Summary of mechanistic investigations by ¹H and ²⁹Si NMR for the reaction of cyclic diamino-hydridosilane **2** with triphenylsilanol (HOSiPh₃) in THF. All energies were determined experimentally from reaction or exchange rates.

3.3.5 Quantum Chemical Investigations and Mechanistic Implications

In order to provide further evidence for the assignment of **10** and **11** quantum chemical calculations were carried out at the PBEh-3c / CPCM(THF) level for geometry optimizations and frequencies, and at the PBE0 / pcSseg-2 or pcJ-2 / CPCM(THF) level of theory to calculate nuclear shieldings and scalar coupling constants using Orca 6.0.0.^[20–29] The feasibility of this calculation scheme was evaluated for [F₃Si(CH₂OAc)], an established pentacoordinate, neutral, silicon compound and yielded very accurate results considering ²⁹Si chemical shifts (see Section 3.7.3.1).^[30,31] In addition, ²⁹Si chemical shifts and ¹J_{SiH} coupling constants of the starting materials HOSiPh₃, **2**, **5** and product **3** have been calculated with excellent agreement to the experimental data with this calculation scheme (see Section 3.7.3.2).

According to the experimental results from NMR described above, and in accordance with literature,^[10,32] the first step in the overall mechanism would be the nucleophilic addition of the silanolate^[10] [OSiPh₃][−] to **2** (see Figure 3.19). Relative energies for the six candidates of resulting pentacoordinate anionic silicon species (Figure 3.15) have been calculated from suitable starting geometries. It was not possible to obtain the optimized geometry for **11-I** ((Dipp)_{N_{ax}} / Ph_{ax}), because it optimized to **10-II**.^[33] The stable isomers are corroborating the structural assignment carried out in Section 3.3.4.1 (Figure 3.15), namely that **11** is correctly assigned to **11-III** with (Dipp)_{N_{ax}}/OSiPh_{3ax} geometry (ΔG_{calc} = 0.0 kJ mol^{−1}), and **10** to **10-II** ((H)_{N_{ax}}/H_{ax}, ΔG_{calc} = +2.4 kJ mol^{−1}). With all other isomers having a relative ΔG_{calc} of 12.0 kJ mol^{−1} or higher (Table 3.4). Repeating the calculations at the PBE0 / def2-SVP / D3BJ / CPCM(THF) level resulted in a similar ΔG_{calc} difference of 4.2 kJ mol^{−1}. Since the accuracy of calculations at this level is usually much less than 5 kJ mol^{−1}, the results corroborate the finding by NMR that **10** and **11** would be energetically very similar. Calculations of the NMR-parameters yielded δ_{29Si} = −98.7 ppm, ¹J_{Hsi} = −245 Hz for **11** and δ_{29Si} = −100.0 ppm, ¹J_{Hsi} = −187 Hz for **10**, further strongly

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

corroborating the structural assignment and mechanistic proposal. The calculated ^1H chemical shifts are also in good agreement with the assigned structures (see Section 3.7.3.3).

All six *N*-*t*Bu substituted pentacoordinate anionic isomers resulting from nucleophilic attack of triphenylsilanolate to **5** (similar to the *N*-Dipp structures depicted in Figure 3.15) were optimized with the same general calculation scheme. The isomer with $(t\text{Bu})\text{N}_{\text{ax}} / \text{OSiPh}_{3\text{ax}}$ was the one with lowest energy ($\Delta G_{\text{calc}} = 0.0 \text{ kJ mol}^{-1}$), similar to the *N*-Dipp case discussed above. In contrast, the isomer with $(\text{H})\text{N}_{\text{ax}} / \text{H}_{\text{ax}}$ had a significantly increased energy ($\Delta G_{\text{calc}} = +26.4 \text{ kJ mol}^{-1}$). The isomers with second lowest energy were found to be the $(t\text{Bu})\text{N}_{\text{ax}}/\text{Ph}_{\text{ax}}$ ($\Delta G_{\text{calc}} = +15.8 \text{ kJ mol}^{-1}$) and $(t\text{Bu})\text{N}_{\text{ax}}/\text{H}_{\text{ax}}$ ($\Delta G_{\text{calc}} = +17.9 \text{ kJ mol}^{-1}$) structures, while $(\text{H})\text{N}_{\text{ax}}/\text{Ph}_{\text{ax}}$ ($\Delta G_{\text{calc}} = +51.5 \text{ kJ mol}^{-1}$) and $(\text{H})\text{N}_{\text{ax}}/\text{H}_{\text{ax}}$ ($\Delta G_{\text{calc}} = +47.7 \text{ kJ mol}^{-1}$) would be even more disfavored.

Thus, it can be inferred, that the H_2 evolution reaction would not (observably) occur with the *N*-*t*Bu substituted silane **5** because the populations of required states with H_{ax} are too low and instead the Si–N cleaved amino-disiloxane **7**, and doubly Si–N cleaved trisiloxane **6** are observed as products.

3.4 Conclusions

In conclusion, we expanded our investigations on cyclic diaminosilanes to diamino-hydridosilanes with *N*-Dipp (**2**) or *N*-*t*Bu (**5**) moieties. It was found, that the starting materials react vastly different with triphenylsilanol in THF, as the former quantitatively yields a formal substitution product of Si–H by Si–OSiPh₃ (**3**) under hydrogen elimination, while the latter is converted to formal addition products of HOSiPh₃ with cleaved Si–N bonds (**6** / **7**). Through extended ^1H and ^{29}Si NMR spectroscopic investigations, we were able to identify pentacoordinate silicon species as key downstream intermediates in the dehydrogenative coupling of *N*-Dipp substituted silane **2**, quantify relative energies, rates and the activation barriers connecting them, thus providing a comprehensive picture of the reaction.

Quantum chemical calculations corroborated our mechanistic proposal, as the populations of pentacoordinate, anionic Si– H_{ax} states were suggested as crucial for the hydrogen evolution reaction. Thus, it should be possible to predict the reaction outcomes of other *N*-substituted diamino-hydridosilanes based on calculations of relative energies.

We hope that the findings serve as helpful guides in the understanding and development of reactions involving silanes, which are often employed across all fields of synthetic chemistry. Future investigations will be focused on isolation of enantiomerically pure silanes and assess their potentials as stereospecific mild reducing agents.

3.5 Acknowledgements

Jonathan O. Bauer thanks the Elite Network of Bavaria (ENB), the Bavarian State Ministry of Science and the Arts (StMWK), and the University of Regensburg (Project N-LW-NW-2016-366) for financial support. Manuel Kümper thanks the Fonds der Chemischen Industrie (FCI) for a Kekulé fellowship. Franz F. Westermair, Ruth M. Gschwind and Jonathan O. Bauer would like to thank the Deutsche Forschungsgemeinschaft (DFG, RTG 2620 IonPairs in Reaction Project 426795949) for funding.

3.6 Conflict of Interest

The authors declare no conflict of interest.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7 Supporting Information

3.7.1 General Considerations

3.7.2 Investigations by NMR-Spectroscopy

NMR spectra were recorded on 600 MHz Bruker spectrometers (Avance III HD 600 MHz or Avance Neo 600 MHz) equipped with either an inverse ^{19}F -selective 5 mm TBI-F (^1H , ^{19}F , X) probe with z-gradient or an observe 5 mm Prodigy BBO (X, ^1H) probe with z-gradient. Temperatures were controlled with Bruker BVTE 3000 or Bruker BVTE 3900 temperature control units. Temperatures below 233 K were achieved via liquid N_2 evaporation. ^1H -NMR spectra were referenced to the residual ^1H solvent signal of THF- d_8 ($\delta_{\text{1H}} = 1.74$ ppm, 3.58 ppm). ^{29}Si spectra were externally referenced to TMS ($\delta_{^{29}\text{Si}} = 0.0$ ppm). ^{29}Si NMR spectra were acquired without ^1H decoupling. Spectra were processed and analyzed with Bruker TopSpin 4.2.0, MestRe MNova 14.3.2 and Python scripts. Figures were created using Perkin Elmer ChemDraw Professional 2022, CorelDraw 24.0.0.301, MestRe MNova 14.3.2 and Python scripts.

3.7.2.1 Activation Barriers from Chemical Exchange

The activation barrier $\Delta G^\ddagger$ of two exchanging species can be approximately determined from the frequency difference in the slow exchange regime, $\Delta\nu$. The rate at the coalescence temperature T_c is then approximately

$$k_{\text{obs}} \approx \frac{\pi \Delta\nu}{\sqrt{2}} \quad (5)$$

$\Delta G^\ddagger$ can be obtained from determination of both $\Delta\nu$ and T_c , and calculating via Eyring-Polanyi according to equation

$$\Delta G^\ddagger = RT_c \ln\left(\frac{k_B T_c}{h k_{\text{obs}}}\right) \quad (6)$$

Since the coalescence temperature is dependent on $\Delta\nu$, some signals with similar chemical shift may appear broadened while those with larger differences in exchanging species remain sharp. This is especially the case for heteronuclei, where $\Delta\nu$ usually is much larger than for ^1H .

3.7.3 Mechanistic Investigations with Density Functional Theory

All quantum chemical calculations have been carried out using Orca 6.0.0.^[20,21] Initial geometries were generated with Avogadro 4.2.1. Geometries and frequencies were calculated using the composite method PBEh-3c^[22] (dispersion correction D3BJ^[23,24] and gCP to account for basis set superposition errors^[25]), with improved resolution of identity approximation (chain of spheres) RIJCOSX,^[26] which was successfully applied previously in literature for similar compounds.^[27] Solvation was included via CPCM(THF).^[28,29] To increase SCF accuracy, integration grid density has been increased with defgrid3. More strict thresholds for the geometry optimization have been set with the tightOpt and tightSCF keywords. All structures have been approved to be energetic minima by the absence of imaginary frequencies ($< 0 \text{ cm}^{-1}$). Relative energies of isomeric structures were compared using the resulting Gibbs free energies G , relative to the lowest lying isomer ΔG .

NMR-parameters were calculated from optimized geometries using the PBE0 functional. Chemical shifts and J -coupling constants were calculated separately, using Jensen's NMR-optimized pcSseg-2^[34] or pcJ-2^[35] basis sets, respectively. Auxiliary basis sets were generated with the AutoAux keyword.^[36] For NMR, the same solvation model was used as for geometries. Chemical shifts were always calculated for all atoms, while J -coupling constants

were only calculated for pairs of nuclei of interest. Absolute shieldings σ of ^{29}Si and ^1H were converted to chemical shifts δ by referencing TMS calculated with the same scheme, using the equation:

$$\delta_{\text{calc}} = \sigma_{\text{calc}} - \sigma_{\text{ref}}$$

An empirical value of 0.7 ppm was further subtracted from the calculated ^1H chemical shifts to account for systematic offset errors of the method.

3.7.3.1 Evaluation of the Method of Choice

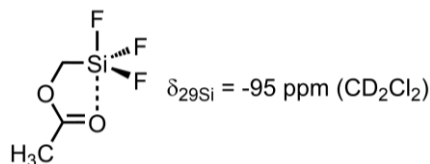


Figure 3.20: Neutral, pentacoordinate silicon compound $[\text{F}_3\text{Si}(\text{CH}_2\text{OAc})]$ (**13**) used for benchmarking.^[30,31]

To determine a good calculation scheme, i.e., delivering correct results for NMR parameters at a reasonable computational cost, various methods were compared: For each method, a geometry optimization of TMS and $[\text{F}_3\text{Si}(\text{CH}_2\text{OAc})]$ with additional calculation of analytical frequencies was conducted. NMR-parameters were then calculated using PBE0 / pcSseg-2 for each geometry. Solvation was included both in the geometry optimization and NMR, when indicated (Table 3.1).

All calculations have been run with the same number of processes (nprocs = 12) on a workstation computer. The NMR calculations of TMS lasted on average 55 s, NMR calculation of the benchmark molecule on average 100 s. The three common composite methods HF-3c,^[37] B97-3c^[38] and PBEh-3c^[22] were tested, along with PBE,^[39,40] PBE0,^[41] B3LYP,^[42–45] TPSSH,^[46] ω B97X-D4^[47,48] and M06-2X,^[49–52] and varying size of Ahlrichs def2 basis sets.^[53]

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

Table 3.1: Benchmarking various DFT schemes for computational cost and accuracy of TMS and **13**, followed by calculation of $\delta_{29\text{Si}}$ by PBE0 / pcSseg-2.

DFT-Method	$\delta_{29\text{Si}}$ / ppm	$ \Delta\delta_{\text{calc-exp}} $	t_{calc} TMS / s	t_{calc} 13 / s	d(Si-O) / Å
exp. ^[31]	-95				
HF-3c	-100.515	5.515	35	196	2.0142
HF-3c + cpcm	-102.949	7.949	43	216	1.9384
B97-3c	-82.133	12.867	60	247	2.2032
B97-3c+ cpcm	-87.709	7.291	87	409	2.0453
PBEh-3c	-90.129	4.871	68	230	2.0768
PBEh-3c + cpcm	-92.036	2.964	78	376	1.9846
PBE / def2-SVP D4	-87.354	7.646	86	169	2.1229
PBE / def2-SVP D4 + cpcm	-88.948	6.052	98	167	2.0316
PBE0 / def2-TZVP D4	-87.654	7.346	512	1640	2.1086
PBE0 / def2-TZVP D4 + cpcm	-91.642	3.358	353	1420	1.9847
B3LYP / def2-TZVP D4	-78.001	16.999	282	1703	2.3019
B3LYP / def2-TZVP D4 + cpcm	-90.161	4.839	341	1285	2.0245
TPSSh / def2-TZVP D4	-90.393	4.607	350	860	2.0854
TPSSh / def2-TZVP D4 + cpcm	-93.155	1.845	372	932	1.9790
ω B97X-D4 / def2TZVP	-85.727	9.273	348	1916	2.1478
ω B97X-D4 / def2TZVP + cpcm	-91.550	3.45	425	1624	1.9932
M06-2X / def2-TZVPP D3zero	-89.366	5.634	554	1063	2.0849
M06-2X / def2-TZVPP D3zero + cpcm	-92.460	2.54	627	1575	1.9770

Employing TPSSh / def2-TZVP with dispersion correction D4 and CPCM(THF) for geometry optimization, followed by calculation of NMR via PBE0 / pcSseg-2 resulted in the smallest error from experiment. Nevertheless, PBEh-3c with CPCM(THF) was chosen for further calculations, as the error is only slightly larger at only a quarter of computational time. Notably, B3LYP / def2-TZVP, undoubtedly one of the most popular calculation schemes, performed very poorly without implicit solvation, while also taking comparably long to compute, showing how important long-range, covalent, and solvent interactions are for calculating correct structures. In addition, the distances of the coordinated oxygen towards silicon in **13** are given in Table 3.1. A clear correlation can be drawn between d(Si-O) and $\delta_{29\text{Si}}$, showing that NMR spectroscopy combined with computational modeling is a highly valuable tool to quantitatively determine atom distances in solution apart from the classical methods of NOE-spectroscopy. The linear open chain conformer of **13** was also run through the calculation scheme and values for $\delta_{29\text{Si}} = -60$ ppm were found, in addition with a $\Delta G = +33$ kJ mol⁻¹ compared to the pentacoordinate conformer.

The accuracy of the NMR calculation method was also evaluated by calculating $\delta_{29\text{Si}}$ for the TMS / [F₃Si(CH₂OAc)] pair with the larger basis sets pcSseg-3 and pcSseg-4, using the geometries obtained by the PBEh-3c + cpcm(DCM) method (Table 3.2).

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

Table 3.2: Benchmarking of varied sizes of Jensens pcSseg basis sets with the geometry obtained from PBEh-3c/cpcm(THF).

Method	$\delta_{29\text{Si}}$ / ppm	$\Delta\delta_{\text{calc-exp}}$ / ppm	t_{calc} TMS / s	t_{calc} 13 / s
exp. ^[31]	-95			
PBE0 / pcSseg-2 + cpcm	-92.036	-2.964	54	104
PBE0 / pcSseg-3 + cpcm	-93.647	-1.353	455	537
PBE0 / pcSseg-4 + cpcm	-93.659	-1.341	1727	1829

Clearly, pcSseg-2 is sufficiently accurate for the calculation of ^{29}Si chemical shifts in this project.

3.7.3.2 DFT-Calculations of NMR Parameters for Starting Materials

Table 3.3: Calculated and experimentally observed NMR parameters of **2**, **3**, **5** and HOSiPh_3

Structure	$\delta_{29\text{Si}}$ calc / ppm	$\delta_{29\text{Si}}$ obs / ppm	$\delta_{1\text{H}(\text{SiH})}$ calc / ppm	$\delta_{1\text{H}(\text{SiH})}$ calc / ppm	$^1J_{\text{HSi}}$ calc / Hz	$^1J_{\text{HSi}}$ obs / Hz
2	-15.1	-13.8	6.14	6.01	-233	233
3	-37.0, -12.7	-38.7, -16.6				
5	-19.3	-18	6.14	6.07	-234	234
HOSiPh_3	-17.1	-16				

3.7.3.3 DFT-Calculations of NMR Parameters of Pentacoordinate States

Table 3.4: Calculated energies and NMR parameters of *N*-Dipp substituted, pentacoordinate species.

Structure	N _{AX}	R _{AX}	$\delta_{29\text{Si}}$ calc / ppm	$\delta_{1\text{H}(\text{SiH})}$ calc / ppm	$^1J_{\text{HSi}}$ calc / Hz	$\Delta G^\ddagger$ / Eh	rel. $\Delta G^\ddagger$ / kJ mol ⁻¹
10_{exp}	NH	H	-87.8 _{exp}	4.81 _{exp}	197 _{exp}		
10_{exp}	NDipp	OSiPh ₃	-92.1 _{exp}	5.91 _{exp}	280 _{exp}		
10-I	NDipp	H	-118.6	6.05	-154	-2385.73340030	+12.82
1011-II	NH	H	-100.1	4.75	-187	-2385.73738102	+2.37
11-I	NDipp	Ph	*	*	*	*	*
11-II	NH	Ph	-101.9	6.83	-213	-2385.72991426	+21.97
11-III	NDipp	OSiPh ₃	-98.7	5.64	-245	-2385.73828349	0.00
11-IV	NH	OSiPh ₃	-117.2	6.62	-184	-2385.73127417	+18.40
1011-II^a	NH	H				-2386.02091303	0.00
11-III^a	NDipp	OSiPh ₃				-2386.01916189	+4.60

* Starting geometries of **11-I** resulted in **10-II**.

^a Calculated with PBE0 / def2-SVP / D3BJ / CPCM(THF)

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

Table 3.5: Calculated energies of *N*-*t*Bu substituted, pentacoordinate species.

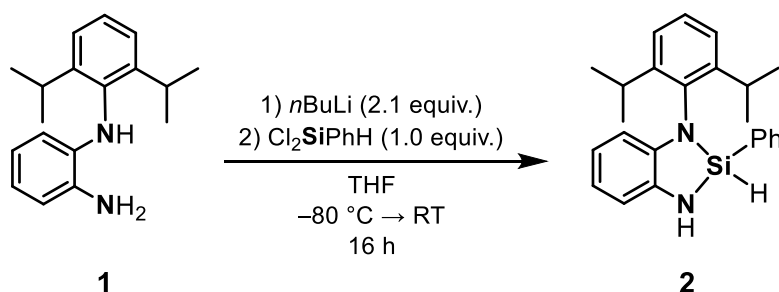
N _{Ax}	R _{Ax}	$\Delta G^\ddagger$ / Eh	rel. $\Delta G^\ddagger$ / kJ mol ⁻¹
N <i>t</i> Bu	H	-2076.14585473	+17.86
NH	H	-2076.14262062	+26.35
N <i>t</i> Bu	Ph	-2076.14665716	+15.75
NH	Ph	-2076.13304031	+51.51
N <i>t</i> Bu	OSiPh ₃	-2076.15265776	0.0
NH	OSiPh ₃	-2076.13450038	+47.67

3.7.4 General Remarks for Syntheses

All experiments were performed in an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated to 140 °C prior to use. Dichloromethane (DCM), diethyl ether (Et₂O), *n*-hexane, tetrahydrofuran (THF) and *n*-pentane were dried and degassed with an MBraun SP800 solvent purification system. *n*-Butyllithium (2.5 M solution in hexane, Merck KGaA), dichlorophenylsilane (96%, abcr GmbH), trichlorophenylsilane (97%, Alfa Aesar) and triphenylsilanol (98%, Merck KGaA) were used as received without further purification. Triethylamine ($\geq 99\%$, Merck KGaA) was heated at reflux over CaH₂ and distilled prior to use. Compounds **1** and **4** were synthesized according to a previously published procedure.^[1,54–56] C₆D₆ ($\geq 99.6\%$, Merck) and THF-*d*₈ (99.5%, Eurisotop) were degassed and dried over molecular sieve (3 Å) prior to use. NMR spectra were either recorded using a Bruker Avance 400 (400.13 MHz) or a Bruker Avance III HD 400 (400.13 MHz) at 298 K. Chemical shifts (δ) are reported in parts per million (ppm). ¹H and ¹³C{¹H} NMR spectra are referenced to tetramethylsilane (SiMe₄, δ = 0.0 ppm) as external standard, with the deuterium signal of the solvent serving as internal lock and the residual solvent signal as an additional reference. For the assignment of the multiplicities, the following abbreviations are used: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet. For simplicity, multiplets of order higher than one are described by approximating them to the closest first-order type. Elemental analyses were performed on a Vario MICRO cube apparatus. High-resolution mass spectrometry was conducted on a Jeol AccuTOF GCX and an Agilent Q-TOF 6540 UHD spectrometer.

3.7.5 Synthetic Procedures

3.7.5.1 Synthesis of Compound 2



Compound **1** was prepared according to a previously published literature procedure.^[1,54,55] Crystals suitable for single-crystal X-Ray diffraction analysis were obtained after recrystallization in diethyl ether at room temperature. The crystal structure has not been published yet; hence it is included.

Compound **1** (2.68 g, 10.0 mmol, 1.0 equiv.) was dissolved in THF (50 mL) and cooled to -80 °C. *n*-Butyllithium (8.0 mL of a 2.5 M solution in hexane, 20.0 mmol, 2.0 equiv.) was added dropwise. The solution was stirred for

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

10 minutes while warming up to room temperature. The resulting brown suspension was cooled to $-80\text{ }^{\circ}\text{C}$ again. Dichlorophenylsilane (1.46 mL, 10.0 mmol, 1.0 equiv.) was added via syringe and the reaction mixture was allowed to warm up to room temperature in 16 hours. Then, all volatiles were removed in vacuo. The residue was extracted with *n*-pentane ($3 \times 5\text{ mL}$) and the remaining solids filtered off via filter cannula. Colorless crystals suitable for single-crystal X-Ray diffraction analysis were obtained after storing the combined filtrates at $-20\text{ }^{\circ}\text{C}$ overnight (535 mg, 1.4 mmol, 14%).

^1H NMR (400 MHz, C_6D_6 , 298 K): $\delta = 0.37$ (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 3H, $\text{CH}(\text{CH}_3)_2$), 1.03 (d, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, 3H, $\text{CH}(\text{CH}_3)_2$), 3.02 (sept, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, 1H, $\text{CH}(\text{CH}_3)_2$), 3.16 (s, 1H, NH), 3.32 (sept, $^3J_{\text{H-H}} = 6.8\text{ Hz}$, 1H, $\text{CH}(\text{CH}_3)_2$), 6.14 (s, 1H, SiH), 6.13–6.17 (m, 1H, H_{Ar}), 6.59–6.62 (m, 1H, H_{Ar}), 6.63–6.69 (m, 1H, H_{Ar}), 6.76–6.82 (m, 1H, H_{Ar}), 7.00–7.09 (m, 3H, H_{Ar}), 7.12–7.18 (m, 2H, H_{Ar}), 7.36–7.41 (m, 2H, H_{Ar}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): $\delta = 23.6$ (s, CHCH_3), 24.8 (s, CHCH_3), 25.0 (s, CHCH_3), 25.5 (s, CHCH_3), 28.2 (s, CHCH_3), 28.5 (s, CHCH_3), 110.3 (s, CH_{Ar}), 11.3 (s, CH_{Ar}), 118.5 (s, CH_{Ar}), 118.7 (s, CH_{Ar}), 124.6 (s, CH_{Ar}), 124.9 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 131.6 (s, CH_{Ar}), 134.1 (s, C_{Ar}), 134.4 (s, C_{Ar}), 135.1 (s, CH_{Ar}), 138.3 (s, C_{Ar}), 141.3 (s, C_{Ar}), 148.6 (s, C_{Ar}), 149.3 (s, C_{Ar}).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, C_6D_6 , 298 K): $\delta = -13.8$ (s, Si).

^{29}Si NMR (79 MHz, C_6D_6 , 298 K): $\delta = -13.8$ (dm, $^1J_{\text{Si-H}} = 233.2\text{ Hz}$, Si).

CHN Analysis $\text{C}_{24}\text{H}_{28}\text{N}_2\text{Si}$: calculated: C 77.37, H 7.58, N 7.52, Si 7.54; found: C 77.38, H 7.17, N 7.30.

HR-MS(FD+) calculated m/z for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{Si}$ $[\text{M}+\text{H}^+]$: 372.20239; found: 372.20163.

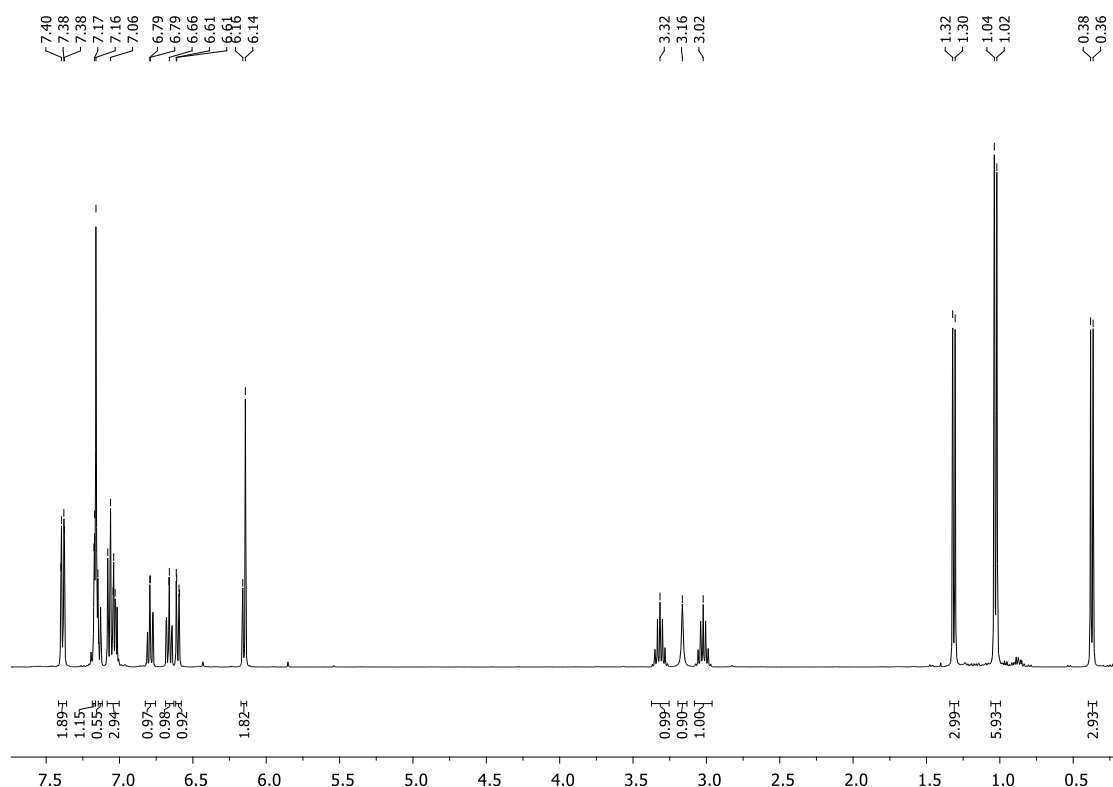


Figure 3.21: ^1H NMR spectrum (C_6D_6 , 298 K) of **2**.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

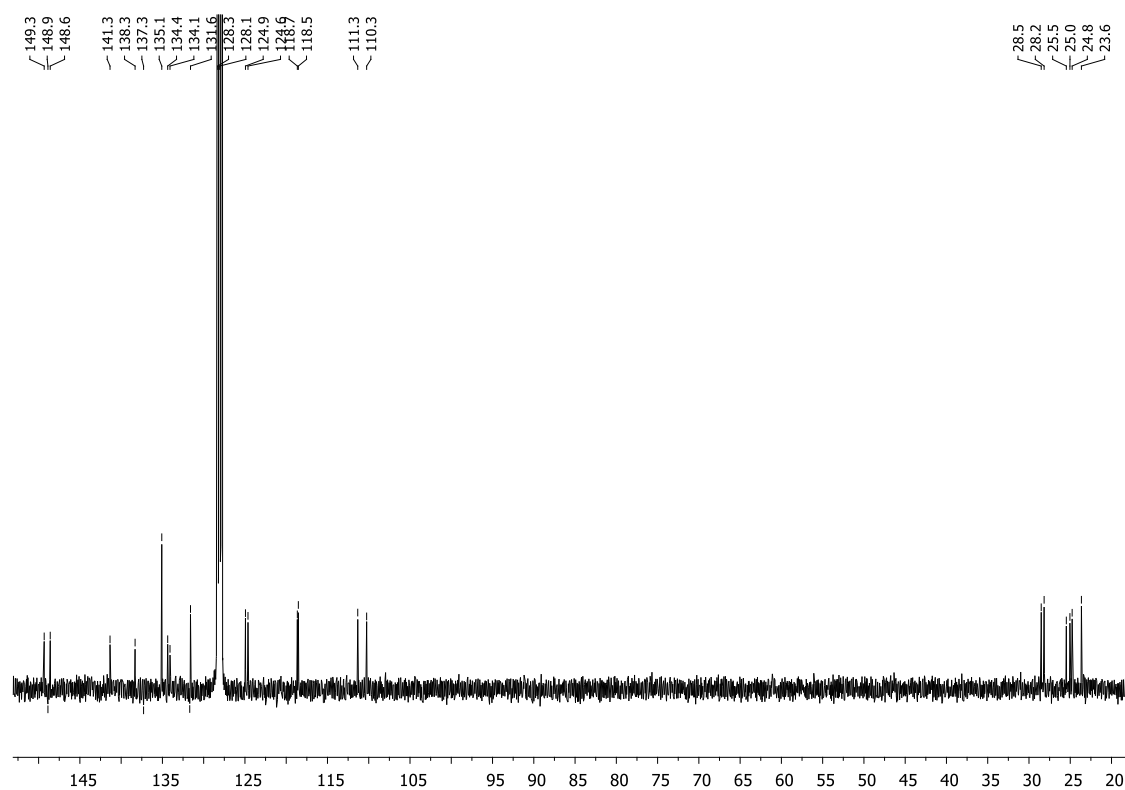


Figure 3.22: ¹H NMR spectrum (C₆D₆, 298 K) of **2**.

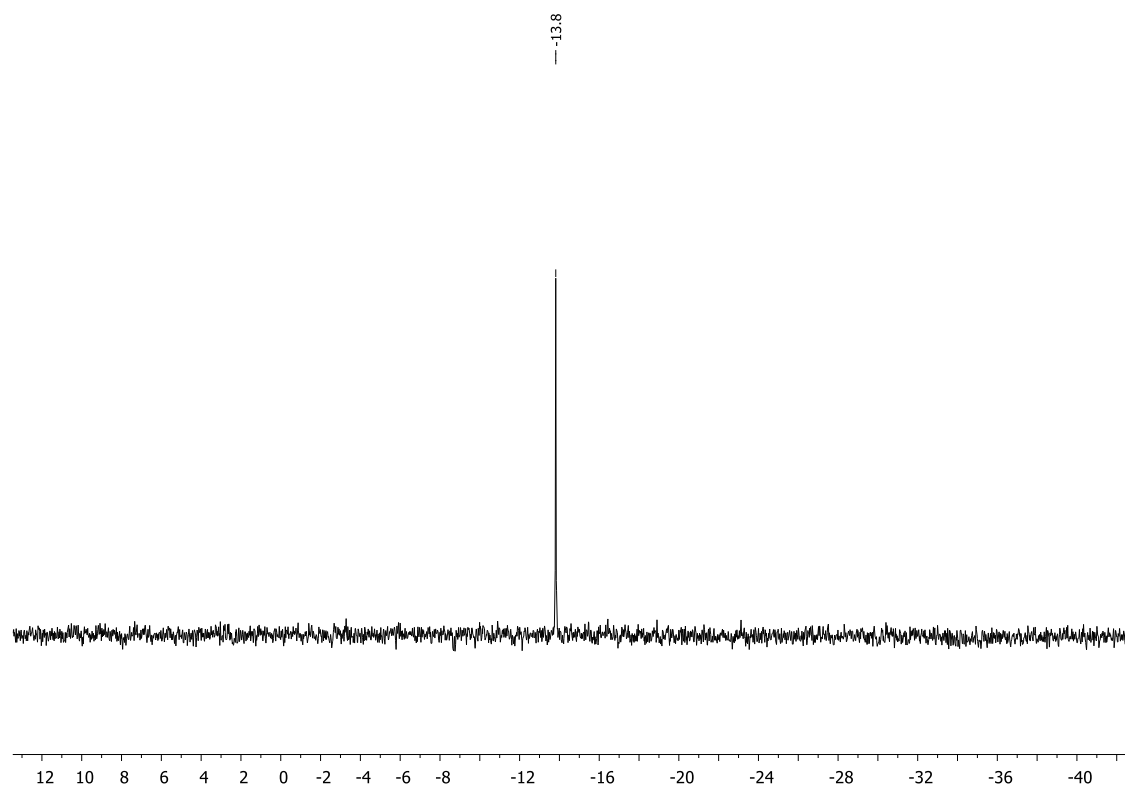


Figure 3.23: ²⁹Si{¹H} NMR spectrum (C₆D₆, 298 K) of **2**.

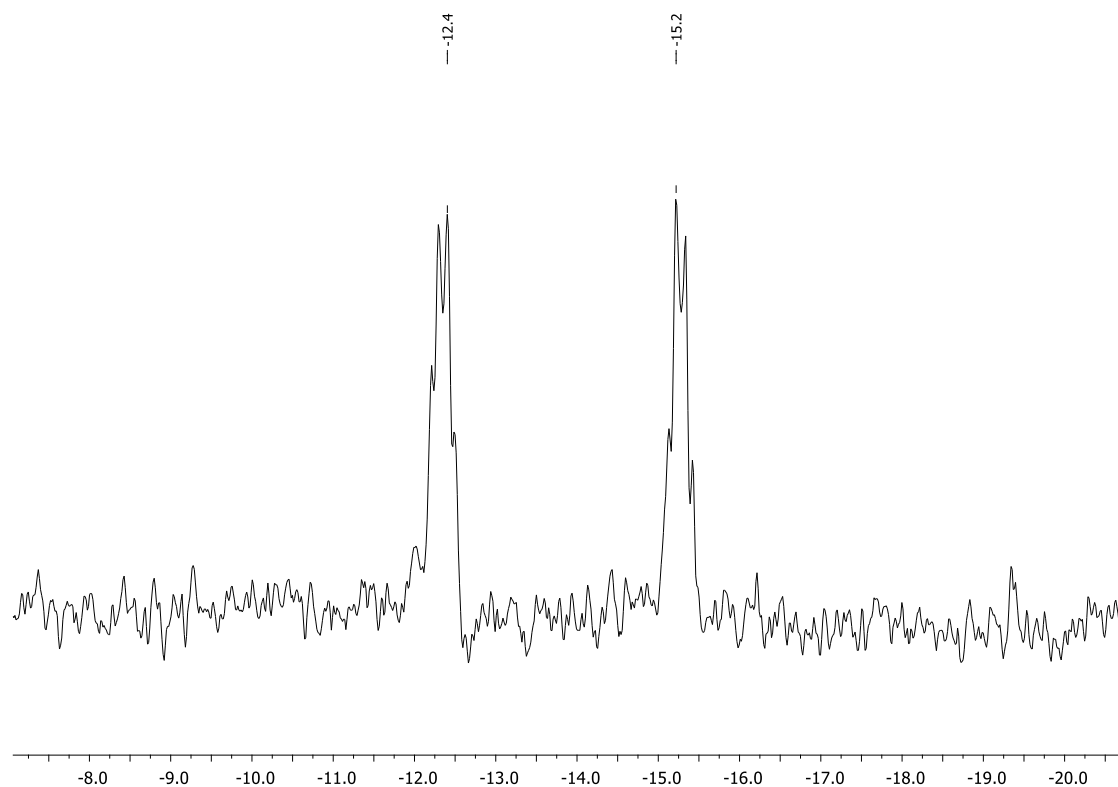
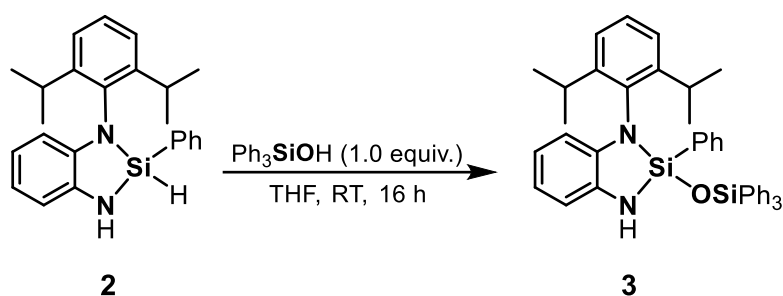


Figure 3.24: ^{29}Si NMR spectrum (C_6D_6 , 298 K) of **2**.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7.5.2 Synthesis of Compound 3



Compound **2** (373 mg, 1.0 mmol, 1.0 equiv.) and triphenylsilanol (276 mg, 1.0 mmol, 1.0 equiv.) were dissolved in THF (20 mL) and stirred at room temperature for 16 hours. Next, all volatiles were removed in vacuo. The residue was washed with *n*-pentane to afford compound **3** as a white solid (471 mg, 0.73 mmol, 73%). Crystals suitable for single-crystal X-Ray diffraction analysis were obtained by recrystallization from *n*-pentane.

^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 0.32 (d, 3H, $^3J_{\text{CH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_3$), 0.91 (d, 3H, $^3J_{\text{CH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_3$), 0.93 (d, 3H, $^3J_{\text{CH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_3$), 0.99 (d, 3H, $^3J_{\text{CH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_3$), 2.83 (sept, 1H, $^3J_{\text{CH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_3$), 3.62 (sept, 1H, $^3J_{\text{CH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_3$), 3.84 (s, 1H, NH), 6.15 (d, 1H, $^3J_{\text{CH}} = 7.6$ Hz, CH_{Ar}), 6.47 (dd, $^3J_{\text{CH}} = 7.5$ Hz, $^4J_{\text{CH}} = 1.1$ Hz, CH_{Ar}), 6.68 (td, $^3J_{\text{CH}} = 7.6$ Hz, $^4J_{\text{CH}} = 1.3$ Hz, CH_{Ar}), 6.80 (td, $^3J_{\text{CH}} = 7.5$ Hz, $^4J_{\text{CH}} = 1.2$ Hz, CH_{Ar}), 7.00–7.13 (m, 14H, CH_{Ar}), 7.17–7.21 (m, 2H, CH_{Ar}), 7.61–7.65 (m, 6H, CH_{Ar}), 7.69–7.72 (m, 2H, CH_{Ar}).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): δ = 23.4 (s, $\text{CH}(\text{CH}_3)_2$), 24.7 (s, $\text{CH}(\text{CH}_3)_2$), 25.5 (s, $\text{CH}(\text{CH}_3)_2$), 25.7 (s, $\text{CH}(\text{CH}_3)_2$), 28.3 (s, $\text{CH}(\text{CH}_3)_2$), 28.4 (s, $\text{CH}(\text{CH}_3)_2$), 111.0 (s, CH_{Ar}), 111.2 (s, CH_{Ar}), 118.7 (s, CH_{Ar}), 118.8 (s, CH_{Ar}), 124.5 (s, CH_{Ar}), 124.9 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 130.4 (s, CH_{Ar}), 130.9 (s, CH_{Ar}), 132.7 (s, C_{Ar}), 134.4 (s, C_{Ar}), 135.5 (s, C_{Ar}), 135.6 (s, CH_{Ar}), 135.9 (s, CH_{Ar}), 136.3 (s, C_{Ar}), 140.1 (s, C_{Ar}), 148.7 (s, C_{Ar}), 149.5 (s, C_{Ar}).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, C_6D_6 , 298 K): δ = -38.7 (s, SiN), -16.6 (s, SiPh_3).

CHN Analysis $\text{C}_{42}\text{H}_{42}\text{N}_2\text{OSi}$: calculated: C 77.97, H 6.54, N 4.33, O 2.47, Si 8.68; found: C 78.25, H 6.65, N 4.19.

HR-MS(FD+), calculated m/z for $\text{C}_{42}\text{H}_{42}\text{N}_2\text{OSi}$ [$\text{M}+\text{H}^+$]: 646.28302; found: 646.28402.

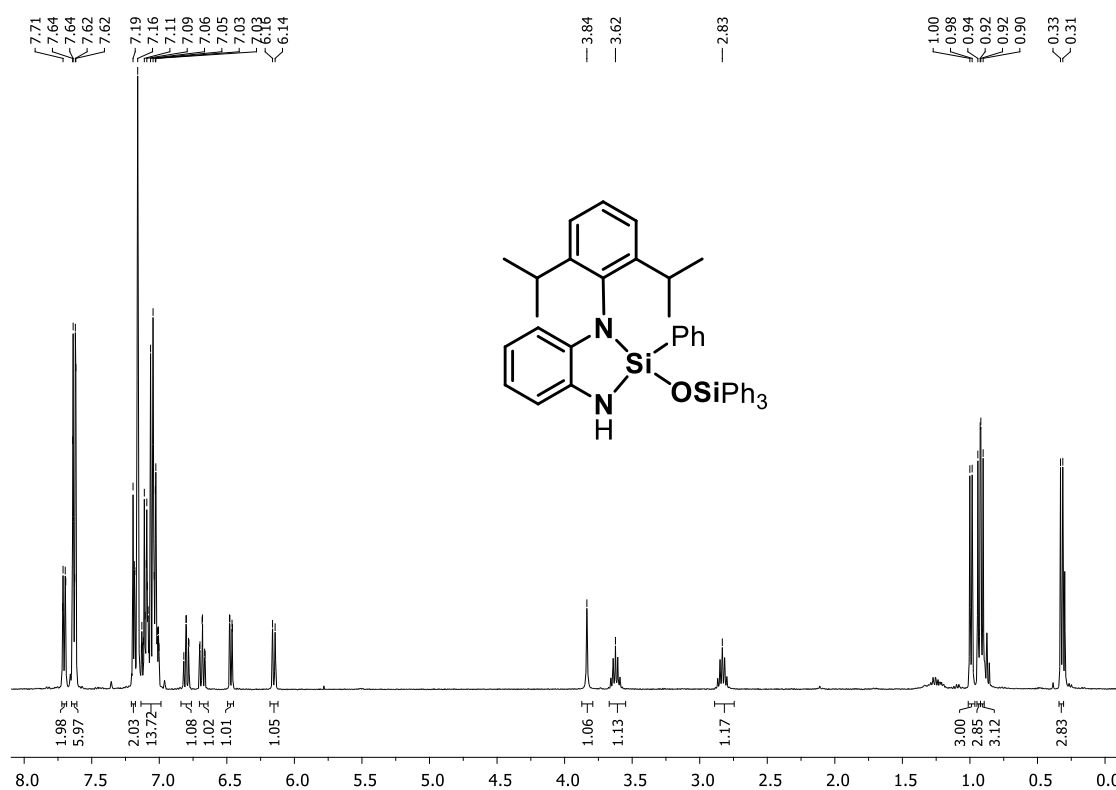


Figure 3.25: ¹H NMR spectrum (C₆D₆, 298 K) of 3.

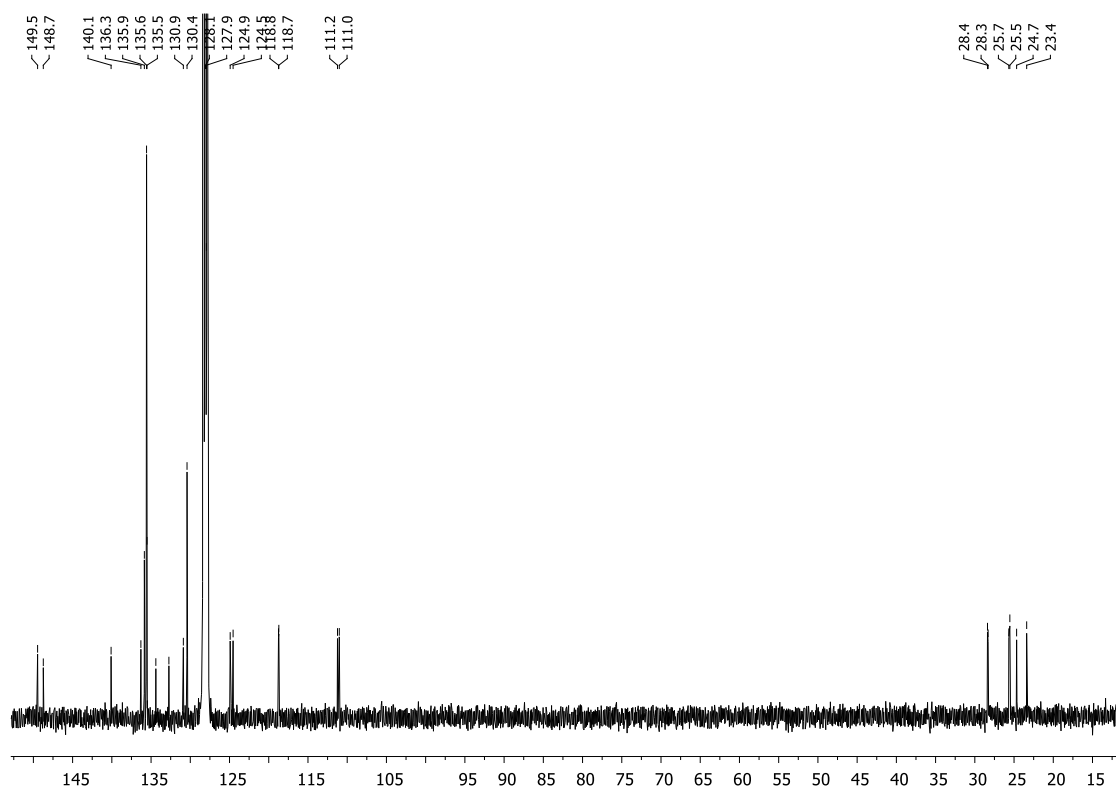


Figure 3.26: ¹³C NMR spectrum (C₆D₆, 298 K) of 3.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

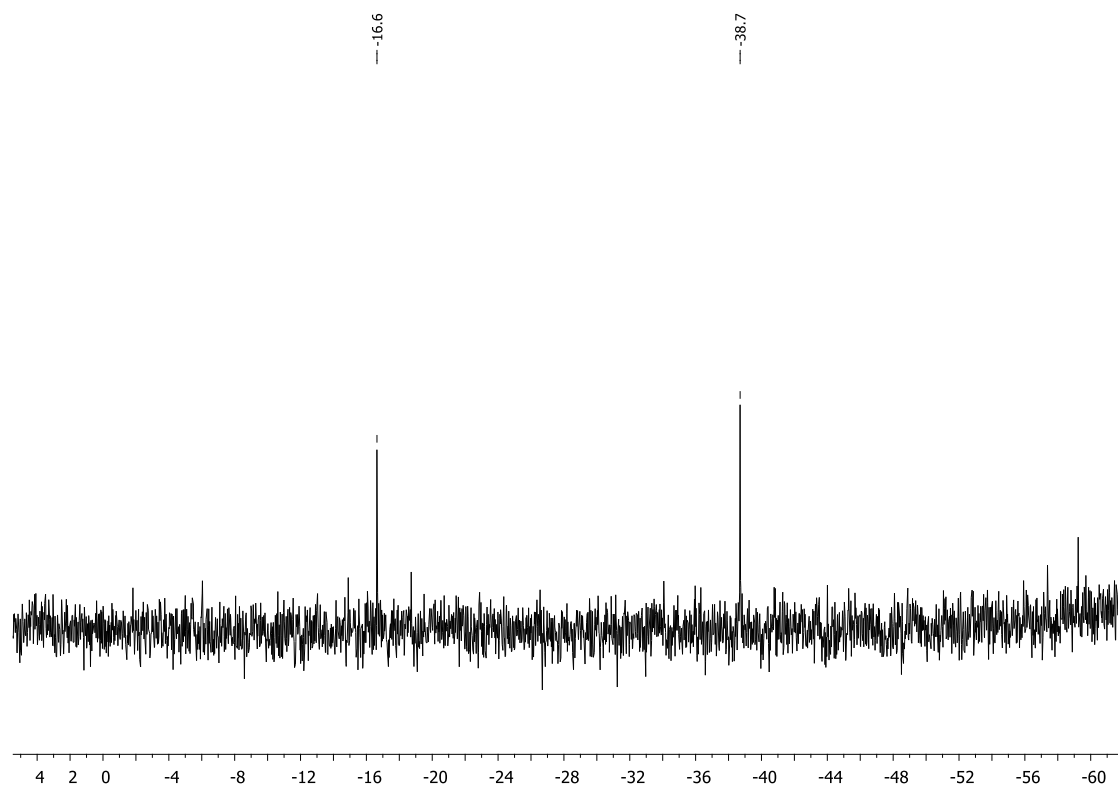
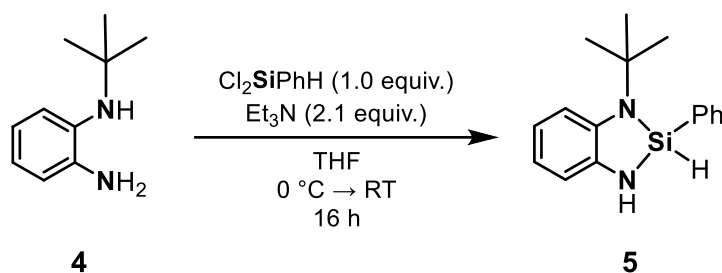


Figure 3.27: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K) of **3**.

3.7.5.3 Synthesis of Compound 5



Compound **4** was prepared according to a previously published literature procedure.^[1,55,56]

4 (1.64 g, 10.0 mmol, 1.0 equiv.) and triethylamine (2.90 mL, 21.0 mmol, 2.1 equiv.) were dissolved in THF (100 mL) and cooled to 0 °C. Dichlorophenylsilane (1.46 mL, 10.0 mmol, 1.0 equiv.) was added via syringe and the mixture was allowed to warm up to room temperature in 16 hours while stirring. The formed precipitate was filtered off via filter cannula. Next, all volatiles were removed in vacuo. The residue was extracted with *n*-hexane (4 × 10 mL) and the remaining solids filtered off via filter cannula. The filtrates were combined and dried in vacuo to afford compound **5** as a brown wax (1.16 g, 4.4 mmol, 44%).

¹H NMR (400 MHz, C₆D₆, 298 K): δ = 1.30 (s, 9H, CHCH₃), 3.00 (s, 1H, NH), 6.14 (s, 1H, SiH), 6.46–6.49 (m, 1H, *H*_{Ar}), 6.73–6.87 (m, 3H, *H*_{Ar}), 6.92–6.96 (m, 1H, *H*_{Ar}), 7.10–7.15 (m, 1H, *H*_{Ar}), 7.16–7.19 (m, 1H, *H*_{Ar}), 7.46–7.51 (m, 2H, *H*_{Ar}).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): δ = 29.6 (s, $\text{C}(\text{CH}_3)_3$), 52.5 (s, $\text{C}(\text{CH}_3)_3$), 11.3 (s, CH_{Ar}), 112.9 (s, CH_{Ar}), 117.7 (s, CH_{Ar}), 117.8 (s, CH_{Ar}), 128.5 (s, CH_{Ar}), 131.1 (s, CH_{Ar}), 134.0 (s, CH_{Ar}), 138.1 (s, C_{Ar}), 138.4 (s, C_{Ar}), 140.7 (s, C_{Ar}).

²⁹Si{¹H} NMR (79 MHz, C₆D₆, 298 K): δ = -18.0 (s, Si).

^{29}Si NMR (79 MHz, C_6D_6 , 298 K): $\delta = -18.0$ (dm, $^1J_{\text{SiH}} = 233.6$ Hz, *Si*).

CHN Analysis C₁₆H₂₀N₂Si • 0.1 DCM: calculated: C 69.83, H 7.35, N 10.12; found: C 69.87, H 7.52, N 10.05.

HR-MS(EI+), calculated m/z for C₁₆H₂₀N₂Si [M+H⁺]: 268.13903; found: 268.13984.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

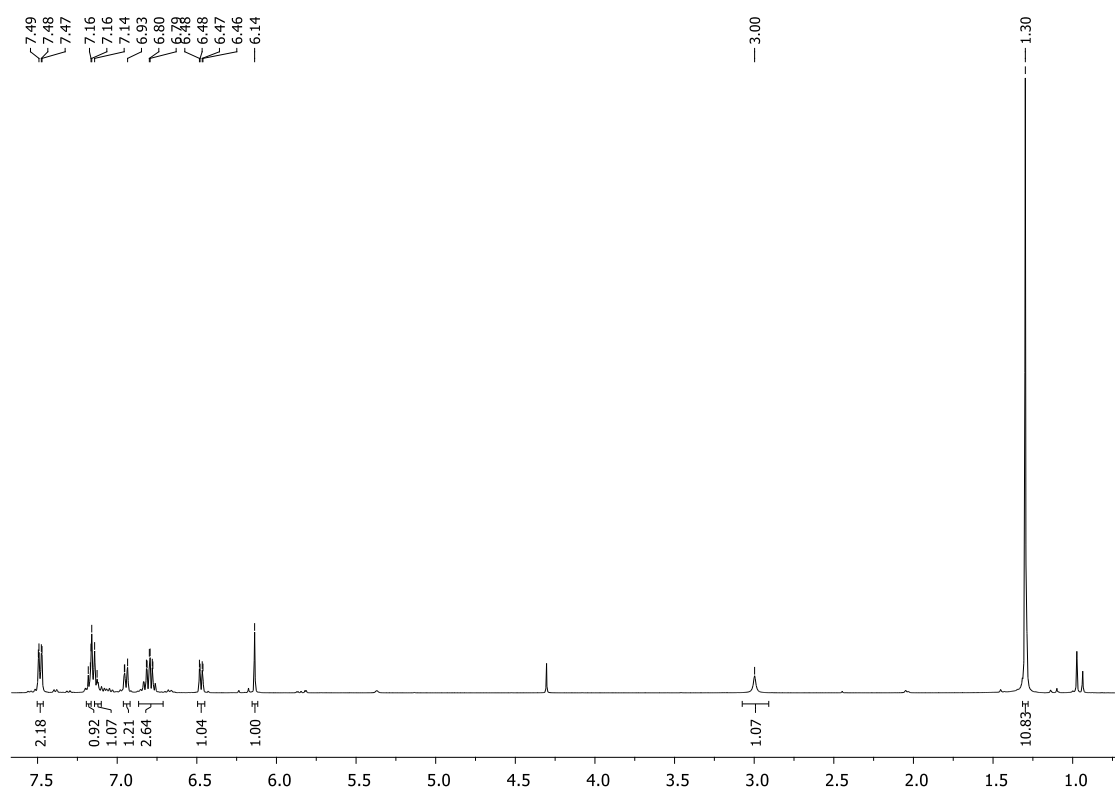


Figure 3.28: ¹H NMR spectrum (C₆D₆, 298 K) of **5**.

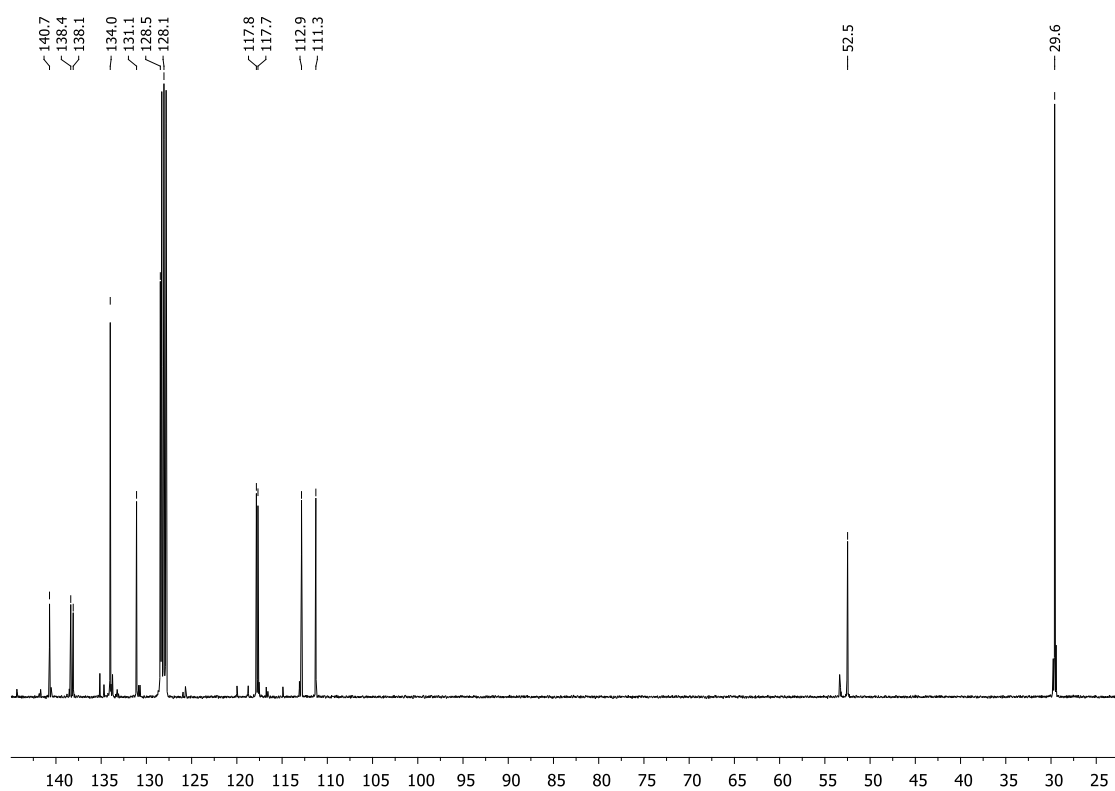


Figure 3.29: ¹³C{¹H} NMR spectrum (C₆D₆, 298 K) of **5**.

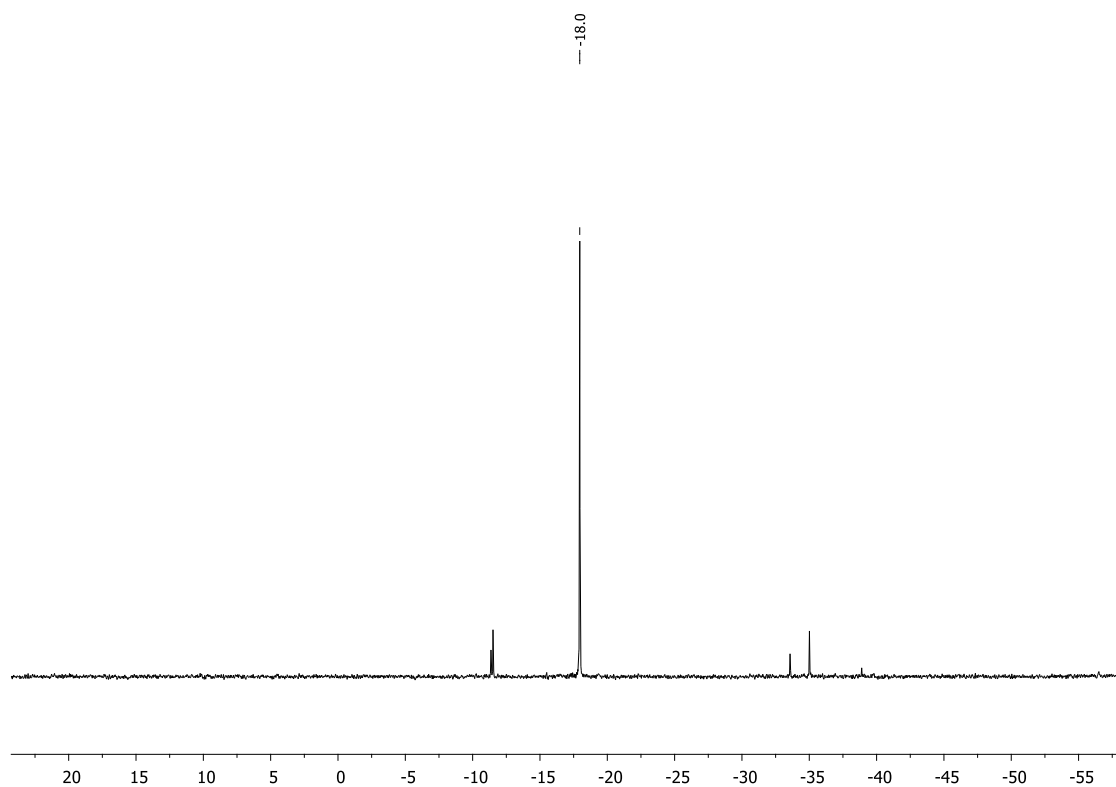


Figure 3.30: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K) of **5**.

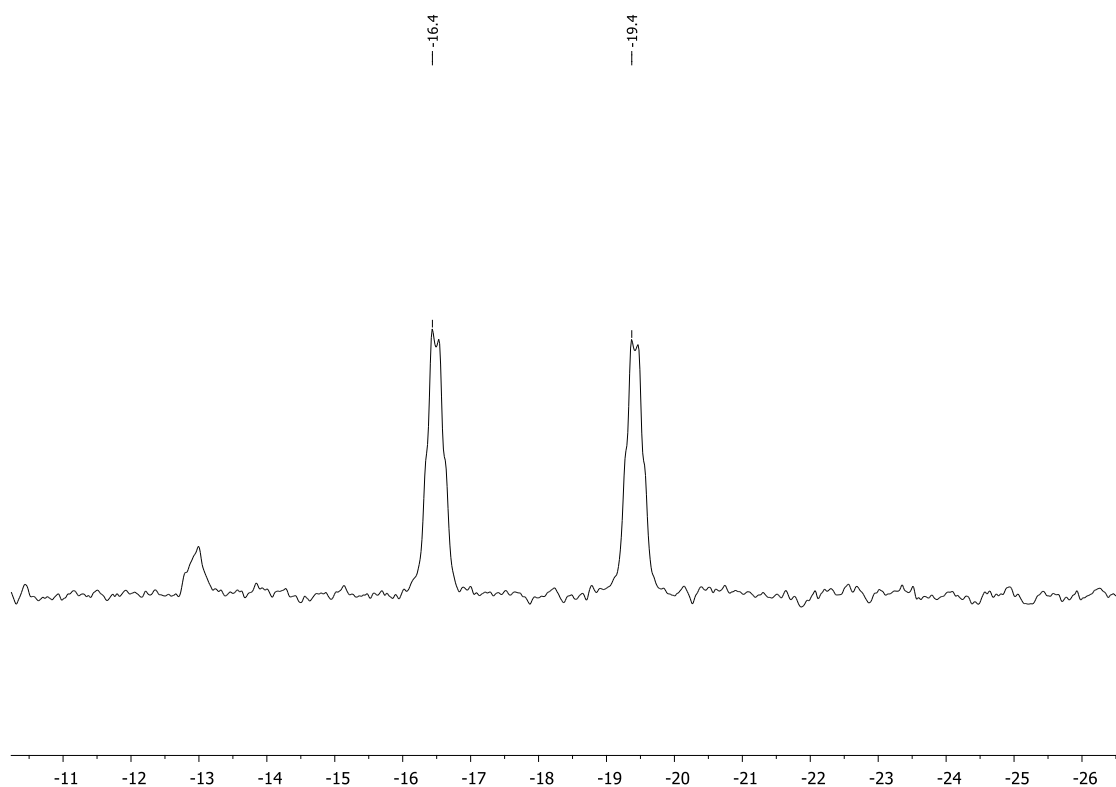
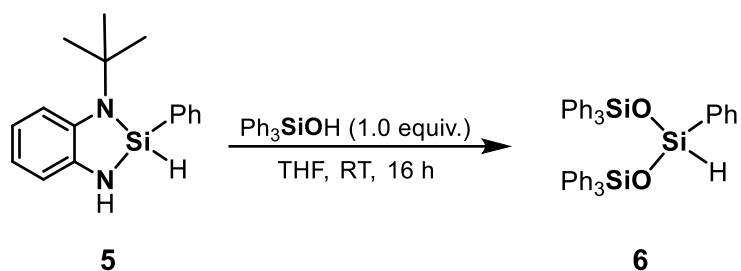


Figure 3.31: ^{29}Si NMR spectrum (C_6D_6 , 298 K) of **5**.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7.5.4 Synthesis of Compound 6



Compound **5** (1.34 g, 5.0 mmol, 1.0 equiv.) and triphenylsilanol (1.38 g, 5.0 mmol, 1.0 equiv.) were dissolved in THF (50 mL) and stirred at room temperature for 16 hours. Next, all volatiles were removed in vacuo. The residue was extracted with *n*-pentane (50 mL) and the solids filtered off via filter cannula. Crystals suitable for single-crystal X-Ray diffraction analysis were obtained by storing the red filtrate at 8 °C for one day. The crystals were isolated via filter cannula and washed with *n*-pentane to afford compound **6** as an off-white crystalline solid (680 mg, 1.0 mmol, 20%).

¹H NMR (400 MHz, C₆D₆, 298 K): δ = 5.80 (s, 1H, SiH), 6.97–7.15 (m, 20H, *H*_{Ar}), 7.17–7.19 (m, 1H, *H*_{Ar}), 7.57–7.61 (m, 2H, *H*_{Ar}), 7.63–7.68 (m, 12H, *H*_{Ar}).

¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ = 138.2 (s, CH_{Ar}), 130.2 (s, CH_{Ar}), 130.7 (s, CH_{Ar}), 138.8 (s, CH_{Ar}), 156.6 (s, CH_{Ar}), 135.9 (s, C_{Ar}).

²⁹Si{¹H} NMR (79 MHz, C₆D₆, 298 K): δ = -46.6 (s, SiH), -17.9 (s, SiPh₃).

²⁹Si NMR (79 MHz, C₆D₆, 298 K): δ = -46.2 (dm, ¹*J*_{SiH} = 250.5 Hz, SiH), -17.4 (m, SiPh₃).

CHN Analysis C₄₂H₃₆O₂Si₃: calculated: C 76.78, H 5.52, O 4.87, Si 12.82; found: C 76.68, H 5.43.

HR-MS(FD+), calculated *m/z* for C₄₂H₃₆O₂Si₃ [M+H⁺]: 656.20176; found: 656.20401.

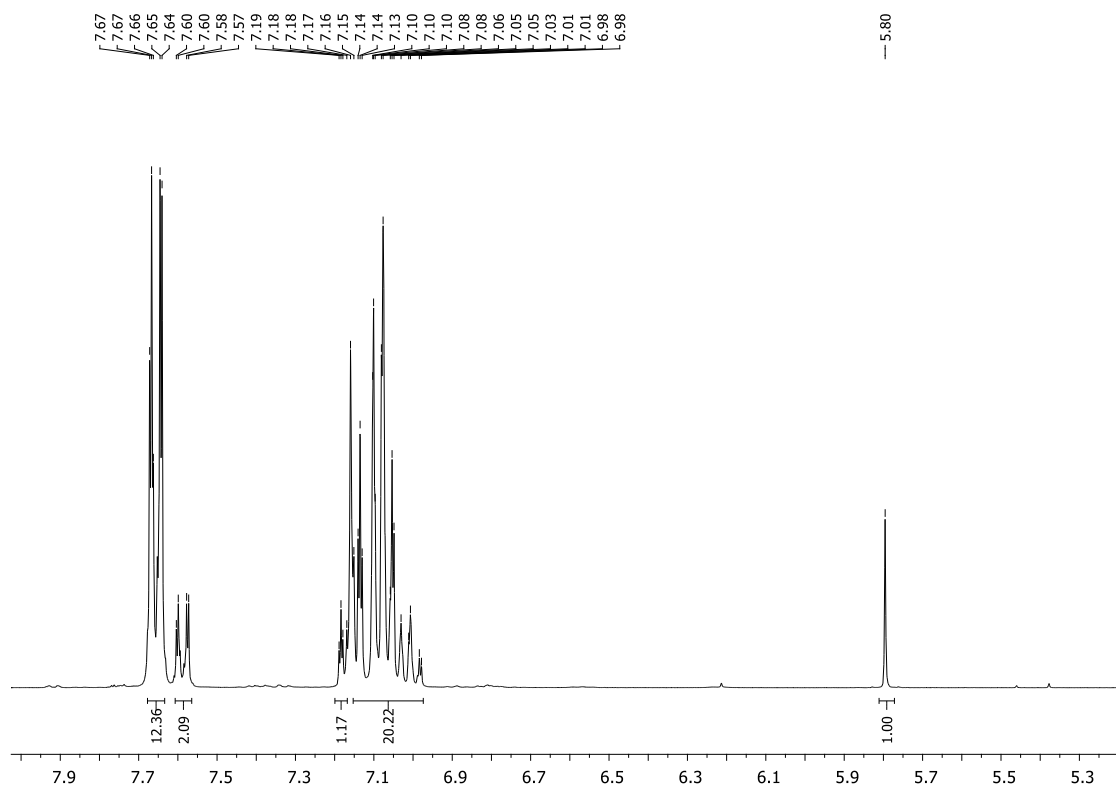


Figure 3.32: ¹H NMR spectrum (C₆D₆, 298 K) of **6**.

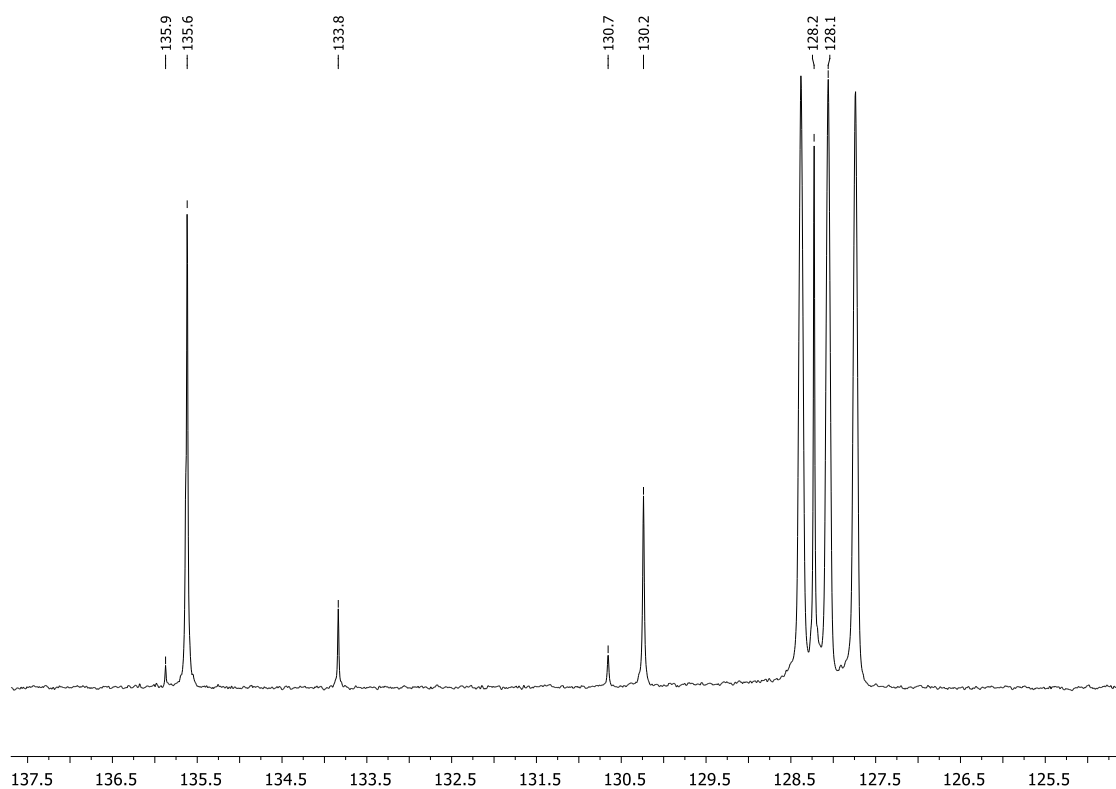


Figure 3.33: ¹³C{¹H} NMR spectrum (C₆D₆, 298 K) of **6**.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

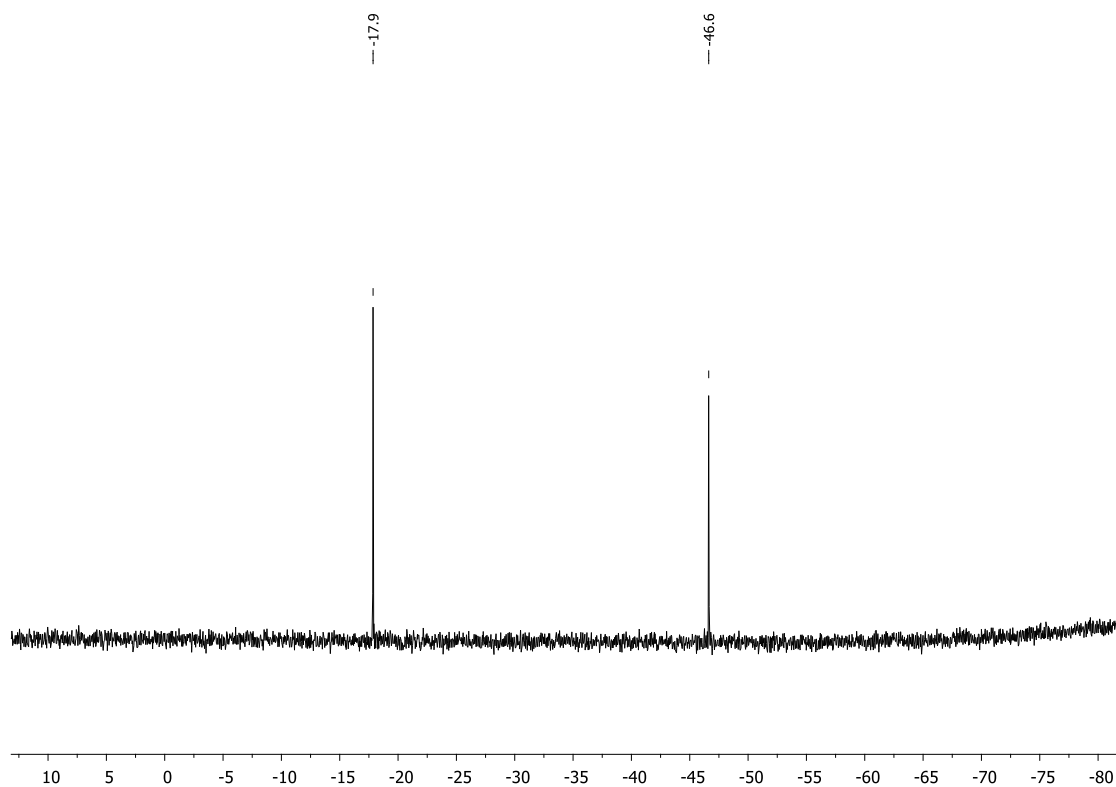


Figure 3.34: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K) of **6**.

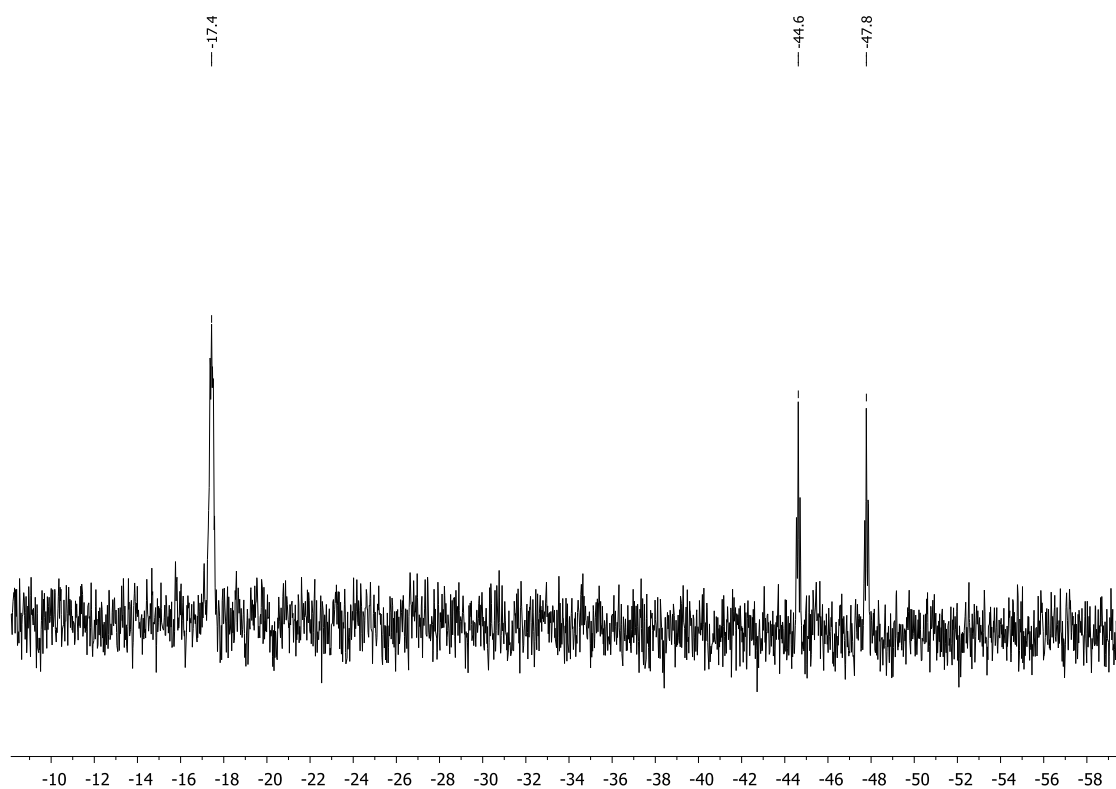
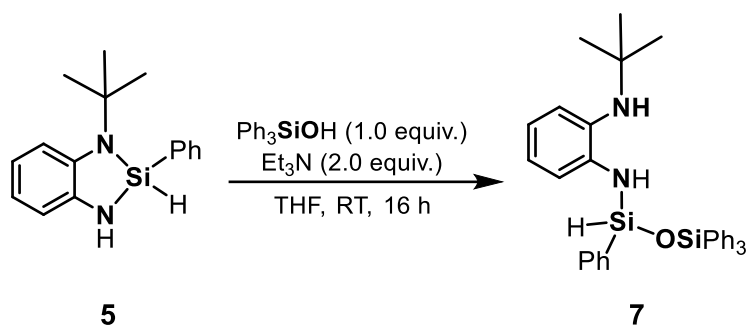


Figure 3.35: ^{29}Si NMR spectrum (C_6D_6 , 298 K) of **6**.

3.7.5.5 Synthesis of Compound 7



Compound **5** (130 mg, 0.48 mmol, 1.0 equiv.) and triethylamine (0.13 mL, 0.96 mmol, 2.0 equiv.) were dissolved in THF (10 mL). Triphenylsilanol (133 mg, 0.48 mmol, 1.0 equiv.) was added and the solution was stirred at room temperature for 16 hours. Next, all volatiles were removed in vacuo. The residue was dissolved in *n*-pentane (20 mL) and cooled to -80 °C, after which precipitation was observed. The solids were isolated via cannula filtration. Upon warming up to room temperature, the solids turned into a brown wax, which was layered with *n*-pentane (1 mL) and stored at 8 °C. Crystals suitable for single-crystal X-Ray diffraction analysis were obtained after two weeks. The crystals were isolated via filter cannula and washed with *n*-pentane to afford compound **7** as a white crystalline solid (8 mg, 0.01 mmol, 3%).

¹H NMR (400 MHz, C₆D₆, 298 K): δ = 0.98 (s, 9H, C(CH₃)₃), 2.03 (s, 1H, *t*Bu-NH), 5.71 (d, 1H, ³*J*_{HH} = 3.0 Hz, Si-NH), 5.81 (d, 1H, ³*J*_{HH} = 3.1 Hz, SiH), 6.67–6.72 (m, 1H, *H*_{Ar}), 6.77–6.83 (m, 2H, *H*_{Ar}), 7.05–7.16 (m, 8H, *H*_{Ar}), 7.16–7.21 (m, 3H, *H*_{Ar}), 7.73–7.78 (m, 8H, *H*_{Ar}).

¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ = 29.8 (s, C(CH₃)₃), 53.4 (s, C(CH₃)₃), 117.0 (s, CH_{Ar}), 118.9 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 130.3 ((s, CH_{Ar}), 130.7 (s, CH_{Ar}), 133.1 (s, C_{Ar}), 134.3 (s, CH_{Ar}), 135.3 (s, C_{Ar}), 135.7 (s, CH_{Ar}), 135.8 (s, C_{Ar}), 144.2 (s, C_{Ar}).

²⁹Si{¹H} NMR (79 MHz, C₆D₆, 298 K): δ = -38.7 (s, SiH), -17.6 (s, SiPh₃).

²⁹Si NMR (79 MHz, C₆D₆, 298 K): δ = -38.7 (d, ¹*J*_{SiH} = 240.6 Hz, SiH), -17.6 (s, SiPh₃).

CHN Analysis C₃₄H₃₆N₂OSi₂: calculated: C 74.95, H 6.66, N 5.14, O 2.94, Si 10.31; found: C 75.00, H 6.53, N 5.10.

HR-MS(FD+), calculated *m/z* for C₃₄H₃₆N₂OSi₂ [M+H⁺]: 544.23607; found: 544.23416.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

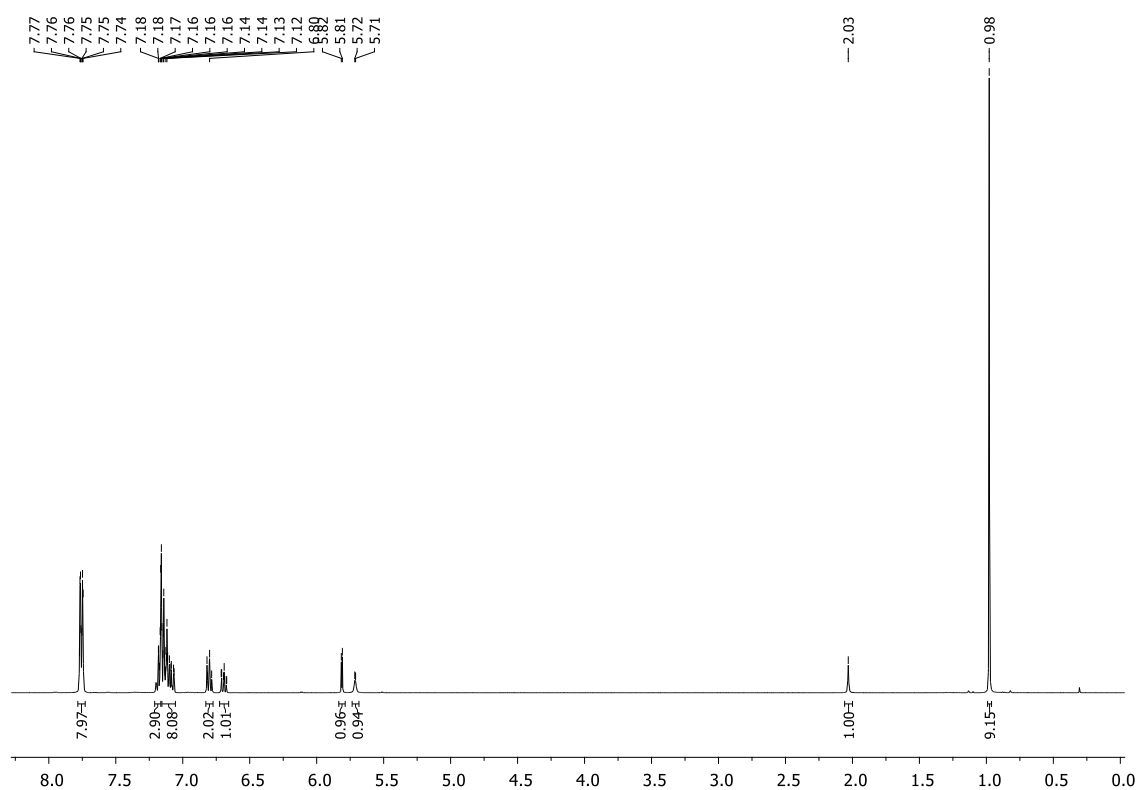


Figure 3.36: ¹H NMR spectrum (C₆D₆, 298 K) of 7.

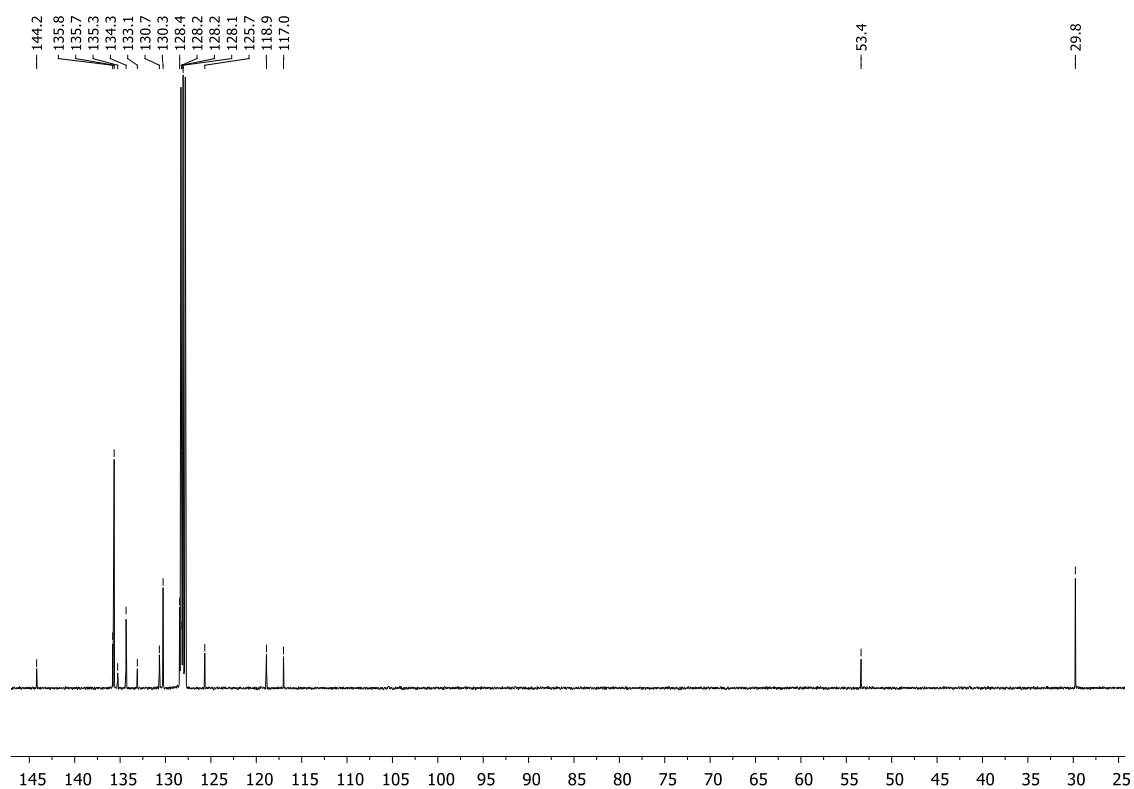


Figure 3.37: ¹³C{¹H} NMR spectrum (C₆D₆, 298 K) of 7.

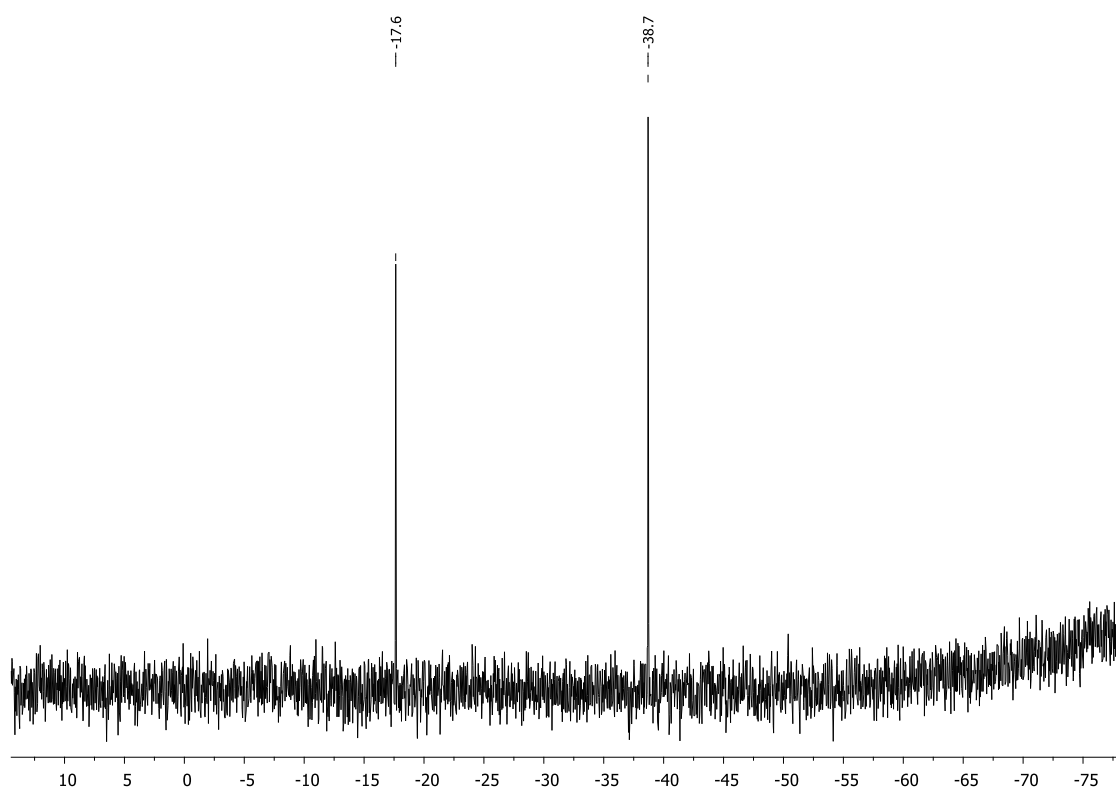


Figure 3.38: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K) of **7**.

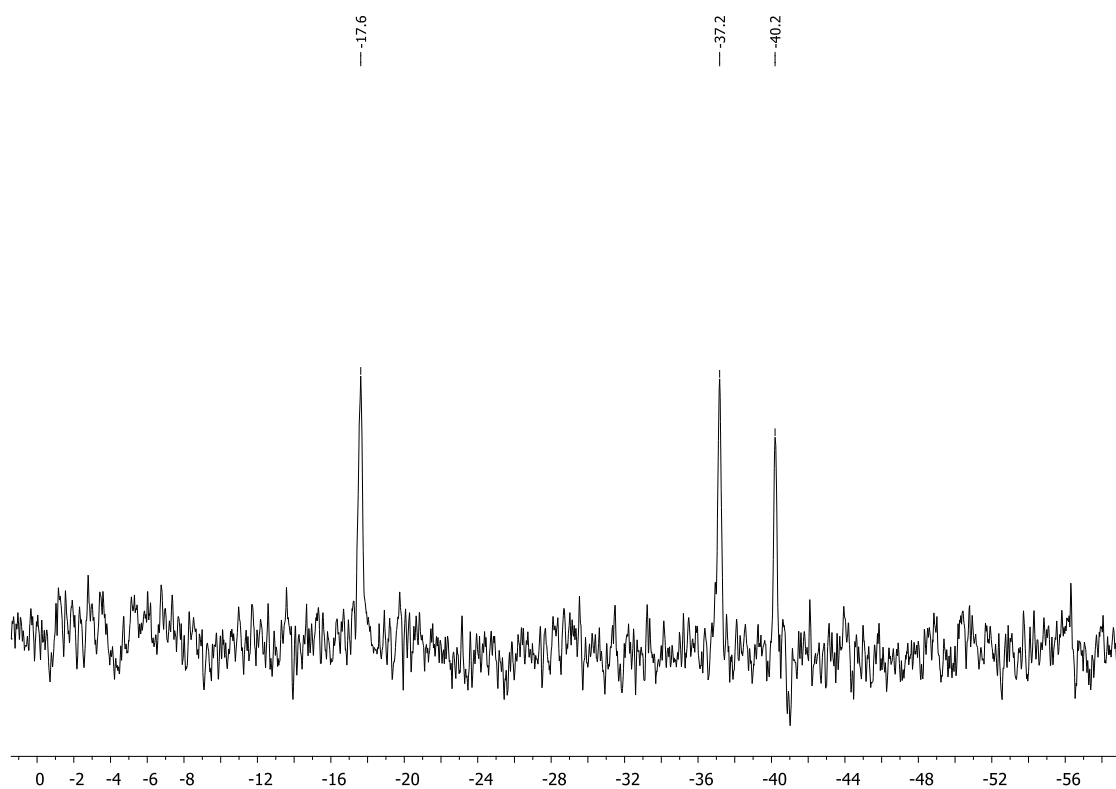
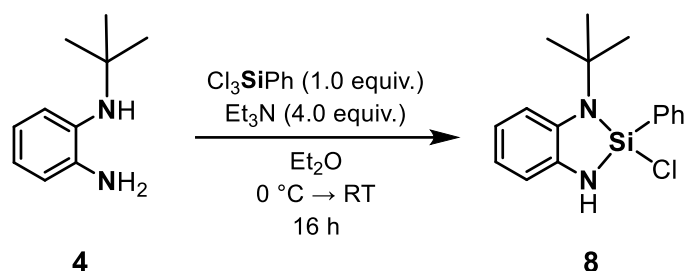


Figure 3.39: ^{29}Si NMR spectrum (C_6D_6 , 298 K) of **7**.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7.5.6 Synthesis of Compound 8



Compound **4** (1.64 g, 10.0 mmol, 1.0 equiv.) and triethylamine (5.58 mL, 40.0 mmol, 4.0 equiv.) were dissolved in diethylether (30 mL) and cooled to 0 °C. Trichlorophenylsilane (1.60 mL, 10.0 mmol, 1.0 equiv.) was added via syringe and the mixture was allowed to warm up to room temperature in 16 hours while stirring. The formed precipitate was filtered off via filter cannula. The filtrates were dried in vacuo to afford compound **8** as a brown wax (3.13 g, 10.0 mmol, 99%).

¹H NMR (400 MHz, C₆D₆, 298 K): δ = 1.35 (s, 9H, C(CH₃)₃), 3.45 (s, 1H, NH), 6.47–6.50 (m, 1H, *H*_{Ar}), 6.80–6.88 (m, 2H, *H*_{Ar}), 7.00–7.04 (m, 1H, *H*_{Ar}), 7.09–7.15 (m, 3H, *H*_{Ar}), 7.72–7.75 (m, 2H, *H*_{Ar}).

¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ = 29.7 (s, C(CH₃)₃), 53.2 (s, C(CH₃)₃), 111.9 (s, CH_{Ar}), 114.0 (s, CH_{Ar}), 118.5 (s, CH_{Ar}), 118.5 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 131.4 (s, CH_{Ar}), 134.9 (s, C_{Ar}), 135.4 (s, CH_{Ar}), 136.4 (s, C_{Ar}), 137.7 (s, C_{Ar}).

²⁹Si{¹H} NMR (79 MHz, C₆D₆, 298 K): δ = -18.4 (s, Si).

CHN Analysis C₁₆H₁₉ClN₂Si: calculated: C 63.45, H 6.32, Cl 11.70, N 9.25, Si 9.27; found: C 63.07, H 6.56, N 9.25.

HR-MS(EI+), calculated *m/z* for C₁₆H₁₉ClN₂Si [M+H⁺]: 302.10005; found: 302.09939.

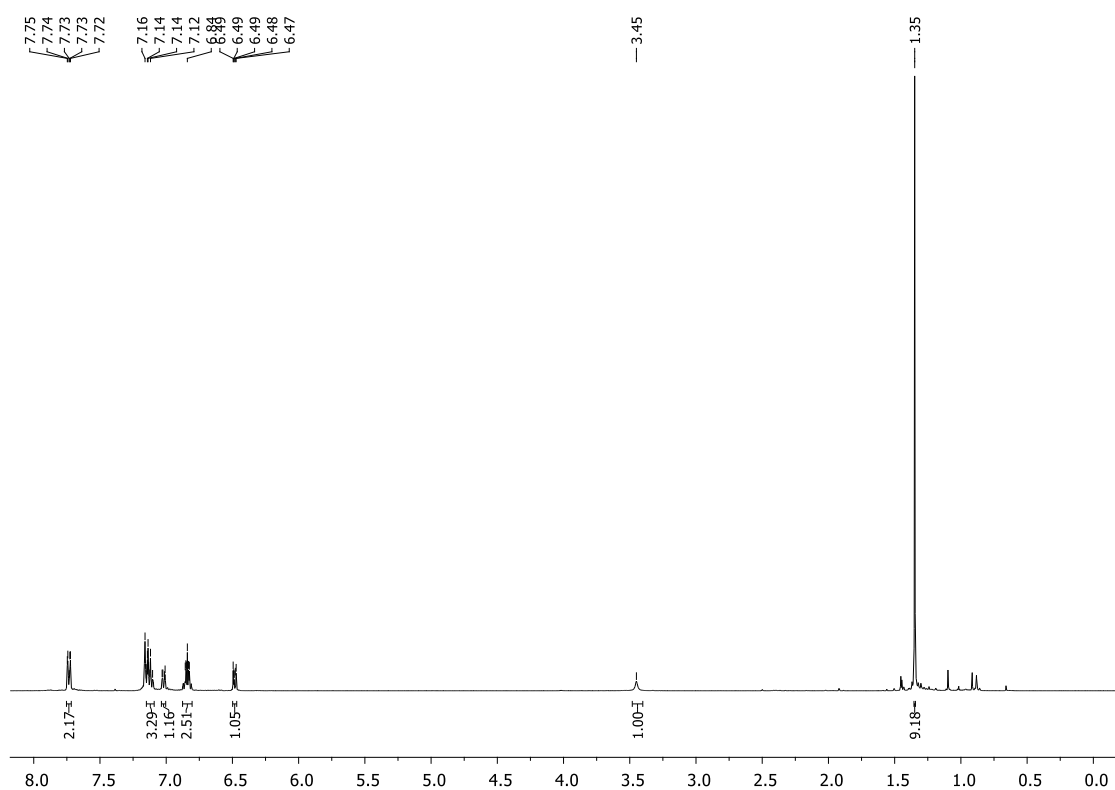


Figure 3.40: ¹H NMR spectrum (C₆D₆, 298 K) of **8**.

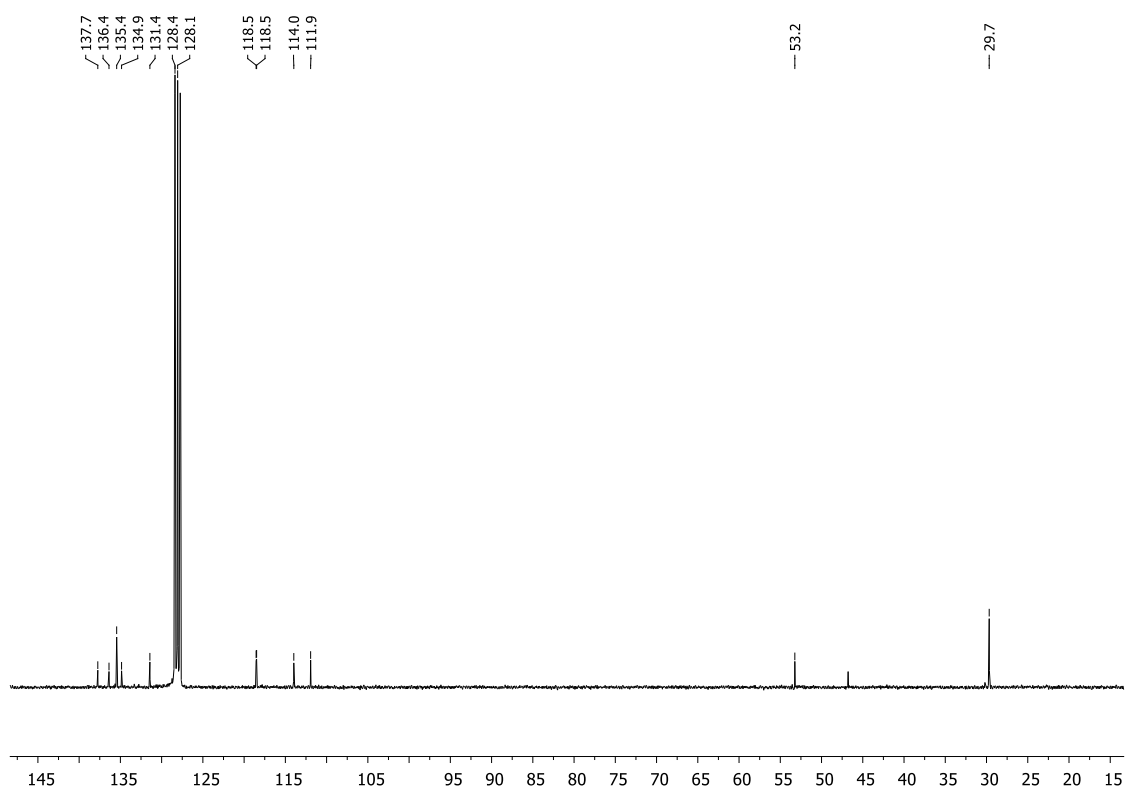


Figure 3.41: ¹³C{¹H} NMR spectrum (C₆D₆, 298 K) of **8**.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

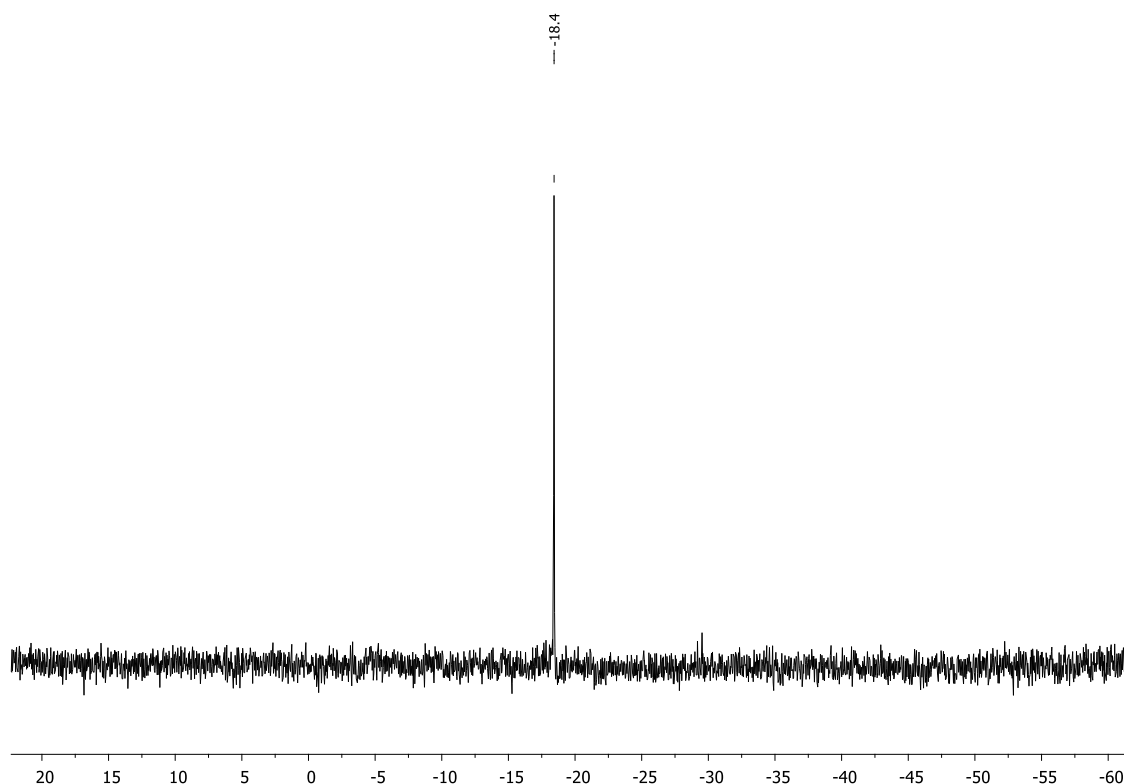
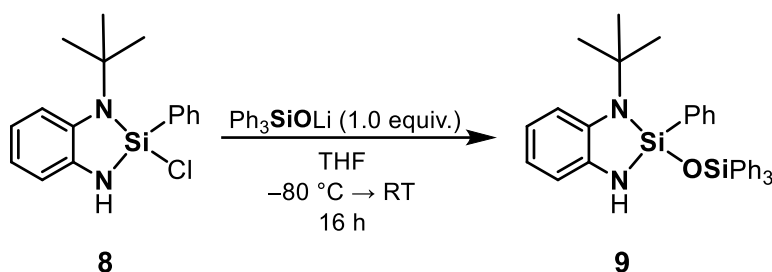


Figure 3.42: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K) of **8**.

3.7.5.7 Synthesis of Compound **9**



Triphenylsilanol (2.76 g, 10.0 mmol, 1.0 equiv.) was dissolved in THF (30 mL) and *n*-butyllithium (4.40 mL of a 2.5 M solution in hexane, 11.0 mmol, 1.1 equiv.) was added dropwise. The mixture was stirred at room temperature for 10 minutes, after which it was cooled to $-80\text{ }^{\circ}\text{C}$. Compound **8** (20 mL of a 0.5 M solution in THF, 10.0 mmol, 1.0 equiv.) was added via cannula and the reaction mixture was allowed to warm up to room temperature in 16 hours. Then, all volatiles were removed in vacuo. The residue was washed with *n*-pentane ($3 \times 20\text{ mL}$). The remaining crude product was dissolved in DCM (20 mL) and the remaining solids filtered off via filter cannula. The brown filtrates were dried in vacuo, resulting in a brownish solid. Crystals suitable for single-crystal X-Ray diffraction analysis were obtained after recrystallization in *n*-pentane (2.36 g, 4.3 mmol, 43%).

^1H NMR (400 MHz, C_6D_6 , 298 K): δ = 1.27 (s, 9H, $\text{C}(\text{CH}_3)_3$), 3.47 (s, 1H, NH), 6.31 (dd, $^3J_{\text{H-H}} = 7.4\text{ Hz}$, $^4J_{\text{H-H}} = 1.4\text{ Hz}$, 1H, H_{Ar}), 6.81 (td, $^3J_{\text{H-H}} = 7.5\text{ Hz}$, $^4J_{\text{H-H}} = 1.0\text{ Hz}$, 1H, H_{Ar}), 6.88 (td, $^3J_{\text{H-H}} = 7.6\text{ Hz}$, $^4J_{\text{H-H}} = 1.4\text{ Hz}$, 1H, H_{Ar}), 6.95–6.99 (m, 1H, H_{Ar}), 7.09–7.16 (m, 11H, H_{Ar}), 7.16–7.19 (m, 1H, H_{Ar}), 7.68–7.73 (m, 6H, H_{Ar}), 7.78–7.82 (m, 2H, H_{Ar}).

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): δ = 29.5 (s, $\text{C}(\text{CH}_3)_3$), 52.5 (s, $\text{C}(\text{CH}_3)_3$), 113.3 (s, CH_{Ar}), 113.1 (s, CH_{Ar}), 117.7 (s, CH_{Ar}), 117.8 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 130.4 (s, CH_{Ar}), 130.6 (s, CH_{Ar}), 135.6 (s, CH_{Ar}), 135.6 (s, CH_{Ar}), 136.3 (s, C_{Ar}), 137.1 (s, C_{Ar}), 138.0 (s, C_{Ar}).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, C_6D_6 , 298 K): δ = -40.0 (s, SiPh_3), -17.0 (s, SiN).

CHN Analysis $\text{C}_{34}\text{H}_{34}\text{N}_2\text{OSi}_2$: calculated: C 75.23, H 6.31, N 5.16, O 2.95, Si 10.35; found: C 74.58, H 6.11, N 5.85.

HR-MS(FD+), calculated m/z for $\text{C}_{34}\text{H}_{34}\text{N}_2\text{OSi}_2$ $[\text{M}+\text{H}^+]$: 542.22042; found: 542.21889.

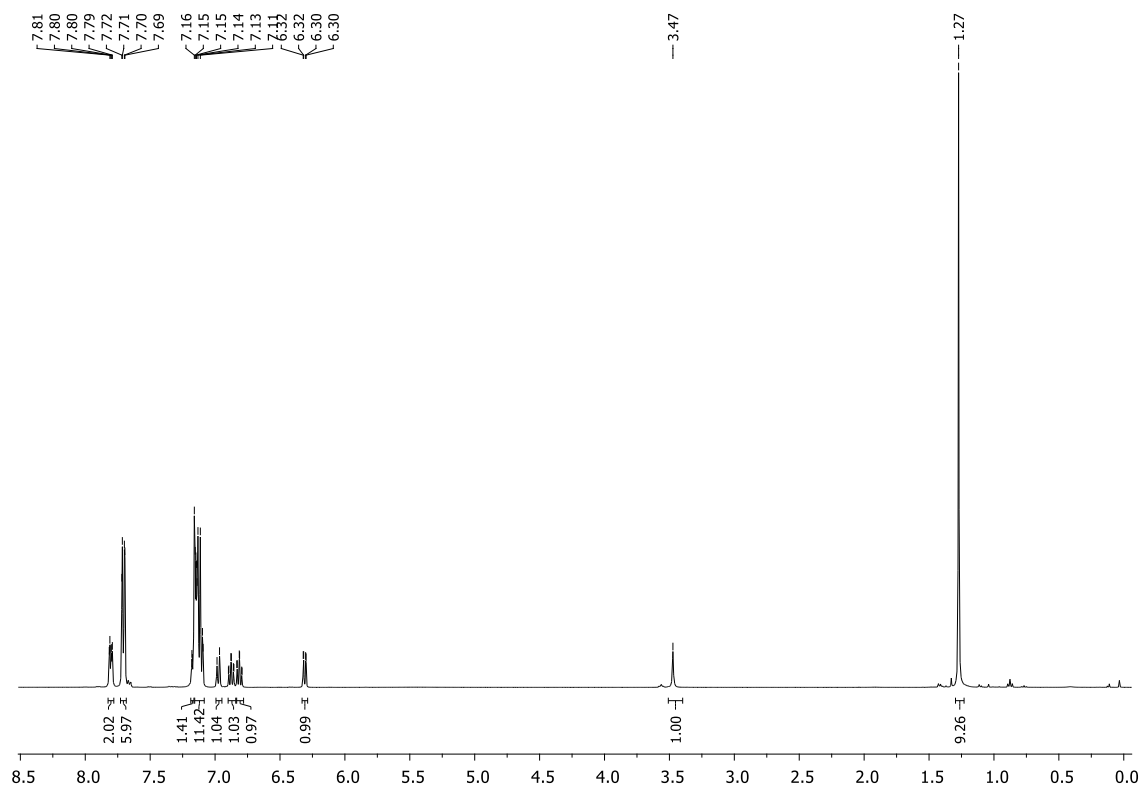


Figure 3.43: ^1H NMR spectrum (C_6D_6 , 298 K) of **9**.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

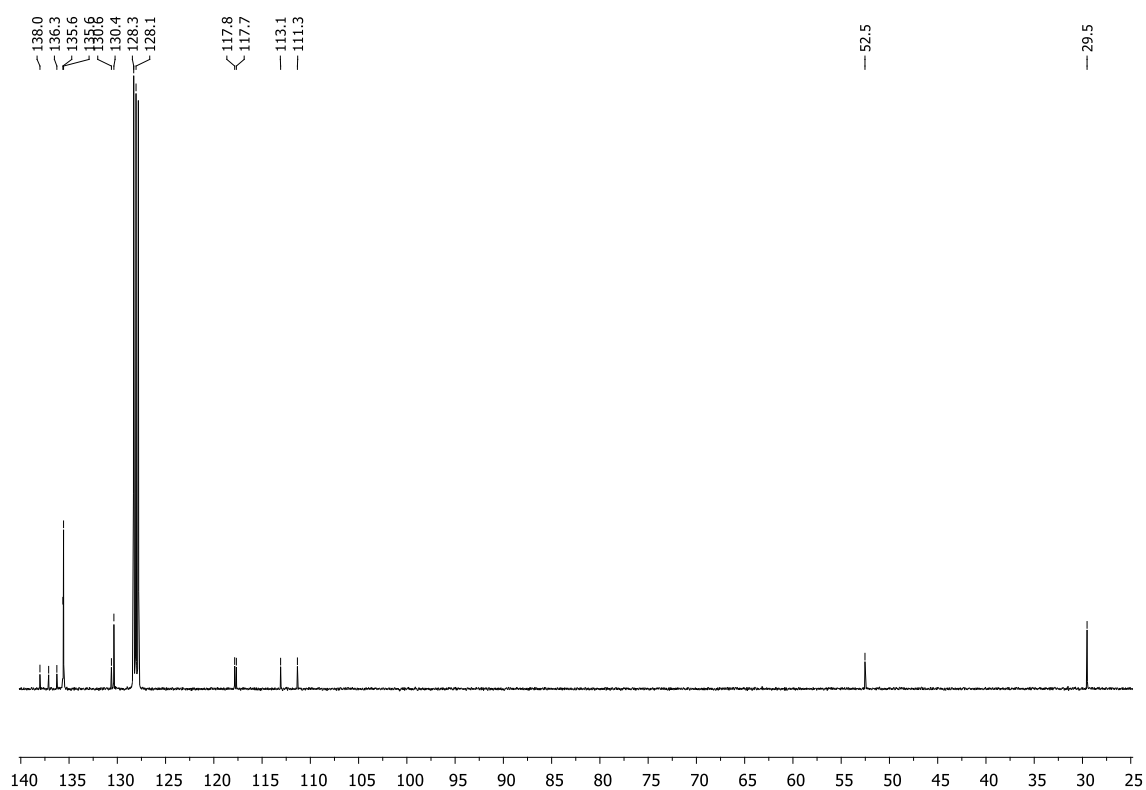


Figure 3.44: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K) of **9**.

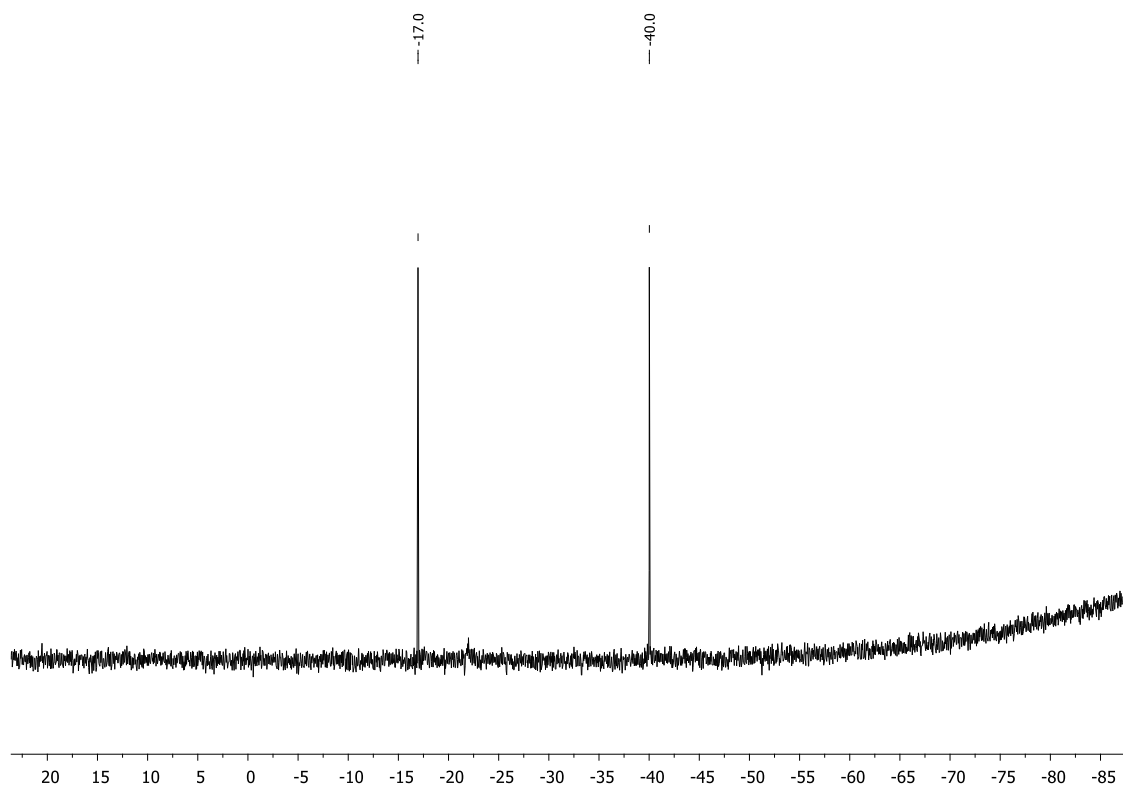


Figure 3.45: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (C_6D_6 , 298 K) of **9**.

3.7.6 Single Crystal X-Ray Diffraction Analysis

The crystals were selected and measured on a Gemini Ultra diffractometer equipped with an Atlas S2 CCD detector (7), XtaLAB Synergy R, DW system diffractometer equipped with a HyPix-Arc 150 detector (6), a GV50 diffractometer equipped with a TitanS2 detector (9) or a Supernova diffractometer equipped with either a TitanS2 detector (1) or an Atlas detector (2, 3). The crystals were kept at T = 123(1) K (1, 2, 3, 9), T = 100(1) K (6) or T = 293(2) K (7) during data collection. Data collection and reduction were performed with CrysAlisPro (Version 1.171.41.54a, Version 1.171.41.76a or Version 1.171.43.36a).^[57] A numerical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK was applied. Using Olex2,^[58] the structures were solved with ShelXT^[59] and a least-square refinement on F^2 was carried out with ShelXL^[60] for all structures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. Figures were created with Mercury Version 3.10.3.^[61]

Compound 1: The asymmetric unit contains one molecule of compound 1.

Compound 2: The asymmetric unit contains one molecule of compound 2.

Compound 3: The asymmetric unit contains one molecule of compound 3.

Compound 6: The asymmetric unit contains one molecule of compound 6.

Compound 7: The asymmetric unit contains one molecule of compound 7.

Compound 9: The asymmetric unit contains one molecule of compound 9.

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

Table 3.6: Crystal data and structure refinement of compounds **1**, **2** and **3**.

Compound	1	2	3
Formula	C ₃₆ H ₄₈ N ₂	C ₂₄ H ₂₈ N ₂ Si	C ₄₂ H ₄₂ N ₂ OSi ₂
<i>M</i> / g·mol ⁻¹	536.78	372.57	646.95
<i>T</i> / K	123.01(10)	123.00(10)	123.00(10)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> / Å	10.3849(2)	10.00150(10)	9.5270(3)
<i>b</i> / Å	12.3450(3)	12.0551(2)	11.1155(4)
<i>c</i> / Å	14.6119(3)	17.7528(3)	16.8771(6)
α / °	110.103(2)	90	98.976(3)
β / °	91.635(2)	94.7500(10)	94.987(3)
γ / °	114.796(2)	90	93.751(3)
<i>V</i> / Å ³	1563.86(7)	2133.09(5)	1755.54(11)
<i>Z</i>	2	4	2
<i>Z'</i>	1	1	1
ρ / g·cm ⁻³	1.140	1.160	1.224
μ / mm ⁻¹	0.506	1.030	1.184
Crystal size / mm ³	0.29 × 0.15 × 0.13	0.24 × 0.20 × 0.10	0.55 × 0.35 × 0.31
λ / Å	1.54184	1.54184	1.54184
Radiation type	Cu K α	Cu K α	Cu K α
θ range / °	4.261 – 67.010	4.436 – 76.113	4.039 – 72.926
Reflections, collected	27565	17365	19642
Reflections, independent	5528	4374	6828
Reflections with <i>I</i> > 2(<i>I</i>)	5115	4125	5924
<i>R</i> _{int}	0.0511	0.0195	0.0287
Parameters	399	256	432
Restraints	27	0	0
GooF	1.058	1.049	1.034
<i>wR</i> ₂ (all data)	0.1567	0.0951	0.0906
<i>wR</i> ₂	0.1530	0.0935	0.0856
<i>R</i> ₁ (all data)	0.0599	0.0350	0.0416
<i>R</i> ₁	0.0571	0.0333	0.0345
$\Delta\rho_{\text{fin}}$ (max / min) / e·Å ⁻³	0.68 / -0.59	0.33 / -0.26	0.36 / -0.30

Table 3.7: Crystal data and structure refinement of compounds **6**, **7** and **9**.

Compound	6	7	9
Formula	C ₄₂ H ₃₆ O ₂ Si ₃	C ₃₄ H ₃₆ N ₂ OSi ₂	C ₃₄ H ₃₄ N ₂ OSi ₂
<i>M</i> / g·mol ⁻¹	656.98	544.83	542.81
<i>T</i> / K	100.01(10)	293(2)	124(1)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> / Å	12.6336(6)	9.9562(2)	10.8425(4)
<i>b</i> / Å	13.1403(6)	11.9185(2)	12.0185(5)
<i>c</i> / Å	13.3843(4)	14.1045(3)	12.4936(4)
α / °	67.363(4)	72.173(2)	104.816(3)
β / °	62.497(4)	74.637(2)	92.098(3)
γ / °	68.033(4)	75.329(2)	109.754(4)
<i>V</i> / Å ³	1765.90(15)	1509.12(6)	1467.69(10)
<i>Z</i>	2	2	2
<i>Z'</i>	1	1	1
ρ / g·cm ⁻³	1.236	1.199	1.228
μ / mm ⁻¹	1.508	1.282	0.952
Crystal size / mm ³	0.26 × 0.10 × 0.08	0.55 × 0.35 × 0.31	0.22 × 0.12 × 0.10
λ / Å	1.54184	1.54184	1.54184
Radiation type	Cu K α	Cu K α	Cu K α
θ range / °	3.754 – 73.537	3.362 – 71.992	3.335 – 74.216
Reflections, collected	54619	36898	21102
Reflections, independent	6889	5848	7807
Reflections with <i>I</i> > 2(<i>I</i>)	5913	5506	6364
<i>R</i> _{int}	0.0399	0.0307	0.0425
Parameters	428	363	359
Restraints	0	0	0
GooF	1.062	1.033	1.043
<i>wR</i> ₂ (all data)	0.1046	0.0842	0.1305
<i>wR</i> ₂	0.1006	0.0827	0.1198
<i>R</i> ₁ (all data)	0.0444	0.0333	0.0583
<i>R</i> ₁	0.0375	0.0316	0.0464
$\Delta\rho_{\text{fin}}$ (max / min) / e·Å ⁻³	0.63 / -0.38	0.35 / -0.30	0.47 / -0.37

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7.6.1 XRD: Compound 1

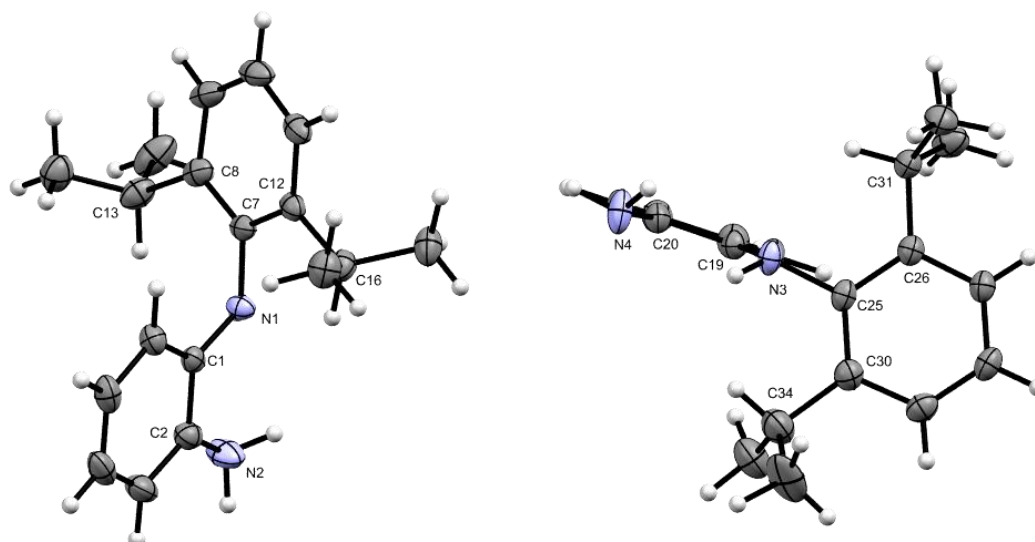


Figure 3.46: Molecular structure of compound **1** in the crystal (displacement ellipsoids of non-hydrogen atoms set at the 50% probability level).

Table 3.8: Selected bond lengths / Å and selected bond angles / ° of compound **1**.

Selected bond lengths / Å		Selected bond angles / °	
N1–C1	1.411(2)	C1–C2–N2	118.7(1)
C1–C2	1.410(3)	N1–C1–C2	117.5(1)
C2–N2	1.400(2)	C1–N1–C7	119.6(1)
N1–C7	1.433(2)	N1–C7–C8	120.8(1)
C7–C8	1.404(2)	N1–C7–C12	118.2(1)
C7–C12	1.406(2)		
C8–C13	1.521(2)		
C12–C16	1.517(2)		

3.7.6.2 XRD: Compound 2

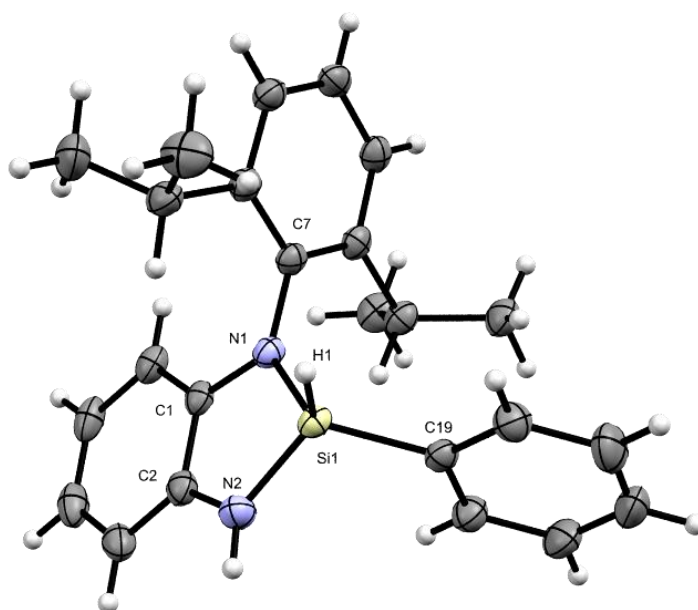


Figure 3.47: Molecular structure of compound **2** in the crystal (displacement ellipsoids of non-hydrogen atoms set at the 50% probability level).

Table 3.9: Selected bond lengths / Å and selected bond angles / ° of compound **2**.

Selected bond lengths / Å		Selected bond angles / °	
N2–Si1	1.724(1)	N1–Si1–N2	91.19(5)
N1–Si1	1.7381(9)	N1–Si1–C19	117.09(5)
C19–Si1	1.850(1)	N2–Si1–C19	113.64(5)
Si1–H1	1.45(2)	N2–Si1–H1	119.1(6)
C1–C2	1.413(2)	N1–Si1–H1	109.8(6)
N1–C7	1.431(1)	C19–Si1–H1	106.0(6)
C1–N1	1.404(1)	C2–N2–Si1	112.52(8)
C2–N2	1.400(1)	C1–N1–Si1	111.82(7)
		Si1–N1–C7	127.45(7)

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7.6.3 XRD: Compound 3

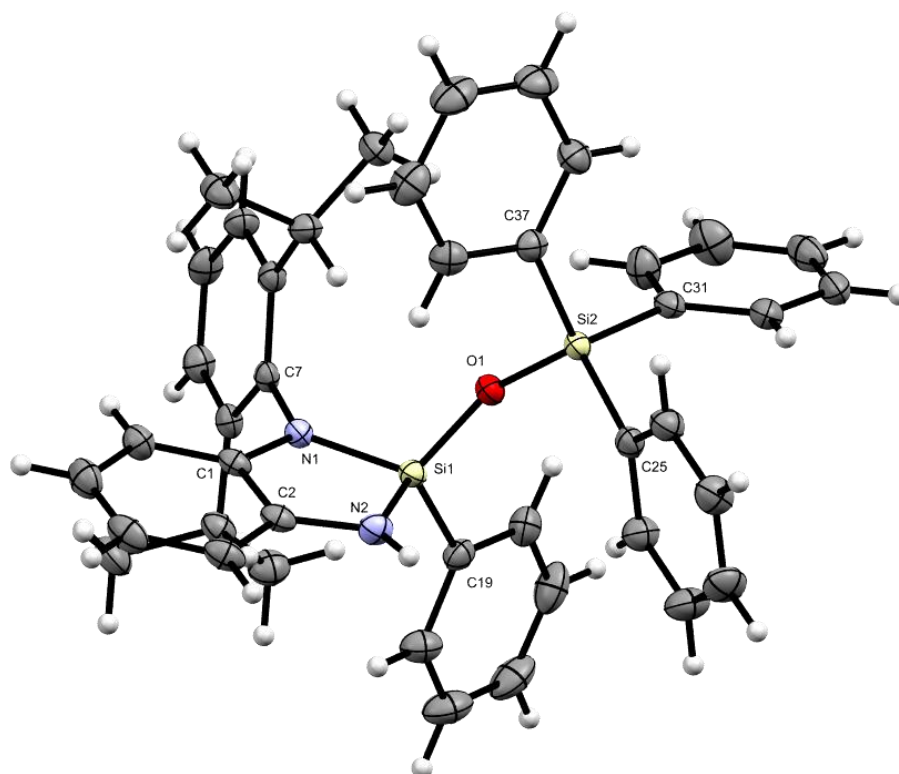


Figure 3.48: Molecular structure of compound **3** in the crystal (displacement ellipsoids of non-hydrogen atoms set at the 50% probability level).

Table 3.10: Selected bond lengths / Å and selected bond angles / ° of compound **3**.

Selected bond lengths / Å		Selected bond angles / °	
N2–Si1	1.724(1)	Si1–O1–Si2	147.82(7)
N1–Si1	1.733(1)	N1–Si1–N2	91.81(6)
C19–Si1	1.852(1)	N1–Si1–C19	113.14(6)
Si1–O1	1.618(1)	N2–Si1–C19	114.46(6)
C1–C2	1.415(2)	N2–Si1–O1	115.86(6)
N1–C7	1.438(2)	N1–Si1–O1	114.13(5)
C1–N1	1.405(2)	C19–Si1–O1	107.14(6)
C2–N2	1.398(2)	C2–N2–Si1	112.14(9)
Si2–O1	1.6420(9)	C1–N1–Si1	111.27(9)
Si1–C25	1.870(1)	Si1–N1–C7	128.30(9)
Si1–C31	1.866(1)	O1–Si2–C25	109.05(6)
Si1–C37	1.866(1)	O1–Si2–C31	106.88(6)
		O1–Si2–C37	108.90(6)

3.7.6.4 XRD: Compound 6

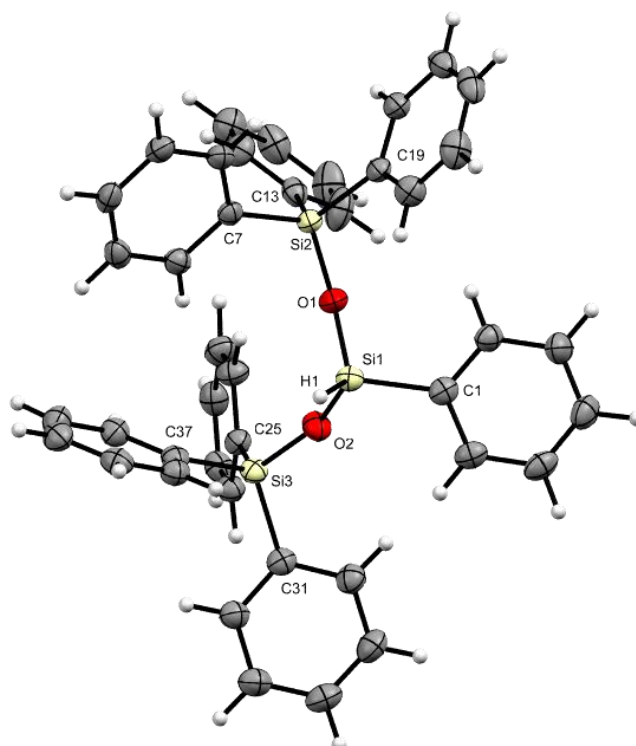


Figure 3.49: Molecular structure of compound **6** in the crystal (displacement ellipsoids of non-hydrogen atoms set at the 50% probability level).

Table 3.11: Selected bond lengths / Å and selected bond angles / ° of compound **6**.

Selected bond lengths / Å		Selected bond angles / °	
Si1–H1	1.42(3)	O1–Si1–O2	108.92(8)
Si1–C1	1.854(2)	O1–Si1–C1	108.90(8)
Si1–O1	1.598(1)	O2–Si1–C1	108.58(8)
Si1–O2	1.611(1)	O1–Si1–H1	109.9(9)
Si2–O1	1.623(1)	O2–Si1–H1	108.1(9)
Si2–C7	1.870(2)	Si1–O1–Si2	165.4(1)
Si2–C13	1.865(2)	O1–Si2–C7	109.71(8)
Si2–C19	1.865(1)	O1–Si2–C13	108.05(8)
Si3–O2	1.632(1)	O1–Si2–C19	109.06(8)
Si3–C25	1.863(2)	Si1–O2–Si3	151.9(1)
Si3–C31	1.863(2)	O2–Si3–C25	108.58(8)
Si3–C37	1.871(2)	O2–Si3–C31	106.21(8)
		O2–Si3–C37	109.89(8)

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7.6.5 XRD: Compound 7

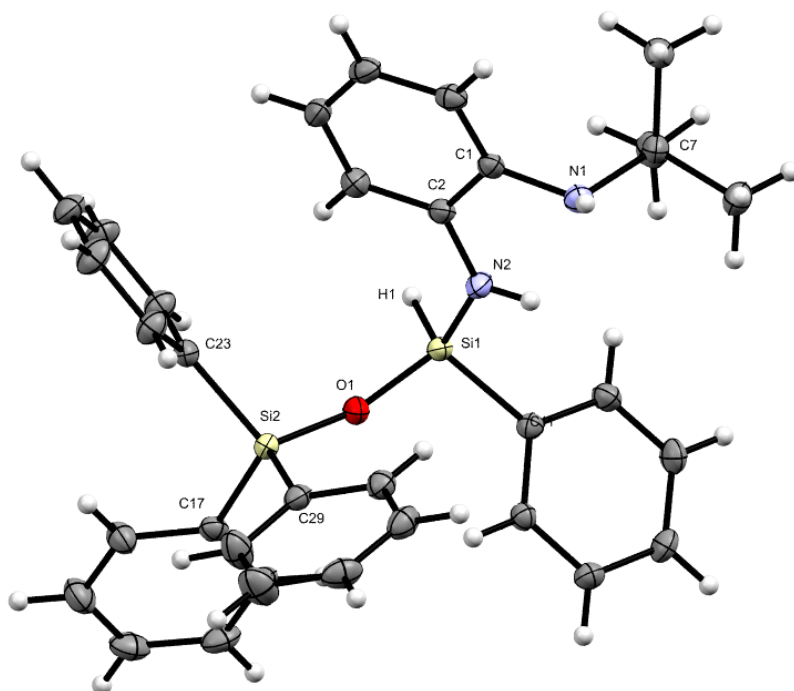


Figure 3.50: Molecular structure of compound **7** in the crystal (displacement ellipsoids of non-hydrogen atoms set at the 50% probability level).

Table 3.12: Selected bond lengths / Å and selected bond angles / ° of compound **7**.

Selected bond lengths / Å		Selected bond angles / °	
N1–C1	1.435(2)	C1–N1–C7	118.5(1)
C1–C2	1.408(2)	C2–N2–Si1	129.8(1)
C2–N2	1.399(2)	N2–Si1–O1	113.60(5)
N1–C7	1.491(1)	N2–Si1–H1	110.2(7)
N2–Si1	1.709(1)	O1–Si1–H1	106.7(7)
Si1–H1	1.37(2)	Si1–O1–Si2	162.46(7)
Si1–C11	1.861(1)	N2–Si1–C11	106.80(6)
Si1–O1	1.6218(8)	O1–Si1–C11	106.46(5)
Si2–O1	1.6239(8)	O1–Si2–C17	107.88(5)
Si2–C17	1.869(1)	O1–Si2–C23	109.99(5)
Si2–C23	1.868(1)	O1–Si2–C29	108.33(5)
Si2–C29	1.866(1)		

3.7.6.6 XRD: Compound 9

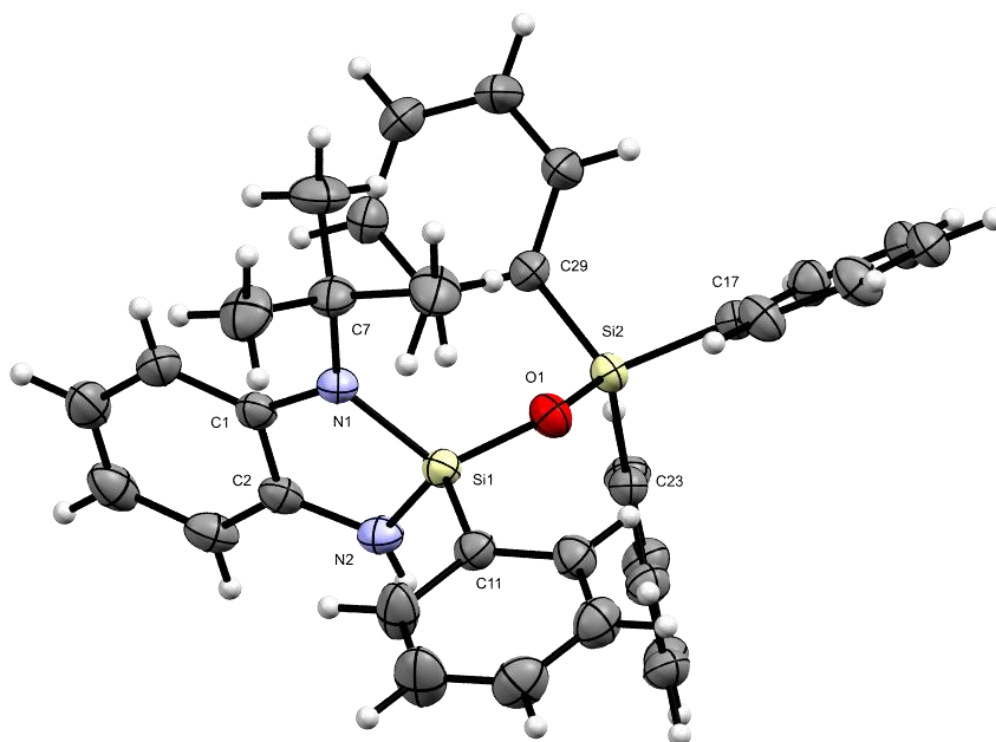


Figure 3.51: Molecular structure of compound **9** in the crystal (displacement ellipsoids of non-hydrogen atoms set at the 50% probability level).

Table 3.13: Selected bond lengths / Å and selected bond angles / ° of compound **9**.

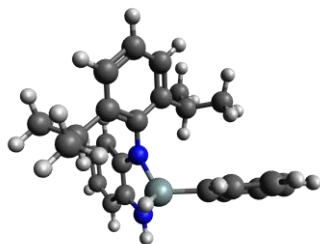
Selected bond lengths / Å		Selected bond angles / °	
N1–C1	1.411(2)	Si1–O1–Si2	140.10(9)
C1–C2	1.415(2)	N1–Si1–N2	92.55(7)
C2–N2	1.400(3)	N1–Si1–C11	115.56(8)
N1–C7	1.485(2)	N2–Si1–C11	113.41(8)
Si1–N1	1.734(2)	N2–Si1–O1	113.78(7)
Si1–N2	1.719(1)	N1–Si1–O1	116.67(7)
Si1–C11	1.856(2)	C11–Si1–O1	105.02(7)
Si1–O1	1.625(1)	C2–N2–Si1	111.5(1)
Si2–O1	1.642(1)	C1–N1–Si1	110.7(1)
Si2–C17	1.862(2)	Si1–N1–C7	123.1(1)
Si2–C23	1.871(1)	O1–Si2–C17	105.93(7)
Si2–C29	1.867(2)	O1–Si2–C23	107.39(7)
		O1–Si2–C29	110.50(7)

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

3.7.7 Cartesian Coordinates of Optimized Structures

All values are given in Å (1 Å = 10⁻¹⁰ m)

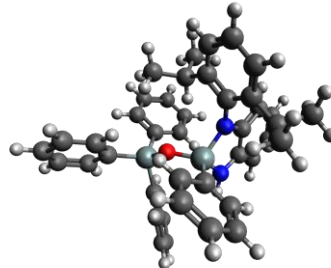
Compound 2



E = -1327.44257191 Eh

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N	-1.19418894700683	3.29908706323714	0.06005078477258
N	-1.53888832089583	0.81848588491572	0.62922129035393
C	1.13280959723246	1.87935506601806	1.55006537442615
C	1.83887120508963	2.50398037816688	2.57694179629979
C	3.21370965329773	2.35477120938591	2.69036894402211
C	3.89835973726527	1.56689701391146	1.77745571470558
C	3.20942708582751	0.92881145669711	0.75444606198165
C	1.83785937696868	1.08695832873941	0.64218125358914
C	-0.94170521176833	4.59821771618057	-0.04423547641331
C	-1.82933507774143	5.50241524174017	0.55720688082859
C	-1.55340353846203	6.86162618669199	0.46327314386948
C	-0.43714254948224	7.31775246758536	-0.21398529166950
C	0.42021367450125	6.41471609400562	-0.81517296760661
C	0.18622854416336	5.04569746293604	-0.74622970959771
C	1.13300806848341	4.09561667364256	-1.44497365566025
C	2.56225860593494	4.23718184721350	-0.92447798423614
C	1.07470762609317	4.28583360606297	-2.96101347956717
C	-3.07468857857531	5.04782885070033	1.28641773458918
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C	-1.99440619984234	2.54392452780286	-0.86727643851986
C	-2.19346577197763	1.18923379834650	-0.54082648877466
C	-2.96791780577780	0.38882330777866	-1.35730673688769
C	-3.54815578649396	0.93337812947852	-2.50279225768061
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C	-2.57176655875034	3.0806650334433	-2.00205504276296
H	-2.41947238012749	4.12362242163369	-2.24741797571312
H	-3.80662380416708	2.68247303664943	-3.70898944239464
H	-4.15516519886204	0.30530123835145	-3.14080593136992
H	-3.12495864134081	-0.65399683337183	-1.10882631260815
H	-3.11395156116139	3.95835474867903	1.25887776985118
H	-3.04546323639938	6.55274344572209	2.86864878997594
H	-2.15964855338667	5.08193360984294	3.26078347132669
H	-3.92232320794098	5.08415186271342	3.28074612567939
H	-5.22884507730743	5.17934333219655	1.09097092941215
H	-4.39152925439140	6.64596433553258	0.59312977449580
H	-4.37275225613311	5.22162377723099	-0.44785418172873
H	-2.22406943176474	7.57710172856426	0.92384991329157
H	-0.23785372775940	8.37966146145990	-0.27752263054707
H	1.28717553779811	6.78206991983889	-1.35087775172870
H	0.80935117762976	3.07583879343158	-1.23584058482688
H	3.21235680436167	3.49672300185693	-1.39252196473262
H	2.97851011602007	5.22254176684660	-1.14267417231129
H	2.61157222877248	4.08366095264927	0.15344282339022
H	1.72312750266954	3.56501098913813	-3.46171776989012
H	1.40310276825141	5.28417059968349	-3.25615302886510
H	0.06290497599955	4.14015449559910	-3.33923978980584
H	1.31116986437927	3.11661327581875	3.29972679506134
H	3.74974660024401	2.84979109516379	3.48953449474599
H	4.97051060250647	1.44702855097469	1.86387328763408
H	3.74425645940432	0.31068049317695	0.04512361274793
H	1.30764508466707	0.58885452148973	-0.16155990577755
H	-1.62976732710253	-0.12845270371915	0.95089950775033

Compound 3



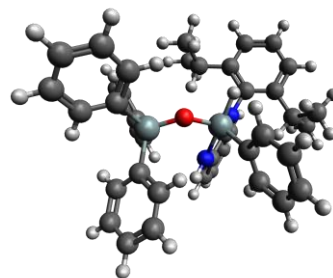
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C	1.90782168909185	2.08538540564599	3.40492254718591
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C	4.13010463116636	1.72100261354430	2.56208676548385
C	3.61110050093629	0.94829514713889	1.53212043030928
C	2.24058920689195	0.75629079092406	1.43471793164363
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C	-2.21643973043169	4.27866776783333	1.89226259024988
C	-2.16849646207235	5.66993352106057	1.88343384176744
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C	0.69587182459626	3.52136300886587	-0.50304191962614
C	2.13283336001587	3.91681612603626	-0.16668069105575
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C	-6.48443342998657	3.90322748146824	2.14569269322821
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C	-1.78470565405617	0.06753808106065	0.20306345710865
C	-2.42381459191928	-0.77001877438391	-0.69338779446486
C	-3.26634440285507	-0.22415826065923	-1.66305191449240
C	-3.46671794151326	1.14455434231687	-1.72608886910512
C	-2.83216421065090	1.99582565279454	-0.81979767943855
H	-2.99445642543422	3.06534771751505	-0.86793571585837
H	-4.12035911060563	1.56417446379496	-2.47951126930514
H	-3.76222775465134	-0.87982380417390	-2.36681884632897
H	-2.26565353025308	-1.84056577796251	-0.64086581475473
H	-3.15320825157417	2.51125703809917	2.61250735919892
H	-3.38807756259138	5.00870332513248	4.35104809101067
H	-2.21208293281177	3.71518541477174	4.58047990363803
H	-3.93333249741550	3.38289858384674	4.75391131145631
H	-5.44434034799450	3.35006794176370	2.70053513440893
H	-4.96008345315459	4.96600834531549	2.22784155210563
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H	2.35741794366820	3.74324273164481	0.88600588001537
H	1.08662735206323	3.19052969123906	-2.60928088359326
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H	-0.61766381813065	3.45040265837182	-2.23939963931652
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H	3.67935047512991	2.89269132350470	4.30292465095690
H	5.19867687162756	1.87675433856622	2.63768741172040
H	4.27358036680937	0.49824713042283	0.80402417234598
H	1.84839683452946	0.15713478772779	0.62126393294298
H	-0.72761726265003	-1.27674035803988	1.36939672111183
O	-1.05392800630842	1.06364398861775	3.73573647571211
Si	-1.98863614426208	0.03941625474900	4.65611319998625
C	-3.79224501687492	0.16863385426174	4.17474695858917
C	-4.20342752622699	-0.19513702401705	2.88821853051983
C	-5.52635729427171	-0.06466306010810	2.49362975043194
C	-6.47001586314409	0.42654384897442	3.38723188691778
C	-6.08378510637897	0.78537136271122	4.67080701610110
C	-4.75534088539665	0.65913913427061	5.05748657731419
C	-1.73280064808177	0.53867393492186	6.43806787867791
C	-1.09132594587045	1.72575705341659	6.79434096608431
C	-0.91791983048958	2.07111121435577	8.12844740823143
C	-1.38527473898281	1.23164520908993	9.12995024776071
C	-2.02370975889485	0.04442200746823	8.79434684248857
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C	-1.36999810109411	-1.70619889471183	4.37111924118423
C	0.00666959886405	-1.95127137134611	4.32628176622224
C	0.50003571782123	-3.23030866029840	4.11466650505955

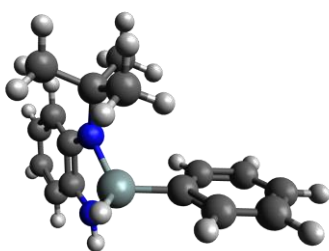
Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

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C	-1.74768003444860	-4.07238277174761	4.00318367138446
C	-2.23627532975435	-2.78825343322670	4.20986109132255
H	-3.48663759835462	-0.58683426888906	2.17617019012653
H	-5.81991433299652	-0.34560271772331	1.49024059705181
H	-7.50385493864257	0.52883403312442	3.08298342698862
H	-6.81562379080034	1.16768756880264	5.37081198364626
H	-4.47182183828227	0.95249415282300	6.06147274011263
H	-0.71661574504653	2.39366539842980	6.02829916191902
H	-0.41641257545853	2.99534003539040	8.38561688965193
H	-1.25030196349315	1.49968262865817	10.17000521052232
H	-2.38678487607471	-0.61555165076078	9.57169591924274
H	-2.68551002286883	-1.23202096017314	7.21798725483249
H	-3.30847970730394	-2.63350160049872	4.23813211796512
H	-2.43607064525672	-4.89839491837589	3.87823925881178
H	0.00354021405490	-5.29322134652710	3.78672622453295
H	1.56877125606655	-3.39839302027178	4.07850768989223
H	0.71205425280461	-1.13734913084363	4.45793800498067

10-II



Compound 5



E = -2385.73828353454 Eh

E = -1018.56432844 Eh

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Si	-0.52822146003930	3.12876713423722	0.55558615033928
H	-0.85698125424877	3.94965631288489	1.75407689737578
N	-0.92127231644010	3.85439397265128	-0.99073620956569
N	-1.61708116493593	1.81282223305668	0.26705747470393
C	1.24474983739023	2.58890842075522	0.77978103157647
C	1.97356191795711	2.95158333301987	1.91063419055878
C	3.28881625267202	2.54036135719438	2.07553957750464
C	3.89278976909401	1.75898244683314	1.10231818574017
C	3.18162429071130	1.38794919593624	-0.03160811849504
C	1.86787969278197	1.79911438839416	-0.18882552200235
C	-0.39701269851026	5.13306731028583	-1.48567040918773
C	-1.80801568338223	3.04185731461895	-1.70856913573124
C	-2.20069062507576	1.89131719567383	-0.98669853213048
C	-3.07257486857862	0.96886956917907	-1.53120713660156
C	-3.57622082372866	1.16427966005115	-2.81415283472603
C	-3.19628069272056	2.27855355530248	-3.53357252399571
C	-2.31540835547796	3.21281418282662	-2.98870534087286
H	-2.04207514169374	4.06452772689397	-3.59138067785160
H	-3.57786324106396	2.43902155964194	-4.53294764356186
H	-4.25982476185107	0.44199476384102	-3.23942623216926
H	-3.35995570070971	0.09629320030215	-0.95664007071295
H	1.51010180521331	3.56654242494156	2.67465872878768
H	3.84196790917141	2.82926139230228	2.95978477857255
H	4.91882302614965	1.43751432465646	1.22622332057689
C	3.65350597364378	0.77743287955739	-0.79052091880694
H	1.32034425247284	1.50273317747626	-1.07660069818671
H	-1.79521035417495	1.00123493197983	0.83054685933045
C	0.47709595719333	5.75990117939772	-0.39533779671446
C	-1.53353348714071	6.12216149652543	-1.76845730545335
C	0.49269230911087	4.92079287502466	-2.71557654537406
H	1.34323707669424	5.14212998068741	-0.15124492916441
H	0.86164035616823	6.71944396103359	-0.74179955308160
H	-0.08683986120699	5.95511732782579	0.51906397245000
H	-1.12505047798368	7.08293754229143	-2.08553781040826
H	-2.12112211288491	6.28862721015769	-0.86480652004744
H	-2.21902345886012	5.78817996201409	-2.54317926328658
H	-0.90397932180106	4.46918028063633	-3.55326201296106
H	0.00103419446271	5.87262725674996	-3.05914454532875
H	1.32980324162203	4.26772696316193	-2.46465288109865

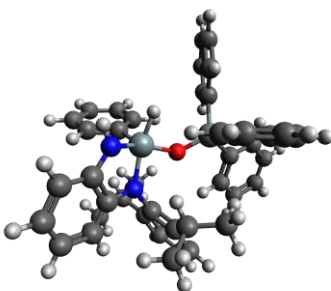
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Si	-0.33533528618344	1.66484820955301	2.53997897061769
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N	-1.29410371995376	2.49475299117737	1.22846454732691
N	-0.97469477041612	0.13615293758623	1.67450928551106
C	1.52889764694040	1.22498307696928	2.35800078639711
C	2.45145939782593	1.84995105768725	3.20163557903302
C	3.81384036475501	1.59068115729938	3.1268986974696
C	4.29727481595242	0.70475595098908	2.17170578187960
C	3.40634595092422	0.08108699910778	1.30852464366523
C	2.04264710525686	0.33422069273067	1.41219910792159
C	-1.37696718311675	3.89462118443900	1.08734782000635
C	-2.38511264798678	4.60461256618812	1.75700328807748
C	-2.44192498451744	5.98825229725531	1.61293846576134
C	-1.53116519611293	6.66214332623273	0.81680834794395
C	-0.54492188544101	5.95172849124055	0.15272709437711
C	-0.45261907299605	4.56827347536140	0.27317604901122
C	0.64912166919198	3.83227380459483	-0.45716719408339
C	2.02407362892278	4.23490913744092	0.07545382379486
C	0.56152908534811	4.03999765074070	-1.96890390741775
C	-3.39345078859864	3.90931987716964	2.64440101887944
C	-4.82710207246064	4.16661702431917	2.18168981638474
C	-3.20427331838309	4.31541744868813	4.10593297818428
C	-1.93184216154363	1.70292649939747	0.29709876126178
C	-1.72675552158325	0.32531029968334	0.56416847861997
C	-2.29740190989427	-0.62226157445137	-0.27833178147364
C	-3.06708951617068	-0.21376334664922	-1.37333760189405
C	-3.26885134977948	1.13076562517279	-1.62655823123170
C	-2.69654274667320	2.09720149566775	-0.78667096170606
H	-2.85302194931338	3.15024088656859	-0.98839646515578
H	-3.86627919333715	1.44544675952165	-2.47296956344447
H	-3.50500164437139	-0.96168407260714	-2.02332616712707
H	-2.14464803495570	-1.67803582885603	-0.08178882052985
H	-3.21813792308471	2.8350226304385	2.57954077303993
H	-3.38427521216736	5.38254149324066	4.25288586915732
H	-2.19088579716231	4.09553869139683	4.44007238721086
H	-3.89721712540822	3.76932086955111	4.74853284073443
H	-5.53016538640592	3.60174189948850	2.79625897319021
H	-5.09727369105127	5.22195609833651	2.25632149121697
H	-4.96865786803614	3.85671986056515	1.14529743463180
H	-3.20962747970786	6.55032792757720	2.13259650783207
H	-1.58867193586569	7.73871883471145	0.71521330720029
H	0.16772441360894	6.48494668508050	-0.46632708591709
H	0.52776892043986	2.76606255946372	-0.26506882774196
H	2.80954663490196	3.65204663125778	-0.40972813758581
H	2.23333139869053	5.29100638192692	-0.10778861372677
H	2.09488087058791	4.056970032865847	1.14886491539180
H	1.32293512521846	3.44771857197688	-2.47978257636753
H	0.71893608311768	5.08447538039424	-2.24558994140251
H	-0.41218732595103	3.73396946290626	-2.35362383974339
H	2.09090617018808	2.56750627952278	3.9319988077575
H	4.50010630240761	2.08393239306143	3.80488759375105
H	5.35936194476693	0.50562930503441	2.09881114549324
H	3.77426069604752	-0.60551542329067	0.55537003127248
H	1.36429493839393	-0.17190971505205	0.73567041139870
H	-0.72647821222944	-0.81458461244442	1.89929721901332
O	-0.88954159184041	1.14060875218922	4.09235339896337
Si	-1.90491896465081	0.01254110042966	4.69680252708490
C	-3.68105637029106	0.16600921663298	4.09168307883323
C	-4.09808097049081	-0.39118179450748	2.88009341323712
C	-5.39569463893140	-0.22400842473964	2.41709492098369
C	-6.31179566322422	0.50355055431990	3.16543687843820
C	-5.92263959854649	1.05818516832931	4.37697480615612
C	-4.62118429758651	0.88789897646242	4.83152014009023
C	-1.93361296836243	0.29448546983334	6.56059450320395
C	-1.45303343454630	1.47714075501864	7.12552872874946
C	-1.50297237467426	1.69138975643861	8.49784970618350
C	-2.3642155147986	0.72080486577415	9.33417936438912
C	-2.51935537956064	-0.46379498775235	8.79202500239267
C	-2.46600105699917	-0.66950528932635	7.42057988098648
C	-1.27935120477830	-1.73590925405834	4.38854532558663
C	0.09011964661497	-1.96544696995734	4.22366963234858
C	0.58744350985475	-3.24727051906958	4.03287628129786
C	-0.27938328122738	-4.33238486727975	4.00918993562697
C	-1.64198262587676	-4.12711363807079	4.17630791593156
C	-2.13296178883217	-2.84077988101232	4.36241105903476
H	-3.40135533913633	-0.95982076217035	2.27874616099273
H	-5.68937873985039	-0.65921151691609	1.47005825222667

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

H	-7.3245233339336	0.63702298315086	2.80639154759436
H	-6.63180095541652	1.62435003572508	4.96781051151686
H	-4.33898163487952	1.32892332825969	5.78067021248077
H	-1.03153736813116	2.24586012235600	6.48921823426419
H	-1.12380139124416	2.61645637461910	8.91396987227011
H	-2.07490409379848	0.88491380687446	10.40369200392671
H	-2.93503342317068	-1.22654072485457	9.43849654700834
H	-2.84555298819159	-1.60329469354639	7.01910762022559
H	-3.20171863726060	-2.70200140752522	4.48144856288492
H	-2.32367874970172	-4.96814399913468	4.15687019004590
H	0.10564769861980	-5.33304033115278	3.85904845731848
H	1.65129122228578	-3.39921385313116	3.90047262844491
H	0.78394052071856	-1.13224540171806	4.23389766812857

10-I

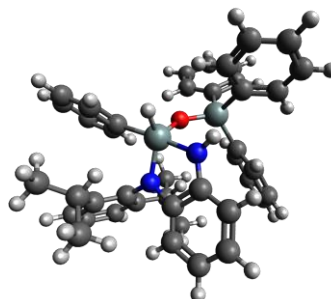


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Si	2.57299258733611	0.05977603107102	0.91052712051703
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N	1.10117489140638	1.21309179052048	1.13565357308234
N	1.85690285880874	-0.11983624210447	-0.74749197783504
C	2.08050458528170	-1.53329032237011	1.84194156529809
C	2.73291885074639	-1.95775150165260	3.00127753286005
C	2.39357492708925	-3.14111821435916	3.64625958105284
C	1.37083691687339	-3.93632551795873	3.14783373686279
C	0.70225460490622	-3.53812342799794	1.99692195528207
C	1.06119236957249	-2.35895375151102	1.35572250491225
C	0.88722655917708	2.19904731271099	2.12311770326437
C	0.25520969494387	1.87444323914087	3.33440619205243
C	-0.00637688642109	2.88242280520053	4.26026673736175
C	0.32939957274788	4.19839868989737	4.00060280148957
C	0.95325329638942	4.51475475449136	2.80505936242775
C	1.24787870514835	3.56460071087693	1.86099849690857
C	1.944809526811996	3.94669306092986	0.58136204285829
C	3.14682711804762	4.85265045547899	0.84797707834139
C	0.97761487116100	4.63346470212118	-0.38528718574936
C	-0.16657149240380	0.46138216211719	3.66428380806489
C	-1.68796014375993	0.33908237354143	3.75657367566337
C	0.49927450162596	-0.03334380126344	4.94753862088273
C	0.15631109184424	1.13487225028726	0.13926356090207
C	0.60029191217147	0.35907088268132	-0.96220807595773
C	-0.21924970112615	0.18801814783518	-2.06745489979932
C	-1.48770193465075	0.77975153719245	-2.09680857689526
C	-1.92475350220548	1.53451661581790	-1.02365290153767
C	-1.10292756948665	1.71691636753492	0.09597340776689
H	-1.45286368241253	2.31805032760457	0.92646398481747
H	-2.90682874670202	1.990806717111089	-1.04091889153907
H	-2.12363850636752	0.63893627255149	-2.96214348023451
H	0.12831432458562	-0.40081162050971	-2.90929741762947
H	0.16653900906391	-0.18418394514444	2.85419597051343
H	0.16554298370435	0.53005534471758	5.82173324980403
H	1.58453119835763	0.05264220477560	4.88607331719874
H	0.26143406200125	1.08431294717249	5.12103339869450
H	-1.97837910780791	-0.69784361189443	3.93729715603220
H	-2.09339472177102	0.94195351447812	4.57219916599279
H	-2.16740073323747	0.66217764184220	2.83158094715639
H	-0.49378825610905	2.63376789875090	5.19631910805529
H	0.11012472028712	4.97332093941994	4.72467755571662
H	1.22015430488008	5.54635487155447	2.60808443327329
H	2.31455534274949	3.04118063446245	0.09752148490590
H	3.71800818375422	5.00162849710297	-0.06981035530333
H	2.84362215157135	5.83845840973893	1.20628314412342
H	3.82106390149805	4.41867188365294	1.58572326354487
H	1.48406933513230	4.88669936436021	-1.31860296012347
H	0.58912804165849	5.56019768459323	0.04390665283855
H	0.13084365709805	3.99240166272286	-0.62758997877533
H	3.52912024900577	-1.35507643693078	3.41950868606703
H	2.92587480435774	-3.43993717103550	4.54157275195714
H	1.09856541039059	4.85728588803325	3.64847332263152
H	-0.09770392245704	-4.14595872239517	1.59663455569367
H	0.52728225395126	-2.07568292159417	0.45576716626894
H	2.29244683919884	-0.66137008987473	-1.47649736289208
H	3.42478714895220	0.99451308710029	2.10637682368656
Si	4.99176995311306	1.36282934865929	2.37836621382386
C	5.72377928147243	2.41418272310668	0.99000636977656
C	6.73378502674748	3.34024877571834	1.26354536627432
C	7.29072016608732	4.12380844114713	0.26181011630643
C	6.84652771821735	3.99529666399617	-1.04726735307832
C	5.84627720264182	3.07963197391099	-1.34278967375254

C	5.29371184348142	2.30089988722677	-0.33445533052655
C	6.11700355956830	-0.13669432448681	2.59073067062317
C	6.89597811334749	-0.61962623939678	1.53732493660984
C	7.69871369366721	-1.74293869031252	1.68825330545088
C	7.73831270479507	-2.40908319346005	2.90567362550465
C	6.97474683240878	-1.94477494836353	3.96862351069650
C	6.17704288617554	-0.81993066172986	3.80848443064167
C	5.04346063079388	2.32780639055195	3.99326230449298
C	6.22958308740981	2.49756519557875	4.71329186549215
C	6.25993629134391	3.22821006087071	5.89343068603230
C	5.09338791528830	3.80172022369464	6.38308555345188
C	3.90343297328751	3.63888778599572	5.68723521572585
C	3.88087296487722	2.90943732105480	4.50518037229038
H	7.09136945374188	3.47042926587452	2.27855336540513
H	8.06817197668653	4.83753779080550	0.50402053735377
H	7.27576588956105	4.60648646657811	-1.83112244555288
H	5.49154807722104	2.97309275244445	-2.36033277704687
H	4.51339013744562	1.59652695533422	-0.59589771591505
H	6.88115928567980	-0.11248795951248	0.57944653699334
H	8.29335523681844	-2.09844233618107	0.85614113649730
H	8.3634845113643	-3.28473110739973	3.02664500563418
H	7.00239891524560	-2.45741861515833	4.92194296837995
H	5.59330441009039	-0.47048718626977	4.65321485982407
H	2.94139171563973	2.79377366969613	3.97918706240629
H	2.98804209996469	4.07823550589310	6.06404533065109
H	5.11226812819474	4.36917940718581	7.30506510960507
H	7.19112549214724	3.34554861416712	6.43339704202007
H	7.14900753186834	2.04526521667388	4.35708644977465

11-II



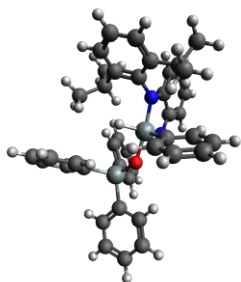
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N	-0.30679680362419	4.86853014303933	2.08938065943423
N	0.68275084068373	3.57660052717675	3.90413546500936
C	0.21117069427874	7.33547208525332	3.31974831001318
C	-0.60348998963588	7.99472466245969	4.23994069016197
C	0.86463941844407	9.36070053003176	4.17120766461403
C	-0.29567927680538	10.12286116957069	3.16235309826742
C	0.53741781298334	9.50217599577152	2.23717894967460
C	0.78095175673914	8.1386287488829	2.32509263999267
C	-0.77659259634104	5.69296325988186	1.04133387750187
C	-2.03670528637011	6.30960819011358	1.14326627259964
C	-2.47644086969322	7.11086674955138	0.09423186621484
C	-1.70479667493993	7.29433894510781	-1.04118346942211
C	-0.47657803845358	6.66589183753536	-1.14128009154892
C	0.00697205045530	5.86057933168218	-0.11374125749144
C	1.34748527620101	5.17592833110833	-0.296805744669251
C	2.47174994135322	6.16381564492951	-0.61102489162653
C	1.27431386506169	4.11427165473543	-1.39702400792553
C	-2.93607581018587	6.08660840275305	2.34102652916448
C	-3.89172737620979	5.81723267143029	2.08669137834000
C	-3.73007672707638	7.32789274268882	2.741502427802457
C	-0.49106847189382	3.50258542768735	1.93934341018835
C	0.06634205669186	2.76717196981348	3.01478428409276
C	-0.07521176482200	1.38275058092400	3.04255755917157
C	-0.74263721454315	0.72413652585977	2.00615941526696
C	-1.27096079220092	1.44248506179482	0.94872884645662
C	-1.14973858466198	2.83863381650774	0.91900431300093
H	-1.58167521969854	3.39559641160321	0.09652916077310
H	-1.78677672573101	0.93534106438818	0.14309055794421
H	-0.84180444775828	-0.35426407874634	2.03656234122491
H	0.34239974463779	0.81838975361694	3.86938031452526
H	-2.30491644222586	5.81723267143029	3.89112781427948
H	-4.50061322441681	7.57866841681964	2.00985207462835
H	3.08306717122290	8.19556514245237	2.86674009481936
H	-4.23812080832601	7.15120564994551	3.69112041762639
H	-4.51605036191815	4.73403084854521	2.96374787481534
H	-4.55484493019183	5.13447298309895	1.24595039369395
H	-3.35276911544578	3.99815508091195	1.86134913453386
H	-3.44065644616205	7.59968918244294	0.15740094074251
H	-2.06427933795052	7.92093246064258	-1.84791245568847
H	0.11726056329019	6.80514516513733	-2.03737922301931
H	1.60682036001063	4.7215113245333	0.63464192648376
H	2.61560468502408	6.88773644809296	0.19081559077586
H	3.41389251993119	5.62901320419673	-0.73757683475029
H	2.28433496548783	6.71860442279347	-1.53212399539677
H	2.22473709630326	3.58255809761343	-1.47377413037458

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

H	1.06614237967354	4.56468597290952	-2.37025651339760	H	-3.15466863883390	2.75770462331326	2.59219883043442
H	0.49782161369480	3.37821118866061	-1.19201910315678	H	-3.51635667807717	4.87295659289734	4.76674601711998
H	-1.04991234953974	7.42172150540709	5.04807383938567	H	-2.39174900194249	3.51224490720100	4.83472259095135
H	-1.58959268453391	9.82794742098063	4.90650336064518	H	-4.12940225886949	3.22530864534359	4.78493508414691
H	-0.48985160353066	11.18666853734570	3.09981489048218	H	-5.44066370944723	3.65099658157623	2.64779219545436
H	0.99967116092754	10.08488597545670	1.44869251950314	H	-4.83472402235649	5.30368326214469	2.54445208469595
H	1.43967822054567	7.6209969924747	1.59154710010271	H	-4.60903857450293	4.19318577660361	1.18979131443552
H	0.94445275602232	3.17387095887687	4.79082803631231	H	-2.69841952963223	6.38306964040854	3.32929612782014
O	2.26457769028186	5.65805925733644	3.45348536216434	H	-0.90000038038968	7.75614677212548	2.36488596471250
Si	3.61597275699102	4.74480934991158	3.58111935741577	H	0.67000057197313	6.76608667754947	0.75004741284580
C	3.87702229840731	3.49471495757097	2.19832383914211	H	0.53931813108850	3.19375236210946	-0.32287866482945
C	4.66102897586993	3.81778197292821	1.08802025341603	H	2.87531511133400	3.93908868694838	-0.49880565521611
C	4.83738293466257	2.92156367430302	0.04155534013705	H	2.50390980299510	5.42694822680731	0.367135368322086
C	4.22968387150331	1.67452647870521	0.08753152796387	H	2.37296276149729	3.86423987244599	1.18518208312094
C	3.45188331676107	1.32939736529199	1.18509343289642	H	1.19884816354734	4.47492710172381	-2.32017365505502
C	3.28290498157762	2.23029468423918	2.22703943109289	H	0.78294856637091	5.99327596036562	-1.53002607599556
C	5.04844616953098	5.96788855082375	3.48554090488049	H	-0.48038372028847	4.82310528901170	-1.91343344346157
C	6.35782206736501	5.55011807997783	3.73883142172273	H	1.76953240239531	1.76473328807113	3.73262537891544
C	7.42600838680062	6.43224758640983	3.66045113962574	H	4.16321776889737	1.61669073443425	3.205684144112574
C	7.20284315607171	7.76196927536358	3.32411445129303	H	4.89946059030763	0.91956044633081	0.94588256427899
C	5.9103128937608	8.19797219572134	3.06985020831674	H	3.20672661843932	0.38378928479059	-0.77993186255783
C	4.84560945745233	7.30788042023442	3.15155630276013	H	0.81282648990617	0.54619013942600	-0.25606894868193
C	3.72342743221206	3.86579376311169	5.24180487996947	H	-1.94940068304504	-0.71342825230839	1.25860350645793
C	3.05674327584769	4.38168938213112	6.35678785317223	O	-0.66687148339309	-0.14616428958376	3.35134500655538
C	3.16541382177990	3.77995202908333	7.60297321793827	Si	-1.65830928271090	-0.74817474861184	4.48648370777743
C	3.95158082534245	2.64579968672398	7.76135350067144	C	-3.37619540772217	-1.12713480764934	1.80767189713138
C	4.62542151652139	2.11960565402091	6.66799492946859	C	-3.78541157997696	-2.42594449739030	3.50385651440003
C	4.50946769208468	2.72578981753519	5.42330696450231	C	-5.01958388780826	-2.67446206689590	2.91342789393661
H	5.14548831907137	4.78563833318568	1.03191492541464	C	-5.86913998850083	-1.61986021421385	2.61179817172411
H	5.44781658101718	3.19757489324522	-0.80917345647587	C	-5.48273894374692	-0.31789666404251	2.90760392102825
H	4.36230808553426	0.97421347584564	-0.72756553017745	C	-4.25185208772429	-0.08120760140436	3.50079966736184
H	2.97269450647435	0.35941879628514	1.22916647727436	C	-1.86306697003158	0.43922560231239	5.9359323387690
H	2.67214240867869	1.94179981974661	3.07171395702642	C	-0.80806131776845	1.28021706600917	6.30104333672213
H	6.55523796833867	4.51646082938255	4.00340407622068	C	-0.91575558379686	2.14506655892994	7.38096165271159
H	8.43160669895688	6.08480773876742	3.86189726756360	C	-2.08950751024461	2.18604232643692	8.12330583363135
H	8.03323906552046	8.45396831310701	3.26219182379725	C	-3.14831302663821	1.35664723099374	7.78099589526842
H	5.72896695820689	9.23312828671255	2.80867250202760	C	-3.03158570599788	0.49357994435907	6.69803002459138
H	3.84374077542544	7.66873495025997	2.95234003453009	C	-0.91011756060613	-2.34939817435937	5.13249992411358
H	5.03858946972691	2.29330425312212	4.58151107916767	C	0.18918414993205	-2.93935668471920	4.50715099282874
H	5.23855251927484	1.23457186554595	6.78295839728623	C	0.73516533048551	-4.12588226008673	4.98228993375152
H	4.03660785946626	2.17381892596881	8.73198241470330	C	0.18667712134420	-4.74615198928497	0.09641719199831
H	2.63531216712997	4.19502054323842	8.45100564506678	C	-0.90784321341258	-4.17451218083715	6.73344938611523
H	2.43228266025893	5.26209479546311	6.25489643774807	C	-1.44544854908526	-2.98839921781391	6.25393663590770
				H	-3.13412128771164	-3.26326029439357	3.72743428603474
				H	-5.31551000796203	-3.69109481164516	2.68667157626327
				H	-6.82881520891502	-1.80974612292454	2.14795922119887
				H	-6.13936951119622	0.51088094288673	2.67422680956462
				H	-3.97048199696072	0.94219742545732	3.72438331806525
				H	0.10861538439682	1.27106682016437	5.72598597729050
				H	-0.80693981630930	2.79145044451937	7.64128117239506
				H	-2.17830947961979	2.86314537022268	8.96348880643317
				H	-4.06662793916250	1.38443073602724	8.35411440764690
				H	-3.87385380402845	-0.13946059476875	6.44212831616388
				H	-2.29667900050301	-2.55523774917484	6.76897775912966
				H	-1.33921910610378	-4.65231258266345	7.60414856582467
				H	0.61071354256448	-5.67023440011367	6.46838032734240
				H	1.58953950876152	-4.56554812007259	4.48292901311467
				H	0.63035811516830	-2.46743339310920	3.63750977389546

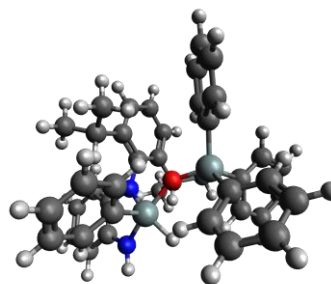
11-III



E = -2385.73738102457 Eh

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Si	-0.74637574740342	1.24313753055941	2.21869407358826
H	-0.89441243342969	2.20105638332518	3.38133663742639
N	-1.32523802338565	2.65293823922462	1.06620467173955
N	-1.74737279941922	0.26051459661575	1.10341061987920
C	1.09805928992805	1.17053585536150	1.77934325423444
C	2.07278008644646	1.46402049200488	2.73463822890532
C	3.42937832530936	1.38055741459397	2.44429204699107
C	3.84391471964605	0.98972849368273	1.17786696251434
C	2.89270567272957	0.69053852948141	0.21069612156022
C	1.53993461820029	0.78352064401175	0.51343305082297
C	-1.21841238724244	4.01584810896649	1.38942901549860
C	-2.13368145229622	4.59041506398267	2.29520686155767
C	-1.99876683700008	5.93320631502201	2.63392082750812
C	-0.99077779827294	6.71250301811237	2.09049056771211
C	-0.10798532586820	6.14927297314180	1.18575707078830
C	-0.20679299805477	4.80887014185582	0.82032127473219
C	0.75363840891195	4.25599389785687	-0.20900199850113
C	2.20732288143702	4.38328046848201	0.24132721408671
C	0.54886496295649	3.92708972649220	-1.56837186467330
C	-3.28856023889966	4.80024362191350	2.87461491171576
C	-4.61804289030136	4.26687930232329	2.27770354512481
C	-3.32925003214208	3.86158720139503	4.40074080507997
C	-2.15560706133920	2.27329402286600	0.05127822983227
C	-2.40338314492336	0.87640746090527	0.07406390455921
C	-3.25052659064216	0.30473397891800	-0.85982590048905
C	-3.85968699429176	1.10524481013511	-1.8356249886756
C	-3.62441225739739	2.46765444542726	-1.85845771116510
C	-2.77657845426233	3.05818300028672	-0.91240346688292
H	-2.60895093634081	4.12859750028912	-0.927097981790145
H	-4.09732966576360	3.089728123804373	-2.60860477640214
H	-4.51694108046710	0.65043853489732	-2.5663300607490
H	-3.44741809280376	-0.76136405708056	-0.82711692143504

11-IV



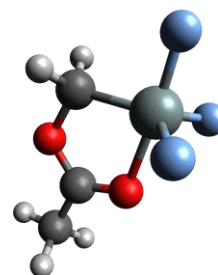
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Si	0.56986179534090	3.83193480623734	3.76892254494499
H	2.02843707579972	3.59794990609117	4.17391863601974
N	-0.55563255484100	4.34514475790697	2.38651242065198
N	0.70266230083903	2.30231495988468	2.75625232454576
C	-0.51351924695448	3.18447436186541	5.22437538827029
C	-0.94230024507580	3.99783722690692	6.27950859126651
C	-1.73008577692728	3.51368417755807	7.31605423318035
C	-2.12154752038108	2.18162884926976	7.33080306119848
C	-1.71317294351258	1.34792059663143	6.29938256193823
C	-0.92339024704058	1.84735706805208	5.26980777667631
C	-1.01483152217393	5.63466034159621	2.03356393407733
C	-2.20229473267147	6.14796047418194	2.57937892349855
C	-2.68282630330292	7.37467399177858	1.28408495876664
C	-2.01140862508419	8.09521036991485	1.15835455539418
C	-0.83210691021561	7.59282883221901	0.63402504185110
C	-0.31723924992713	6.36995093892049	1.05441810673571
C	0.95608179727343	5.85194106922712	0.41749054325271

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

C	2.02134086993775	6.93599253818592	0.25971044838866
C	0.67032038849019	5.21303190860406	-0.94439822756064
C	-2.98722565161721	5.40701773879790	3.63826273765460
C	-4.33816266983740	4.92971980885968	3.10319553552274
C	-3.17979044718422	6.26052366234661	4.89209958194822
C	-0.97295218283774	3.31078286619599	1.57110618671648
C	-0.23492729773774	2.11977468238721	1.79308193930452
C	-0.51629724169041	0.98372909368996	1.04471623541024
C	-1.52416195305607	1.01502963315143	0.07506321067884
C	-2.24405925823195	2.17562784637091	-0.14223985645966
C	-1.96616708925141	3.32839994920362	0.60436937286436
H	-2.52664863923009	4.23590466167462	0.41610806172196
H	-3.02559061978102	2.20313874168477	-0.89137377455266
H	-1.73835317046396	0.12329113914298	-0.50143625131094
H	0.05249847619790	0.07558982488553	1.21212499549782
H	-2.41550701534387	4.52553259119624	3.92531882907892
H	-3.81752903229254	7.12599309810543	4.69968998776004
H	-2.22737947156117	6.62849480382975	5.27464289505046
H	-3.65189810123978	5.67396855348116	5.68230391598735
H	-4.87179106228877	4.35843264328395	3.86548292428351
H	-4.97441216112263	5.76964740026424	2.81512151249393
H	-4.21593728458054	4.28692236419657	2.23105794289603
H	-3.60197502943831	7.77284484236067	2.54301357294610
H	-2.40078383666967	9.04546901243140	0.81425694251039
H	-0.30867280858297	8.16349972362956	-0.12362275917727
H	1.36528938065656	5.07739702996005	-1.06954014271992
H	2.96078525534923	6.48981500896650	-0.06983921711162
H	1.74011004133505	7.67957194586666	-0.48854311514397
H	2.21565035720447	7.45512650211431	-1.19774307711683
H	1.58672369146822	4.80591484936101	-1.37697072394373
H	0.27533801916913	5.95449735059568	-1.64318025084053
H	-0.0534293030064	4.40334071437642	-0.86751225091587
H	-0.66348062154741	5.04354403265607	6.3006723563913
H	-2.03998596307412	4.17930929870202	8.11286135176021
H	-2.73637473632327	1.79879979934741	8.13602907793449
H	-2.0104008988230	0.3059734092303	6.29453222908811
H	-0.62109530337400	1.17321178975548	4.47816492298552
H	1.31450567305593	1.53241063147681	2.97489325616769
O	0.69364619341741	5.50924711404031	4.25338601581148
Si	1.60681905160058	6.64421676026372	4.96492106591116
C	0.49572761751978	8.11695241411935	5.33814882970642
C	-0.12808119658215	8.78481786626486	4.27932516346343
C	-1.01510732908121	9.82670530708937	4.50748746746606
C	-1.30114854823549	10.22336146407850	5.80772126743729
C	-0.69833037381541	9.57023326204107	6.87362156953624
C	0.18985951365040	8.52787158088219	6.63664192132772
C	3.01929079090972	7.19863329145872	3.84811725848119
C	3.85020499313789	6.23137516320933	3.27383618900001
C	4.94074119843208	6.58928932453166	2.49539203812913
C	5.22397137783572	7.93128271849240	2.27215026239203
C	4.41329757348730	8.90709471390434	2.83388650446951
C	3.32398954851717	8.54017073750760	3.61604157067789
C	2.44706519036757	6.09337651527728	6.56266791049566
C	3.24024379466119	7.01551043941385	7.25434244225713
C	3.90887245576582	6.66705798242165	8.41887886760992
C	3.80421830407807	5.37376007824810	8.91631033810092
C	3.03183039268829	4.44037220502805	8.24063442204529
C	2.36223799614050	4.79944246746869	7.07646579847607
H	0.06278302084909	8.47993952954125	3.25584111416071
H	-1.48932683084391	10.32299311852980	3.67008451370272
H	-1.99466522543470	11.03491099869920	5.98891683538750
H	-0.92159586957778	9.86953452181173	7.89003968700428
H	0.64437786439861	8.02755778963647	7.48381569000408
H	3.64210305882827	5.17845703657261	3.43384308098822
H	5.56914832654900	5.82298290995582	2.05889095677341
H	6.07316219510539	8.21390580444757	1.66278648726528
H	4.62819771304526	9.95474436874426	2.66369770841185
H	2.70342044058992	9.31783719030905	4.04643279750161
H	1.76997429076209	4.05240453371377	6.56514941541633
H	2.94968246397555	3.42876273214984	8.61808043262078
H	4.32572853837701	5.09583730727115	9.82354554006814
H	4.51344350915308	7.40119362405890	8.93657593884831
H	3.34432761290930	8.02865197851265	6.87905894386259

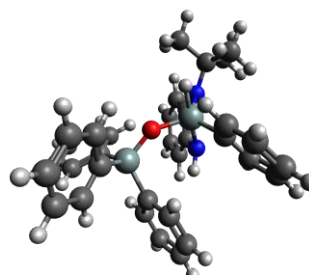
Compound 13



E = -855.49317598

0 1			
Si	0.09967016174790	-0.49597740867601	0.17302200194331
C	-1.68554658509360	-0.52602160291392	-0.45093374199828
C	-2.17587073971683	-1.87468554201916	-0.58856179317061
O	-1.31230357645250	-2.78322624958477	-0.25862193110770
C	-1.75250990153949	-4.19504260767838	-0.35755061487775
O	-0.18474630163169	-2.45957916394744	0.12796319217652
H	-2.72511754229232	-4.28346150948191	-0.83191394436025
H	-1.01444388401942	-4.76925549935731	-0.91560302771659
H	-1.80352530199410	-4.61998840921966	0.64584846701221
F	0.21992129099144	1.14201320790692	0.16914156167172
F	0.44491830869688	-0.70683864787863	1.73869281123876
F	1.34232722938663	-0.77896253850985	-0.82243693522164
H	-1.77993400794643	-0.04895889521780	-1.42748849662590
H	-2.36008915013646	-0.00705513342206	0.23208245103620

tBu-silane NH_{ax}/H_{ax}



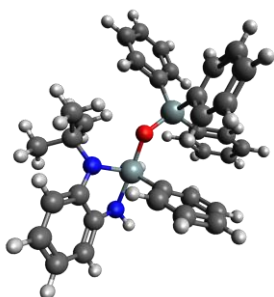
E = -2076.14262062 Eh

-1 1			
Si	-0.59748397188512	2.58268738644711	1.23686116498867
H	0.43278811168517	3.58396646387565	1.78646383346186
N	-1.00942641469494	3.69143843635800	-0.16728442025880
N	-1.90124404714004	1.51146128181420	0.44375564805094
C	0.68708478913405	1.14726171425327	1.32680761346020
C	1.73698000541421	1.26302624223843	2.24122893221202
C	2.67714970296591	0.25557730009128	2.41887247987025
C	2.60325383400719	-0.90078236411221	1.65260148588898
C	1.58233181480808	-1.03565123159384	0.72045848494759
C	0.63775083297928	-0.02663088445821	0.57004154765366
C	-0.13699416079212	4.72601523382499	-0.74001983205885
C	-2.33104038682410	3.54464844293831	-0.55359665883835
C	-2.83597067334859	2.25902381847619	-0.19839684727759
C	-4.14907028653375	1.91310473030785	-0.49478208041925
C	-4.99807572768009	2.83295121835593	-1.11453942545787
C	-4.53494529454190	4.10031748017233	-1.41395756182616
C	-3.21107419890593	4.45832234481766	-1.12311664350015
H	-2.89926913505016	5.47038935812516	-1.33869665061122
H	-5.19110374469945	4.83159767646338	-1.86975074678115
H	-6.01988724486677	2.55377511958800	-1.34158795315891
H	-4.51167103526972	0.92639481933161	-0.22693242535309
H	1.81898212781490	2.17234386913935	2.82919638284820
H	3.47019613135481	0.37308316371966	3.14774367747018
C	3.33735502170871	-1.68728928219247	1.77744936820290
H	1.52069855012661	-1.93028331112036	0.11218016147694
H	-0.15850134346159	-0.15536685726873	-0.15282528914811
H	-2.24676600043442	0.66311277580186	0.86705776341325
C	1.33736344600293	4.31487259442924	-0.59695993888579
C	-0.33745973870327	6.07839768127653	-0.04590914025015
C	-0.35394823566537	4.86368233549818	-2.25657119469679
H	1.50603716366861	3.32704091028865	-1.03093087872709
H	1.96727832677151	5.02702035886831	-1.13321279572623
H	1.66785484152573	4.28913724704925	0.43699019165440
H	0.32328956300509	6.84072682479882	-0.46507765101194
H	-0.11717171154400	5.98847852106966	1.01879992603088
H	-1.36189663047414	6.43928169274638	-0.14423545636862
H	-1.32344895620334	5.26360121451835	-2.53920424731012

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

H	0.40097192053966	5.53542594999827	-2.66850228313055	H	-0.82903883378853	5.63621216196514	-2.02574670715988
H	-0.23874571903283	3.89472399672684	-2.74609055754020	O	0.31838776013268	4.67289260936058	2.69551329709648
O	-1.48315360397216	2.76760959149503	2.71993186128105	Si	1.40237715894236	4.57867137166903	3.89595883223734
Si	-2.55708808033772	2.08479143955957	3.73113855393037	C	1.92534464045119	2.81454497154530	4.3175035431316
C	-2.98537389817075	0.30370342195271	3.29704890440970	C	1.67845110163520	2.25596777451496	5.57229745831015
C	-2.00120916935022	-0.68651297600228	3.38021315570301	C	2.03083760225044	0.94353341965988	5.86287972649735
C	-2.2647125615022	-1.99628264418494	3.00633347545156	C	2.64418076241250	0.15988405077428	4.89577571950907
C	-3.52908480608292	-2.34480508331640	2.54667921093038	C	2.90709085002252	0.69694066148716	3.64151563364059
C	-4.52239892163472	-1.37917964407790	2.46407111623689	C	2.55105725563052	2.00864271111396	3.36118611098940
C	-4.24891926866347	-0.06812342285740	2.83568458693538	C	0.72500186057056	5.36254800822313	5.47239993388424
C	-1.80343126957385	2.06678511517919	5.45621805329671	C	-0.64113184546921	5.34656614176367	5.76141343330391
C	-2.27272265169527	1.20374457863415	6.44966047536083	C	-1.13363398666886	5.88312437398339	6.94427055260643
C	-1.73177385545805	1.21309295698686	7.72864619265902	C	-0.26422919855037	6.45022107854044	7.86635630362135
C	-0.69853941568576	2.08806479760705	8.03707818280163	C	1.09829486376580	6.47722698955900	7.59843063316104
C	-0.21175946457662	2.94860575211708	7.06196147453435	C	1.58234853263299	5.93894375342711	6.41323441660876
C	-0.76101319092897	2.93601723186009	5.78640639141068	C	2.96908754549627	5.54593197187126	3.46444242970117
C	-4.14366422075578	3.09574752550681	3.74908460582957	C	4.25309743712768	5.03181648662350	3.65173227348672
C	-4.49108119972895	3.89359086195982	2.65664632946274	C	5.38525682729092	5.78444815847113	3.35933841750654
C	-5.67679677276793	4.61735811831209	2.64448987842785	C	5.25272914479723	7.07653174695676	2.87244712528948
C	-6.53886415601001	4.55895721692846	3.73087137910512	C	3.98424338278382	7.61192080424364	2.68304578228510
C	-6.20955631151710	3.77425599215398	4.82887858335243	C	2.86105410162201	6.85344958489400	2.97896169474057
C	-5.02349588805546	3.05277451809645	4.83352040501379	H	1.19306150992450	2.84804057829612	6.33923459056178
H	-1.00739762150602	-0.43409445027542	3.73380630361751	H	1.82383735171010	0.53251111372032	6.84310482302980
H	-1.48512315374018	-2.74480232817602	3.07134481252315	H	2.91779315192034	-0.864088391872846	5.11718660811099
H	-3.73805177532258	-3.36603205841443	2.25402823354804	H	3.38756694032744	0.09248230708706	2.88234913325278
H	-5.5094254279874	-1.64526525251780	2.10710239528132	H	2.76061306324402	2.40561336327255	2.37446496024186
H	-5.03350477316571	0.67528310447854	2.75478966866350	H	-1.33590842032830	4.90701474904407	5.0564553588042
H	-3.06869919521862	0.5020603563236	6.22434678671231	H	-2.19765863578000	5.85852415887104	7.14494208939349
H	-2.11150673567466	0.53452166870103	8.48216543192605	H	-0.64590232307802	8.7065323377337	8.78834440594744
H	-0.27113934416845	2.09567571481907	9.03182284823136	H	1.78277306653743	6.91998313304226	8.31130118015498
H	0.5984026727954	3.62830632637713	7.29476973027567	H	2.64918031733630	5.97527916899570	6.22102785258359
H	-0.36362044031469	3.60915818950547	5.03596666274558	H	1.88189083333084	7.29249306392050	2.82416015615835
H	-4.78348254569240	2.450184409731225	5.70395722246084	H	3.87192312817888	8.62061538829605	2.30517676999670
H	-6.87550046433382	3.72657206971679	5.68138696487028	H	6.13185481151752	7.66510372586402	2.64218955498902
H	-7.46295255349031	5.12323982934764	3.72374816711732	H	6.36994526162797	5.36043785814416	3.51183600726061
H	-5.92543257342132	5.22611035583682	1.78412955286581	H	4.38124018362684	4.02531477176677	4.03232220687270
H	-3.83768919847201	3.94883275708253	1.79394441973366				

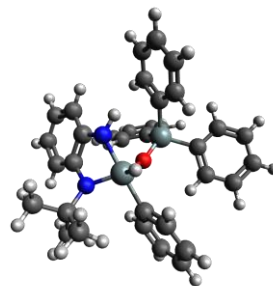
tBu-silane NH_{ax} / OSiPh_{3ax}



E = -2076.13450038 Eh

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Si	-0.63753585694407	3.59494362853055	1.60522348321029
H	0.55156074746432	2.71912420883286	1.33890903650310
N	-1.21640082380017	4.95946880119206	0.56516713109135
N	-1.67658136329704	2.54981351996920	0.39830969649242
C	-1.76436336627597	3.08672996605364	3.06149871508841
C	-2.93072881248104	3.79195234513195	3.37885963899670
C	-3.75016226541176	3.41090811056564	4.43532412046443
C	-3.41884376316189	2.3105009326279	5.21560454445635
C	-2.26783828993678	1.59234916872309	4.91828506062956
C	-1.46165680882676	1.97521508065117	3.85270728588684
C	-0.45224829216355	6.11835742650529	0.06910072020331
C	-2.49627247007680	4.68019466725903	0.08842876256400
C	-2.74605488821411	3.28102438033083	-0.00663714403059
C	-3.99036648374014	2.83304029539529	-0.44577864548248
C	-4.99146777175287	3.74570949903507	-0.78406507392665
C	-4.76510917844729	5.10416545852912	-0.65599121479292
C	-3.52338611679355	5.56576900299290	-0.19946990940487
H	-3.38345975178481	6.62971599787161	-0.05905815859506
H	-5.54621006216215	5.81699414977411	-0.88911615914818
H	-5.95176262440645	3.38215897560950	-1.13017461102078
H	-4.17598449827391	1.76718491132246	-0.52481312172463
H	-3.20721923671505	4.66589512773468	2.79957955515252
H	-4.64553022491046	3.98042081395685	4.65509432582559
H	-4.04985645035601	2.01646832660531	6.04507904094042
H	-1.99482085227486	3.73297907894564	5.51939518696244
H	-0.56741784863219	1.39586360777284	3.64777039600263
H	-1.87367117780048	1.57342193309655	0.56837702856309
C	1.03416850277552	7.25025992157185	-0.04458761713901
C	-0.62316223600836	7.33732687254063	0.98177684002147
C	-0.86495800780555	6.50217748636475	-1.36216607102934
H	1.164827632317038	4.91272615969650	-0.73137948151484
H	1.59576521855479	6.59854119199310	-0.44503942811776
H	1.47737645574868	5.48706393891811	0.90855254600874
H	-0.03483904668434	8.1875559564236	0.166412216484909
H	-0.30498496260429	7.10506692090670	1.99668500382018
H	-1.66693521792857	7.65417724113851	1.02302361442202
H	-1.8570220926348	6.93953219210081	-1.43867318607688
H	-0.15999759196252	7.24248995441527	-1.74389717119774

tBu-silane NH_{ax} / Ph_{ax}



E = -2076.13304031 Eh

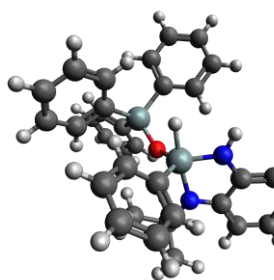
-1 1			
Si	-0.68577554891954	2.43421599657794	0.89897162805907
H	0.26451927490101	1.25810422442484	0.71322071947856
N	-1.19144589623068	3.67593403235211	-0.34185071266098
N	-2.05961302375111	1.41798733932874	0.11128706195017
C	0.74454523754651	3.46925626315936	1.77687782521465
C	0.54828454252226	4.74474871550650	2.31956501891082
C	1.51847232629821	5.38257058177057	3.08100781021566
C	2.73093327239588	4.74978261295552	3.33849816272090
C	2.95245567534249	3.4808996754895	2.82270245427976
C	1.96799098912032	2.86218214642001	2.05644376538515
C	-0.35132443640691	4.43222037181055	-1.29046388130286
C	-2.56230352379527	3.55893438238682	-0.57297299150675
C	-3.05092061775701	2.24929912582412	-0.30148618814779
C	-4.40662084347159	1.96954072638900	-0.46126349390035
C	-5.28646063221552	2.96762668370298	-0.88133303167076
C	-4.82075659833849	4.24754856474025	-1.12657933413442
C	-3.46107199333171	4.54092167023279	-0.96160187887711
H	-3.12237257053703	5.55351564920691	-1.13847821454956
H	-5.50093961343941	5.02988116970217	-1.43970365278594
H	-6.33812179369101	2.73704099720371	-1.00534947315199
H	-4.77237236741820	0.96919468574850	-0.25676775421325
H	-0.39455199822640	5.25513319934434	2.15166874638006
H	1.32940809653899	6.37082931718344	3.48453243935650
H	3.48962289321305	5.24051642575822	3.93583787705051
H	3.88962926361680	2.97271793425344	3.01911756004755
H	2.15884786685666	1.86608431233527	1.66496623420822
H	-2.7401504739570	0.54128058158472	0.50328859126880
C	1.07429856239619	3.86847149232186	-1.31279402701157
C	-0.26716513648299	5.92396787732086	-0.94222458035342
C	-0.7785408601126	4.27846894449869	-2.72672694310712
H	1.06975504384393	2.79500334151598	-1.51471216073050
H	1.64525109386173	3.35229876320983	-2.107520364219362
H	1.60628270121999	4.03691575801180	-0.38099520722576
H	0.36103487939463	6.45421466636684	-1.66177802256313
H	0.06593148346575	7.04718604247397	0.04718604247397
H	-1.24649771377250	6.40265324976120	-0.94985443058174
H	-1.85259430015908	4.73604325945736	-2.88323054219362
H	-0.18229988898370	4.75109395289178	-3.42240562766021
H	-0.95701111913038	3.22343563276847	-2.99685910176680

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

O	-1.55906474855884	2.57663884603132	2.38278298952949
Si	-2.51780656276545	1.92636859165858	3.51793368918140
C	-3.18268828201609	0.22776881974311	3.05212328141582
C	-2.31395537595885	-0.86610684890033	2.98278447050704
C	-2.76310364728840	-2.11945870317350	2.59233889066991
C	-4.10141439406478	-2.30517888542198	2.26675345674535
C	-4.98167775662928	-1.23477152710597	2.33599607431269
C	-4.52275524656607	0.01813656102112	2.72509716462126
C	-1.52354922893074	1.72486189324144	5.10317047883182
C	-1.9350600899850	0.85767140790099	6.11863038936779
C	-1.21086360046135	0.73101118399638	7.29675400945529
C	-0.04884243941991	1.46978656392346	7.47776196125031
C	0.38157072239084	2.33137992494947	6.47747837064767
C	-0.35050363003461	2.45733283547917	5.30379150868327
C	-3.97287365903412	3.07921536003724	3.82074756097861
C	-4.47998500355117	3.86313215328884	2.78059160794857
C	-5.57237687064237	4.69759989088800	2.97911514004271
C	-6.17964396501748	4.76586944352908	4.22588557372241
C	-5.68892414832405	3.99628359036995	5.27257477315510
C	-4.5963076237762	3.16397152718010	5.06762227865378
H	-1.26634653856077	-0.74127805299713	3.23532321661490
H	-2.07197294808342	-2.95138704642905	2.54164262751880
H	-4.45574456702894	-3.28185325972528	1.96215618872652
H	-6.02579263479263	-1.37405476715364	2.08521806798604
H	-5.22338367923090	0.84395252043237	2.76676416347523
H	-2.83202059855839	0.26117190818250	5.99006245440405
H	-1.54892819108760	0.05268680832222	8.07011849314295
H	0.52129283169049	1.37029157723004	8.39287324863606
H	1.29055170950333	2.90514007999346	6.60906199755664
H	0.00564678169751	3.12864117719881	4.53076644578551
H	-4.22401055975039	2.57844715014300	5.90104902948607
H	-6.15474846539411	4.04719671479431	6.24877118468385
H	-7.03043356832558	5.4171004151349	4.38236311342940
H	-5.94803151471845	5.29454199893693	2.15733326977073
H	-4.02765593765583	3.82179395075825	1.79629250404120

Si	2.02754076471560	4.17943711797787	3.34978930571042
C	2.59085526406362	2.38422628687391	3.24912204508712
C	3.60889519529159	1.97237810425268	4.21393628092034
C	4.08474697412058	0.66870895155265	4.19946328949350
C	3.55046428619170	-0.25348595733053	3.30844912661675
C	2.54200870581244	0.13686009362813	2.43833131306331
C	2.06849669548225	1.44288667651449	2.46133105710025
C	1.59604786319998	4.70436393944592	5.10264258103228
C	1.50836067732738	6.06413411005196	5.4129307143245
C	1.09093917011551	6.49189363380033	6.66560854133472
C	0.75463352158630	5.55968166862809	7.63879629533160
C	0.84234874062315	4.20365281845650	7.35352723344897
C	1.25704793013960	3.78451291717411	6.09614876609119
C	3.49745113547767	5.22046267316005	2.79598961476714
C	3.66943281895618	5.55447793278725	1.45076499683869
C	4.77655076821034	6.27430725668037	1.02151483892827
C	5.74261594090765	6.67313085929645	1.93566997583280
C	5.59433124384809	6.34756100467113	3.27728730741481
C	4.48249019129983	5.62958787211273	3.69819780425085
H	4.04325450202889	2.67690658881922	4.91571617257327
H	4.87156367950427	0.37194940414271	4.88154904230955
H	3.91942983278185	-1.27124907960147	3.29295464065336
H	2.12110626505755	-0.57672342612751	1.74108395826703
H	1.27516413165439	1.72438986294554	1.77955138583280
H	1.76143460185372	6.80771305682028	4.66503276910679
H	1.02446749273198	7.55062519811340	6.88215683383093
H	0.42667242461730	5.88922729931152	8.61658905453115
H	0.58097691122977	3.47287218757740	8.10846156861876
H	1.30585643973867	2.72232023555800	5.88701723542786
H	4.38289440656396	5.39332048277011	4.75190610233704
H	6.34258722539824	6.65646149085305	3.99641834517930
H	6.60617227292162	7.23593450213885	1.60444538860577
H	4.88461865673793	6.52477369034787	-0.02637627715810
H	2.92783624443355	5.25166171707669	0.72160129380640

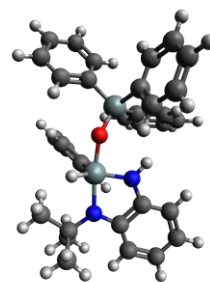
tBu-silane NtBu_{ax} / H_{ax}



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N	-1.11553745977687	4.83630857093816	0.55182999057398
N	-1.29893202276511	2.49132330406871	1.30283115381024
C	-2.17193648998217	4.83982663600776	3.20578372114028
C	-3.42046377379199	5.10010546495992	2.63674817005256
C	-4.45386211643263	5.67393304536310	3.36890423400970
C	-4.25303739101780	6.02591389297292	4.69712628224635
C	-3.02206167708858	5.77094664711189	5.28896286705898
C	-2.01034254903433	5.16553658791129	4.55442156918022
C	-0.92302929948300	6.26847268859049	0.27500425983620
C	-1.48042899419205	3.98703857269215	-0.45848605877474
C	-1.60331730249072	2.63295283669110	-0.02276379637061
C	-1.98174331736634	1.61803579109374	-0.881352149198820
C	-2.25200157830659	1.89079967136811	-2.22694079658430
C	-2.12799196397536	3.18860882799398	-2.67852536594047
C	-1.74444975439683	4.22207609517957	-1.81472479853623
H	-1.66312331651140	5.20996067327239	-2.23955466303283
H	-2.32702141424486	3.42740866058172	-3.71653826803273
H	-2.54977461326357	1.09304958431797	-2.89570818353057
H	-2.06416316498166	0.60566689446549	-0.49992580349701
H	-3.59117710183577	4.85334050479211	1.59559550278363
H	-5.41505776195074	5.85120630987690	2.90109130821940
H	-5.05016497884487	6.48604601586966	5.26798279236912
H	-2.85421046530135	6.93216479380627	6.32716768841053
H	-1.07161671685930	4.04199453078917	5.04801922644925
H	-1.32197552243412	1.56692406766289	1.70008816058550
C	-0.53719532120666	7.06235606590208	1.53225829819563
C	-2.22210913715291	6.93236409832710	-0.22338751394286
C	0.22488029158012	6.49592776856082	-0.72549975083157
H	0.41645669541581	6.74875481904166	1.94847164528032
H	-0.44717503083709	8.115625955610366	2.5865418113766
H	-1.29386029644732	6.99412579960866	2.31132321234660
H	-2.03776045555510	7.97920977747993	-0.47413153771109
H	-2.97603301710274	6.9105083679831	0.56444250866252
H	-2.65609409936685	6.46036104577049	-1.10114009426978
H	0.07195980017650	6.01397709260773	-1.68841122836600
H	0.36334452433494	7.56298136466717	-0.91274701933689
H	1.15716114281137	6.10952292577477	-0.31230163098905
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tBu-silane NtBu_{ax} / OSiPh_{3ax}



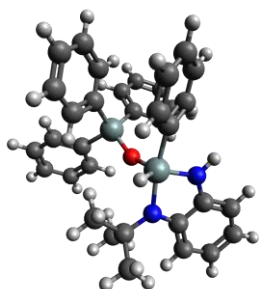
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N	-0.06799905368592	3.61335798381299	-0.16171718382083
N	-1.81683511990934	3.06323950003358	1.47561782837690
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C	1.97959868734588	1.22350412455388	2.41051437795275
C	2.65409351594863	0.0127652117976	2.31133154541933
C	2.27624566207523	0.91546179124049	1.34910735404571
C	1.23408625872478	-0.61089185886234	0.48316465839865
C	0.58317228452838	0.61295852198793	0.58065253178121
C	1.10036767929892	4.01533909110500	-0.94977531463576
C	-1.29248534791026	3.46547317265429	-0.74987757752476
C	-2.30803501551398	3.14820676034064	0.20101954858829
C	-3.62468284088024	2.9587729259504	-0.17346033314136
C	-4.00241440980587	0.07486214911902	-1.51711254967890
C	-3.03929626838974	3.38008562944163	-2.45637859243780
C	-1.70193610205489	3.57225439603725	-2.08456199672515
H	-0.99860613823414	3.80416611146529	-2.86932127769738
H	-3.30658319384612	3.47335797066897	-3.50232257899531
H	-5.03499527118998	2.92484276882419	-1.80631413143614
H	-4.36215548714477	2.71766758555394	0.58507173062522
H	2.28166725347408	1.92128978989290	3.18265053783311
C	3.46821880353779	-0.21043324441653	2.99067819073611
H	2.79050599487821	-1.86568622049122	1.27384982404166
H	0.92856553569922	-1.32812594485949	-0.26931612166332
H	-0.21897530481347	0.83175260562180	-0.11520980077911
H	-2.47326952413931	8.2444126297071	2.19972203269613
C	2.34089463383026	4.18082165247485	-0.06058516573523
C	0.88561842320953	5.38882813571076	-1.61079573426311
C	1.47714381785873	2.95538026091891	-2.00067938503870
C	2.58605385948074	3.26941836174276	0.4838949185459
H	3.19642407331519	4.42258281281911	-0.69417744052388
H	2.2275593296469	4.98794297282604	0.66097382378987
H	1.78431791027282	5.6962413323272976	-2.14995043088558
H	0.68406515119406	6.14044683743292	-0.84505855983680
H	0.05966745663948	5.41286565607849	-2.31785396380680
H	0.7150975735844	7.2633855027041	-2.69503240306227
H	2.33278056943906	3.29070395452865	-2.59124704491364
H	1.75678524232409	2.02397897126790	-1.50654900159566
O	-0.30301365718728	2.93096743611085	3.50983191692025
Si	-0.88685254203743	1.89605639851530	4.60668429834999

Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes 3

C	-1.77929132296708	0.39750984631964	3.88507382924124	H	-1.38990649080290	8.10956519176076	-0.48630442766450
C	-1.06515395573975	-0.67618673205650	3.34527992294383	H	-2.59516198947866	7.13358601833737	0.35337158061678
C	-1.71640117837092	-1.76321982855368	2.77951244689999	H	-2.11324675828540	6.72354468654984	-1.28553007746085
C	-3.10439293453267	-1.79818179137251	2.73688289907185	H	0.47909632453599	5.75813774220977	-1.57597019456588
C	-3.83428456969720	-0.74208982575942	3.26420389503445	H	0.95725298391910	7.25546978665691	-0.79021709631612
C	-3.17416927103476	0.33998798496062	3.83347648732453	H	1.43819228523242	5.70473315089356	-0.10598693325341
C	0.48259571365916	1.27020395206096	5.74119079349192	O	0.61068580680763	3.90856927703889	2.32142216437386
C	1.61083561012553	2.06069610739785	5.97556156473579	Si	1.92201205785393	3.65643091017689	3.25444527371091
C	2.61690460407811	1.64595939693659	6.83725672001078	C	2.52238187291237	1.88761413624331	3.04241202810688
C	2.51256616191199	0.42367002194274	7.48945317204464	C	3.68596827015858	1.44425137461933	3.67724684172472
C	1.39903272648484	-0.37630634489824	7.27405229942960	C	4.16821915965823	0.15754008672744	3.48255532677874
C	0.39778324094920	0.04641547340785	6.40801072655845	C	3.49762995917657	-0.71187150954252	2.63138950202235
C	-2.14225091718689	2.81223272842964	5.68017312115925	C	2.34993750371599	-0.28539865635676	1.97773262674352
C	-2.71343577551313	4.00916653763286	5.24389170962613	C	1.87015419151338	1.00220637941268	2.18304373460125
C	-3.66030268306147	4.67823401422476	6.01046790641651	C	1.65328071271655	4.10023910976149	5.05952365640585
C	-4.05292689058245	4.16019914018083	7.23671536949038	C	1.20114013584212	5.38485531683069	5.37675359909914
C	-3.49509784203145	2.97138123017178	7.69094186935231	C	0.98848452240827	5.77019686775114	6.69184468475882
C	-2.55150643768577	2.30929499585359	6.91772571089359	C	1.22419218386675	4.87063365576651	7.72418285800741
H	0.018764462924590	-0.66522259020013	3.35600101535003	C	1.67230343864209	3.590826184648925	7.43090695863194
H	-1.13971594530409	-2.58092938173330	2.36553106921715	C	1.88499139802438	3.21368687972911	6.11034381833755
H	-3.61419231981571	-2.64443987001520	2.29370493155678	C	3.31430337993828	4.74887706619260	2.59930272820054
H	-4.91653227549315	-0.76100733653461	3.23399987568836	C	3.65427804235276	4.67206209911367	1.24447821277243
H	-3.76332384432632	1.15174288052591	4.24528929705300	C	4.68173656417862	5.43677434733106	0.71242456372745
H	1.71282293081569	3.01424047538087	5.47019097605322	C	5.40202249410645	6.29717063960970	1.53264628747352
H	3.48373615175952	2.27444042906715	6.99931527071280	C	5.08807631451930	6.38293360473052	2.88101923221291
H	3.29670389563412	0.09615581880662	8.16037673393707	C	4.05425918649073	5.61467819469303	3.40511798993778
H	1.31177392553538	-1.33152576877841	7.77658871895656	H	4.23503679631458	2.11310974588286	4.33198194946103
H	-0.45902327664617	-0.598340411242493	6.24689459879271	H	5.06853050855077	-0.165800909041256	3.98971693030198
H	-2.12572232257906	1.38480030643756	7.29340485341370	H	3.87219291728134	-1.71548440373595	2.47443547905120
H	-3.79483801450597	2.56261365463345	8.64790475989977	H	1.82782323294843	-0.95477178598189	1.30560809214827
H	-4.78861422918828	4.68020592933827	7.83729257721465	H	0.97457397301804	1.31877088416818	1.66128780717175
H	-4.09013552164774	5.60486929055021	5.65076873620313	H	1.00427356900721	6.10161021089869	4.58644413356028
H	-2.41808285121314	4.42953000600502	4.28950899386799	H	0.63550998067900	6.76972913440604	6.91256755956794
				H	1.05674973396711	5.16631601272539	8.75216479677228
				H	1.85207095619268	2.88266056642802	8.22997647036184
				H	2.2099820449809	2.20443221241469	5.90432890224360
				H	3.82567995680931	5.69869070842879	4.461021278226574
				H	5.64660727134481	7.04903400973507	3.52670267562897
				H	6.20515787118472	6.89544903267879	1.12125034050799
				H	4.92237026261018	5.36222477630104	-0.34065783865226
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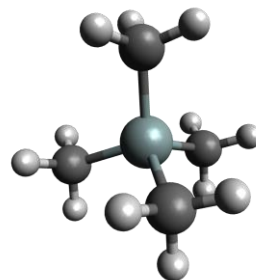
tBu-silane NtBu_{AX} / Ph_{AX}



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H	-1.72154930817831	5.16416731018755	2.91181369102800
N	-1.0998533077607	4.85505589809610	0.54028978968767
C	-1.90419003338466	2.67427981493880	1.33733209431454
C	-1.37708824341607	2.93825306639102	3.94601222328555
C	-1.92550170423679	3.58842211692859	5.05304852630743
C	-2.15757946353087	2.94493588152198	6.26394493863245
C	-1.84082800486768	1.60013779963028	6.40491529593256
C	-1.29746368660015	0.91776115272583	5.32342019079948
C	-1.07521446717865	1.58191634610368	4.12245528689416
C	-0.63025767108768	6.22006656223721	0.28234639205309
C	-1.55020998897942	4.06940707991550	-0.48094809702622
C	-2.03068541775969	2.80726741624043	-0.01907112435080
C	-2.55852866759847	1.86493487590292	-0.88144247930056
C	-2.62854565286736	2.12238760711701	-2.25535228887363
C	-2.160676302330559	3.33120623391260	-2.73009131519398
C	-1.62781201691586	4.29234309702108	-1.86274053615183
H	-1.28186334166290	5.21501555192200	-2.30209171671361
H	-2.20121595169240	3.55367322556579	-3.78985528154679
H	-3.04165202754539	1.38134557371066	-2.92804146270128
H	-2.91771321480874	0.92241742665681	-0.48136759169326
H	-2.17749160918766	4.64200733382458	4.96656115839569
H	-2.58319881143284	3.49073583174300	7.09820137827488
H	-2.01589404919729	1.08986930995022	7.34421280835724
H	-1.04627344009793	-0.13259531473628	5.41703646962360
H	-0.65001648317602	1.01378523395483	3.30137763890081
H	-2.24549409231690	1.82350273911348	1.75285750384498
C	-0.22700551521192	6.93958118112007	1.57821653593374
C	-1.74476364462485	7.08860360263072	-0.32978631453861
C	0.62522362433684	6.23101755032293	-0.60736399279770
H	0.56311329464642	6.41727607839617	2.11519313269266
H	0.15274063917497	7.93041021054481	1.32133519477427
H	-1.06821486992856	7.07530145851027	2.25527003075712

TMS



E = -448.36800014 Eh

0 1			
Si	-1.25204444775515	-1.29371729416827	0.48788562973826
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C	0.56267352076965	-1.51657844945836	0.95353396658244
C	-2.29219491394403	-1.16260380345586	2.05652320931856
C	-1.82769697670753	-2.77720630611132	-0.52585290472054
H	-1.98509701571068	-0.31221936205151	2.66830062094814
H	-3.35064274791420	-1.03316500589501	1.82269292114654
H	-2.19951988977227	-2.05966927787198	2.67170427979864
H	-2.87651538885142	-2.68050723074487	-0.81286029190591
H	-1.24509214824940	-2.88312077879913	-1.44297390746489
H	-1.72600321897977	-3.70734095708905	0.03652008165965
H	0.92965063024336	-0.67307735017667	1.54138454164381
H	1.19430413248157	-1.59790807228852	0.06686522876304
H	0.71306019361991	-2.42025013827494	1.54726871022468
H	-0.86203481932718	0.23750855140315	-1.45046130496702
H	-1.12529985656656	1.16066194858971	0.02536148081343
H	-2.49258959490359	0.44077889357562	-0.81835434771807

3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

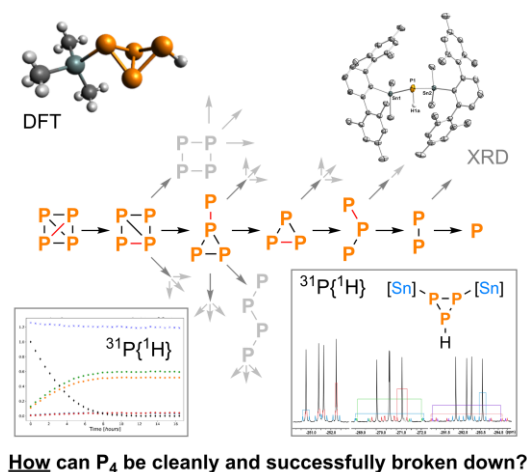
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3 Mechanistic Investigations on Diamino-Hydrido-Cyclosilanes

4 UNRAVELLING WHITE PHOSPHORUS: EXPERIMENTAL AND COMPUTATIONAL STUDIES REVEAL THE MECHANISMS OF P₄ HYDROSTANNYLATION



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English version:

Angew. Chem. Int. Ed. **2024**, e202408423

DOI: 10.1002/anie.202408423

German version:

Angew. Chem. **2024**, e202408423

DOI: 10.1002/ange.202408423

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Mechanistic calculations were performed by Jose Cammarata and Peter Coburger. Design, synthesis, and characterization of the new tin hydrides ArSn(Me)₂H (Ar = Ter, Ter*, Fluid) were performed by Daniel Duvinage and Marvin Jansen, and supervised by Jens Beckmann. In situ NMR monitoring experiments and calculations of NMR parameters were carried out by Franz F. Westermair and supervised by Ruth M. Gschwind. XRD for [TerSn(Me)₂]₂PH was carried out by Jose Cammarata and Maria K. Uttendorfer. All other experimental work was performed by Jose Cammarata. The project was overseen and coordinated by Robert Wolf and Daniel J. Scott. The manuscript was prepared by Daniel J. Scott, with assistance from all other authors.

[†] These authors contributed equally to this work.

4 Unravelling White Phosphorus

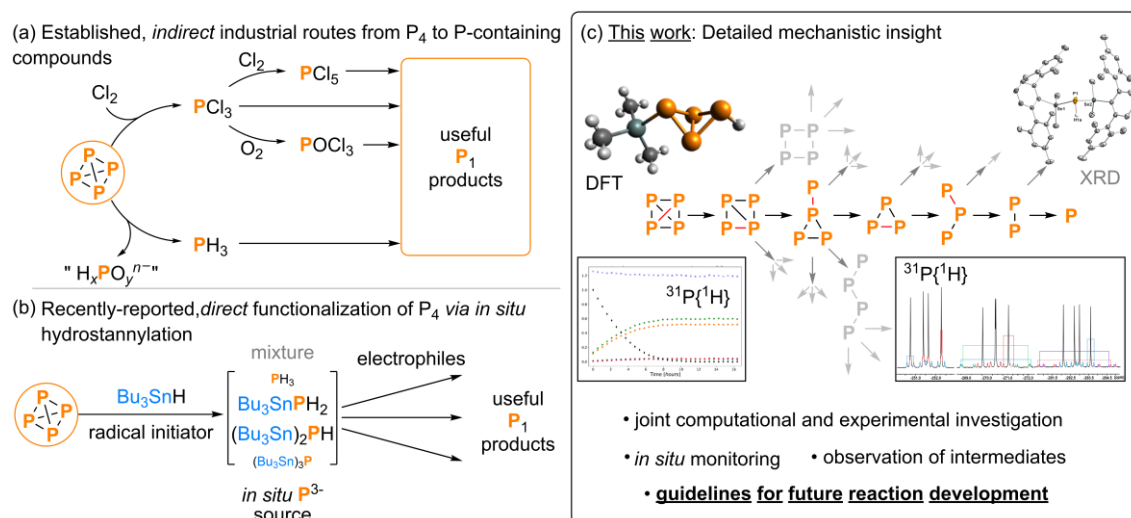
4.1 Abstract

The hydrostannylation of white phosphorus (P_4) allows this crucial industrial precursor to be easily transformed into useful P_1 products via direct, ‘one pot’ (or even catalytic) procedures. However, a thorough mechanistic understanding of this transformation has remained elusive, hindering attempts to use this rare example of successful, direct P_4 functionalization as a model for further reaction development. Here, we provide a deep and generalizable mechanistic picture for P_4 hydrostannylation by combining DFT (Density Functional Theory) calculations with *in situ* ^{31}P NMR reaction monitoring and kinetic trapping of previously unobservable reaction intermediates using bulky tin hydrides. The results offer important insights into both how this reaction proceeds and why it is successful and provide implicit guidelines for future research in the field of P_4 activation.

4.2 Introduction

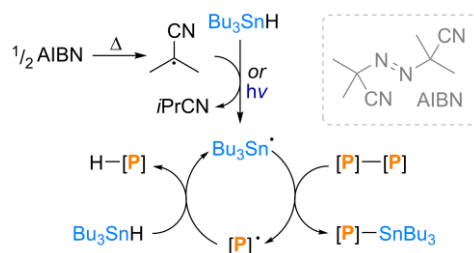
White phosphorus (P_4) provides a common starting point from which effectively all commercially relevant phosphorus compounds are currently prepared (with wet process H_3PO_4 and derived phosphate salts as the major exceptions).^[1] This is achieved industrially through multistep procedures in which P_4 is first transformed into simple P_1 precursors such as PCl_3 (via reaction with Cl_2) or PH_3 (via disproportionation).^[2] These can then be reacted in subsequent steps with suitable reagents (typically nucleophiles or unsaturated organic substrates, respectively) to eventually yield the target P_1 products of interest. (Scheme 4.1a).^[3]

The drawbacks of these industrial methods have long been recognized, with many critics emphasizing their use of extremely hazardous reagents and intermediates (e.g. Cl_2 , PH_3), their poor step economy, and their production of undesirable stoichiometric waste. This has prompted extensive investigations over the last several decades into the fundamental reactivity of the P_4 molecule, in the hope that a better understanding of its basic chemistry might aid the development of new, improved methods for the transformation of P_4 that could eventually replace the current industrial state-of-the-art.^[4] Particularly prominent has been the goal of achieving *direct* transformations in which P_4 would be converted into the target P_1 compounds in a single reaction, thus optimizing step economy while also bypassing the hazardous intermediates required currently.



Scheme 4.1: (a) Industrial routes for the utilization of P_4 and (b) recently reported ‘one pot’ transformation into useful products via hydrostannylation,^[9] (c) whose mechanism is investigated herein.

Despite comprehensive and extended research in this area, it is only very recently that examples of direct P₄ conversion into genuinely useful P-containing products (and particularly organophosphorus products) have begun to appear in the literature.^[5-7] As such, the number of total systems reported remains very low, and those that have been disclosed continue to suffer from substantial drawbacks and limitations. Nevertheless, the independent emergence of several such reports has raised hopes for a new phase in P₄ chemistry research that will see an ongoing expansion in the number and variety of direct P₄ functionalization methods, alongside steady improvements in reaction performance (practicality, atom economy, turnover, etc.). However, if this hope is to be realized, it is crucial for chemists to understand in detail *why* previous examples have been successful, in order to provide guidelines for future reaction development.^[8]



Scheme 4.2: (a) Industrial routes for the utilization of P₄ and (b) recently reported ‘one pot’ transformation into useful products via hydrostannylation,^[9] (c) whose mechanism is investigated herein.

As part of the recent advancement of this field, it was reported that the functionalization of P₄ can be achieved very simply using the inexpensive, ‘classical’ radical reductant Bu₃SnH in combination with a source of radical initiation (light, or a chemical radical initiator).^[9,10] This results in net hydrostannylation of P₄ to yield a clean mixture of the P₁ products (Bu₃Sn)_xPH_{3-x} (x = 0–3), with Bu₃SnPH₂ and (Bu₃Sn)₂PH as the major components. This mixture can then be treated directly with electrophiles to yield a wide variety of useful monophosphorus compounds in ‘one pot’ fashion (Scheme 4.1b).

The hydrostannylation reaction was proposed to proceed via a relatively simple radical chain mechanism as shown in Scheme 4.2, in line with both initial experimental observations and the well-established, broader radical reactivity of Bu₃SnH.^[11] Crucially, however, in that report it was possible to suggest only a very rough outline of the overall mechanism, which did not offer any meaningful insight into the specific sequence of steps by which the P–P bonds of the P₄ tetrahedron are broken down. This is a critical omission, since P₄’s tetrahedral structure means that its cleavage into P₁ species requires many distinct elementary reaction steps. In this case, hydrostannylation of a single P₄ molecule requires cleavage of six P–P bonds and formation of six P–H and six P–Sn bonds, with each step being in principle mechanistically different from every other. Indeed, mechanistic complexity is a general feature of P₄ chemistry,^[5] and one which is exacerbated by the known ability of P_n moieties to adopt an extremely wide range of stable structural motifs,^[12] which can make it very difficult to target specific products in reactions involving P₄. In fact, even many of the previous efforts in this area have been hampered by competing formation of undesired (and often insoluble) polyphosphorus products.^[13]

It is thus very important to understand *why* the hydrostannylation of P₄ is able to proceed so cleanly and efficiently. As well as providing fundamental insight into the reactivity of P₄, such understanding would be a powerful tool as we and others seek both to generalize and optimize this P₄ hydrofunctionalization reactivity, and to develop entirely new mechanistic strategies for P₄ functionalization. With this goal in mind, we report herein a thorough study of the mechanism of P₄ hydrostannylation, which we have pursued both computationally and experimentally (Scheme

4 Unravelling White Phosphorus

4.1c). From our results we are able to highlight several key factors that enable the success of this reaction, which will be valuable signposts for future studies targeting direct P_4 functionalization.

4.3 Results and Discussion

To begin, the time course of the P_4 hydrostannylation reaction using Bu_3SnH was tracked by in situ $^{31}P\{^1H\}$ -NMR spectroscopy. As shown in Figure 4.1, combination of P_4 with stoichiometric Bu_3SnH (6 eq., equating to 1 eq. per P–P bond) and 20 mol% azobis(isobutyronitrile) (AIBN) as initiator at 298 K resulted in smooth consumption of the starting material over several hours, alongside concomitant, synchronous formation of the expected product mixture.^[14] No significant loss in overall ^{31}P intensity was observed and, crucially, no signals corresponding to intermediates or side-products were observed in any of the individual spectra. This latter observation is consistent with previous ex situ $^{31}P\{^1H\}$ -NMR analyses of reactions halted at partial conversion, which also showed only the final products and unreacted starting material.^[9]

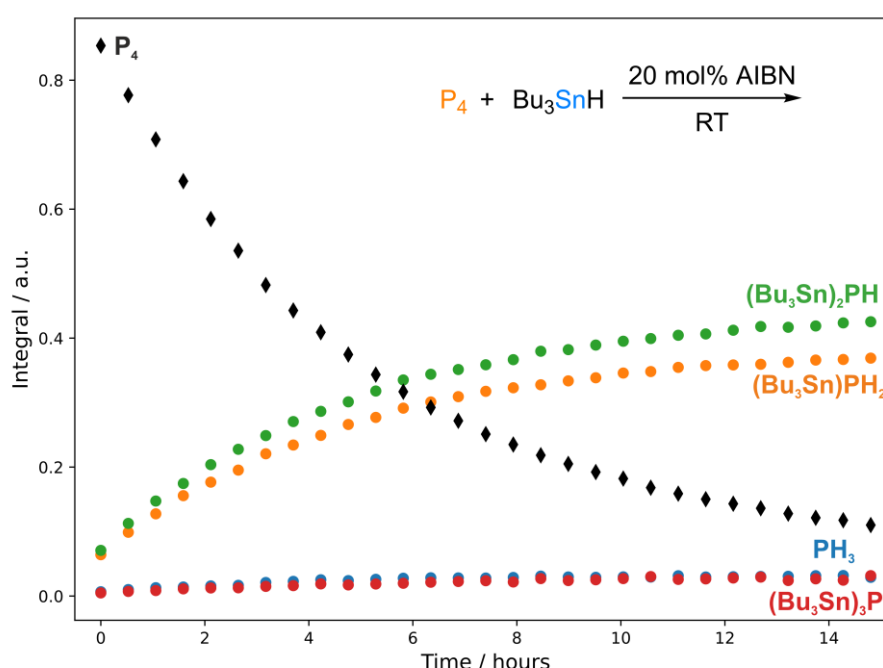


Figure 4.1: Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. Bu_3SnH initiated by 20 mol% AIBN at 298 K in C_6D_6 as monitored by in situ $^{31}P\{^1H\}$ NMR spectroscopy.

A very similar evolution of the $^{31}P\{^1H\}$ -NMR spectrum was observed using an in situ 455 nm light source instead of AIBN (see Figure 4.15), indicating a comparable mechanism. However, for reasons of both practical convenience and theoretical simplicity, AIBN initiation was chosen as the model system for further investigations.^[15]

4.3.1 Computational Investigation

In the absence of any spectroscopically observable intermediates, investigation of the hydrostannylation mechanism was continued through computational methods. DFT calculations were performed at the PBE-D3(BJ)/def2-TZVP level of theory on a model system in which the Bu_3Sn moiety was truncated to Me_3Sn for the sake of computational efficiency (for full details see Section 4.8.3).^[16] Thermal fragmentation of AIBN is well known to result in formation of 2-cyanoisopropyl radicals, $\cdot C(CN)Me_2$, that can then form $Me_3Sn\cdot$ radicals through H atom abstraction (cf. Scheme 4.2).^[14] And, indeed, these steps were both calculated to occur over moderate free

energy barriers, consistent both with previous experimental determinations and our own bond dissociation energies (BDEs), which are higher for H-C(CN)Me_2 than for $\text{Me}_3\text{Sn-H}$ (84.8 kcal mol⁻¹ and 75.3 kcal mol⁻¹, respectively; see Sections 4.8.3 and 4.8.3.2.1).^[14,17] An alternative initiation in which the AIBN-derived $\cdot\text{C(CN)Me}_2$ radical instead adds to P_4 was also calculated. However, this was found to be much less feasible and substantially uphill, which is consistent with experimental observations that AIBN does not react directly with P_4 alone even upon heating (see Sections 4.8.3.2.1 and 4.8.3.2.2).

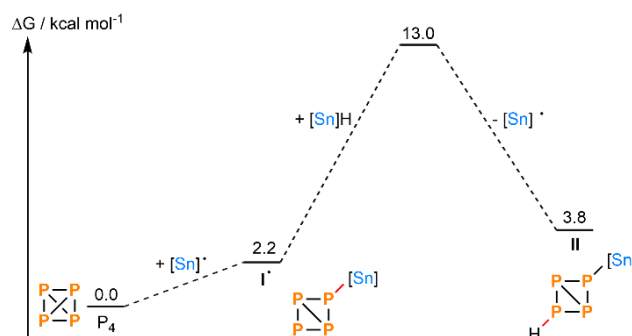


Figure 4.2: Calculated mechanism for hydrostannylation of the first P–P bond in P_4 by Me_3SnH , with relative free energies in kcal mol⁻¹. $[\text{Sn}] = \text{Me}_3\text{Sn}$. For simplicity, stereochemistry is not shown (see Figure 4.20).

First P–P cleavage: Following its formation, $\text{Me}_3\text{Sn}^\bullet$ is calculated to add to P_4 in a slightly uphill (2.2 kcal mol⁻¹) but otherwise essentially barrierless reaction to form the *exo* ‘butterfly’ radical **I**[•] (Figure 4.2). Alternate *endo* attack was calculated to be much less feasible (see Figure 4.20). **I**[•] can then abstract a H atom from a further equivalent of Me_3SnH . This is again slightly uphill (by 1.6 kcal mol⁻¹), and consistent with the slightly lower BDE calculated for **I**–H than $\text{Me}_3\text{Sn-H}$ (73.9 kcal mol⁻¹ and 75.3 kcal mol⁻¹, respectively), but this time proceeds over a modest activation barrier of 10.8 kcal mol⁻¹. This closes the initial stage of the radical chain by re-forming $\text{Me}_3\text{Sn}^\bullet$, while also generating the closed shell intermediate **II** (with *endo* attack again being less favorable than *exo*; Figure 4.20). The ‘butterfly’ structure of **II** is reminiscent of many examples in the literature where selective activation of only a single P–P bond in P_4 has been achieved, either by radical or polar mechanisms.^[18]

The combined activation barrier for this stage is just 13.0 kcal mol⁻¹, which is consistent with the experimental observation of a radical chain process that occurs rapidly at around room temperature. However, comparison with later steps (see below) shows that initial P–P cleavage in fact possesses both the highest individual activation barrier,^[19] and the highest-lying transition state in the overall reaction mechanism. This is also the only P–P cleavage step that is endergonic overall. These calculations therefore suggest that cleavage of the first P–P bond in P_4 is the slowest step and hence rate-limiting for the radical chain part of the hydrostannylation mechanism in which P_4 is involved. This is fully in accordance with the lack of P-containing intermediates observed experimentally during the reaction of P_4 with Bu_3SnH (see above) and, interestingly, also highlights a common misconception recently pointed out by Cummins and co-workers, amongst others: That the P–P bonds in P_4 are unusually strained and therefore especially reactive due to P_4 ’s small, 60° bond angles.^[20] Clearly, in this case it is the P–P bond of the intact P_4 tetrahedron that are actually *least* reactive towards hydrostannylation (both kinetically and thermodynamically), out of any in the overall mechanism. This is presumably a consequence of P_4 ’s noted spherical aromaticity.^[21]

4 Unravelling White Phosphorus

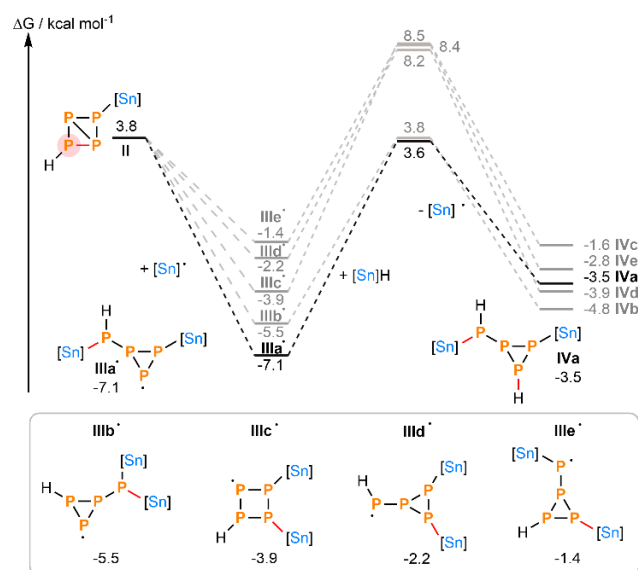


Figure 4.3: Calculated mechanisms for hydrostannylation of the second P–P bond in P_4 by Me_3SnH , with relative free energies in $kcal\ mol^{-1}$. For simplicity, stereochemistry is not shown (see Figure 4.21). $[Sn] = Me_3Sn$.

Second P–P cleavage: While the first step offers only a single set of equivalent P–P bonds to cleave, the second step is significantly more complicated. Following the first hydrostannylation step and formation of **II**, the second $Me_3Sn^\bullet$ attack can in principle occur in at least five different ways, resulting in the five constitutional isomers **III**[•] shown in Figure 4.3 (for further details see also Figure 4.21). Like attack on P_4 each option is calculated to be barrierless, but unlike for P_4 each option is exergonic, with the most favorable option found to be attack at the existing PH position leading to formation of intermediate **IIIa**[•] containing a *cyclo*- P_3 ring (Figure 4.3). Notably, though the alternative *cyclo*- P_3 intermediate **IIIb**[•] is less than $2\ kcal\ mol^{-1}$ higher in energy, suggesting only limited thermodynamic preference for one over the other. (Note that the lack of apparent activation barriers implies that formation of **IIIc**[•]–**IIle**[•] should be no less kinetically feasible than formation of **IIIa**[•] or **IIIb**[•]. However, the former should preferentially equilibrate to the latter rather than react further; see below, and Section 4.8.3.2.3 for more detailed discussion). Once formed, H atom transfer to the lowest energy isomer **IIIa**[•] proceeds over an activation barrier slightly smaller than that for **I** ($10.7\ kcal\ mol^{-1}$), giving intermediate **IVa**. The corresponding transition state is lower lying than those for H atom transfer to any of the other isomers **III**[•], but in the case of **IIIb**[•] the difference is very modest: Only $0.2\ kcal\ mol^{-1}$ (likely within the calculations' margin of error). While the H atom transfer step is slightly uphill the net P–P hydrostannylation that transforms **II** into **IVa** (or **IVb**) is exergonic, in contrast to the hydrostannylation of P_4 to **II** (see above). Notably, this general pattern of downhill, barrierless $Me_3Sn^\bullet$ attack followed by slightly uphill H atom transfer from Me_3SnH resulting in net exergonic P–P cleavage is repeated in step 3 (see below).

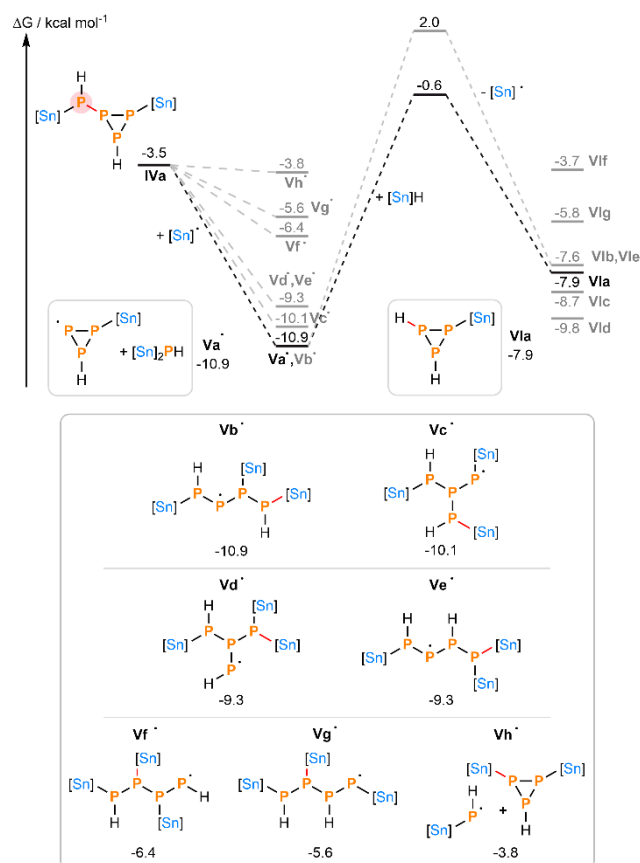


Figure 4.4: Calculated mechanisms for hydrostannylation of the third P–P bond in P₄ by Me₃SnH, with relative free energies in kcal mol⁻¹. For simplicity, stereochemistry is not shown (see Figure 4.22). [Sn] = Me₃Sn.

Third P–P cleavage: The complexity noted in the second P–P cleavage step is compounded in the third, with five constitutional isomers **IV** each offering multiple options for the next Me₃Sn• addition. Of these isomers, formation of **IVa** and **IVb** appears to be kinetically preferred (for a more detailed discussion, see Section 4.8.3.2.3) but for the sake of practicality, calculations were limited to only isomer **IVa**, which was formally calculated to offer the lowest energy transition state.

Even after imposing this limitation, addition of Me₃Sn• to **IVa** still leads to eight possible constitutional isomers **V**•, as shown in Figure 4.4 (also Figure 4.22). As in the second step these additions are all downhill and all essentially barrierless, with *five* lowest energy isomers again being all rather similar in energy, separated by a span of just 2 kcal mol⁻¹, while the two lowest (**Va**• and **Vb**•) are almost identical in energy. H atom transfer from Me₃SnH to **V**• then gives the closed shell intermediate isomers **VI**, which for the lowest-energy isomers of **V**• is again slightly uphill. The relative conformational flexibility of many of these isomers makes calculation of the corresponding transition states more demanding and time consuming than in steps 1 and 2. Nevertheless, these were computed for the two lowest energy isomers, **Va**• and **Vb**•. These again revealed only modest barriers of 10.3 kcal mol⁻¹ and 12.9 kcal mol⁻¹, respectively. The former is thus kinetically preferred (see Section 4.8.3.2.3) and, notably, involves release of the first of the final P₁ products, (Me₃Sn)₂PH, alongside the *cyclo*-P₃ product Me₃SnP₃H₂, **VIa**.

4 Unravelling White Phosphorus

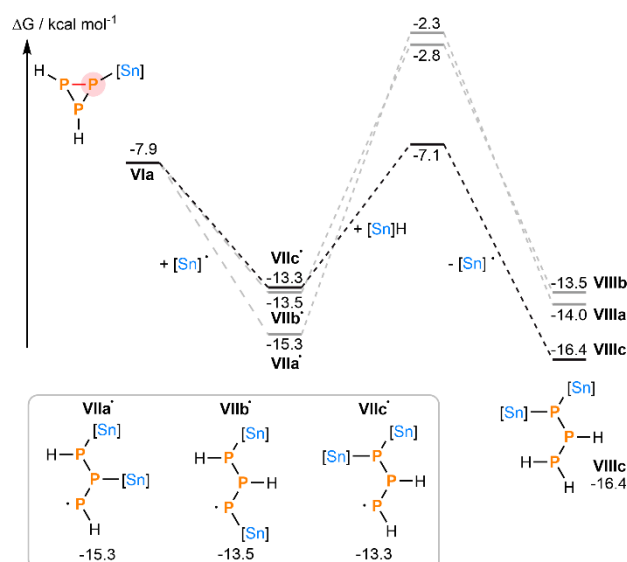


Figure 4.5: Calculated mechanisms for hydrostannylation of the fourth P–P bond in P₄ by Me₃SnH, with relative free energies in kcal mol⁻¹. For simplicity, stereochemistry is not shown (see Figure 4.23). [Sn] = Me₃Sn.

Fourth P–P cleavage: The fourth Me₃Sn[•] attack step could again proceed from any of several different isomers **VI**, and for pragmatic reasons a single, representative example was again chosen as a focus for further calculations. In this case **VIa** was selected, as it is kinetically preferred out of the two products derived from the lowest energy isomers of **V**[•], **Va**[•] and **Vb**[•], which are also the two isomers whose pathways were calculated in the most detail in the previous step (see also Figure 4.23). From **VIa** only three regiochemical options for Me₃Sn[•] attack are available, leading to the intermediates **VII**[•]. H atom transfer from Me₃SnH then gives isomeric intermediates **VIII** (Figure 4.5). In this case all three regiochemical pathways were calculated in full. As for the previous steps, initial Me₃Sn[•] attack is consistently downhill and effectively barrierless, and there is limited preference between the isomers **VII**[•], which are all separated by a span of just 2 kcal mol⁻¹. However, there is a slightly more pronounced preference between the subsequent H atom transfer steps, with isomer **VIIc**[•] providing an appreciably lower activation barrier than **VIIa**[•] or **VIIb**[•], leading to the ring opened P₃ chain **VIIIc**. Notably, this step is slightly exergonic, in contrast to the slightly endergonic H atom transfers calculated for steps 1–3.

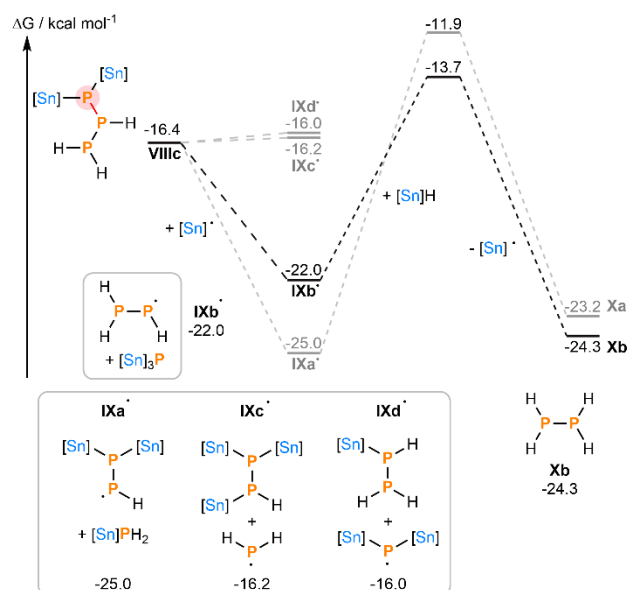


Figure 4.6: Calculated mechanisms for hydrostannylation of the fifth P–P bond in P_4 by Me_3SnH , with relative free energies in $kcal\ mol^{-1}$. For simplicity, stereochemistry is not shown (see Figure 4.24). $[Sn] = Me_3Sn$.

Fifth P–P cleavage: Proceeding from **VIIIc** (as the kinetically preferred product of the previous step; see Section 4.8.3.2.3) four options are available, leading initially to intermediates **IX** (Figure 4.6; also Figure 4.24). Of these, two (**IXa*** and **IXb***) form exergonically, as in steps 2–4, but formation of the two higher energy isomers (**IXc*** and **IXd***) is slightly uphill (cf. step 1). Transition states for subsequent G atom transfer from Me_3SnH were calculated for the former pair, with **IXb*** found to lead to a lower energy barrier, and formation of P_2H_4 (**Xb**) as the kinetically preferred product (see Section 4.8.3.2.3). As for the fourth, this fifth H atom transfer is exergonic. This combined fifth step also yields the second P_1 product of the overall pathway, $(Me_3Sn)_3P$.

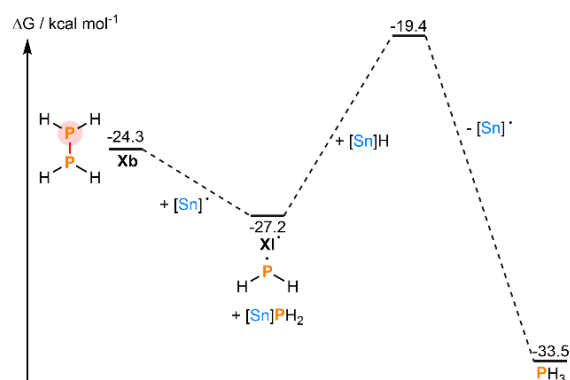


Figure 4.7: Calculated mechanisms for hydrostannylation of the final P–P bond in P_4 by Me_3SnH , with relative free energies in $kcal\ mol^{-1}$. $[Sn] = Me_3Sn$.

Final P–P cleavage: The symmetry and reduced size of **Xb** (P_2H_4) ensure that, gratifyingly, the final P–P bond cleavage calculation involves only a single regiochemical possibility (Figure 4.7). Me_3Sn attack yields the third P_1 product of this sequence, Me_3SnPH_2 , and the simple P_1 radical H_2P (**XI***). As in steps 2–5 this is downhill and effectively barrierless. A final H atom transfer from Me_3SnH then yields the final P_1 product, PH_3 . As in steps 4 and 5 this transfer is also downhill and proceeds over a modest activation barrier ($7.8\ kcal\ mol^{-1}$).

4 Unravelling White Phosphorus

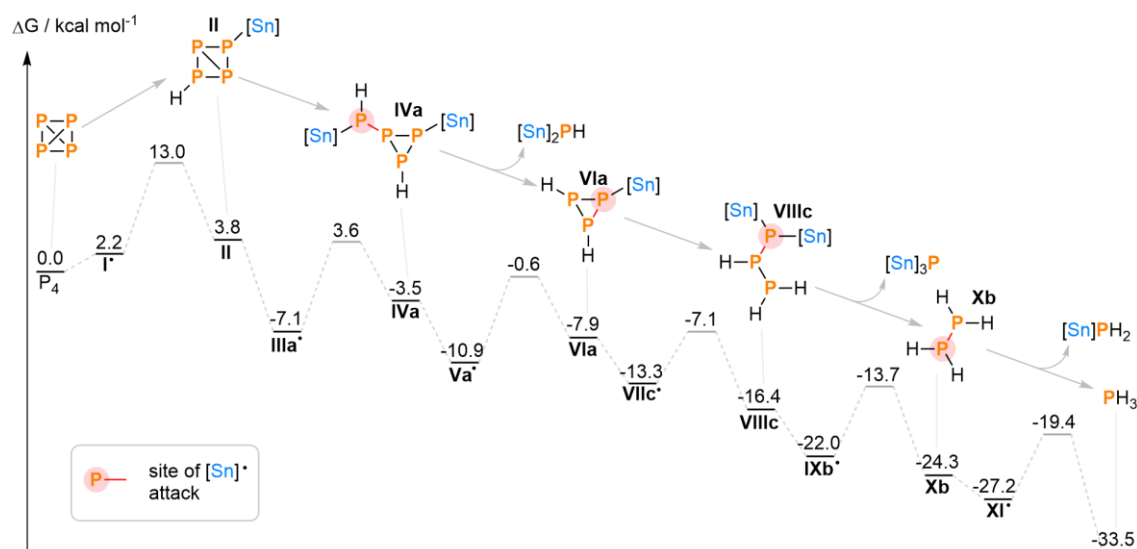


Figure 4.8: Combined calculated pathway for P₄ hydrostannylation, with relative free energies in kcal mol⁻¹. For simplicity, initiation, stereochemistry, addition of [Sn]•, loss of [Sn]H, and competing pathways are not shown (for these details, see Figures 4.2–4.7 and Section 4.8). [Sn] = Me₃Sn.

General observations: Comparing Figures 4.2–4.7, and the combined summary in Figure 4.8, it is possible to identify clear similarities between the multiple P–P cleavage steps. With the exception of the first, each is calculated to begin with exergonic, effectively barrierless attack of a Me₃Sn• radical. The resulting P-centered radical intermediate then abstracts an H atom from Me₃SnH. This latter step becomes less endergonic as P₄ is broken down (e.g. for I→II, IIIa→IVa, and Va→VIa) and is eventually exergonic during the final three P–P bond cleavages. Notably, each of the net hydrostannylation steps proceeds via Me₃Sn• addition that is exergonic to a similar extent (ca. 5–10 kcal mol⁻¹), and a H atom transfer that has a similar activation barrier (ca. 10 kcal mol⁻¹). Crucially, this ensures that there are no significant thermodynamic sinks at which intermediates would be expected to accumulate. This can be attributed to the fact that *each step is in practice very chemically similar*, involving hydrostannylation of a comparable P–P single bond (see below).

The combined pathway shown in Figure 4.8 correctly predicts the formation of all four products observed experimentally: PH₃, Bu₃SnPH₂, (Bu₃Sn)₂PH and (Bu₃Sn)₃P. However, it should be emphasized that *at every step there are clearly alternative, energetically accessible pathways*, often with only very small energetic differences between the competing options. For example, it has already been noted that in the second step, the two isomeric products IVa and IVb are both likely to be kinetically accessible, and while downstream pathways have so far been calculated exclusively from IVa it seems likely that similar investigation of IVb would reveal competing pathways with comparable activation barriers. Similarly, in the third step the *five* lowest energy isomers of intermediate V• span an energy range of well under 2 kcal mol⁻¹. Combined with the experimental observation that the four hydrostannylation products are not formed in equal amounts, these results strongly suggest that the product distribution is likely attributable less to the existence of a single, inherently preferred kinetic pathway, and more to simple statistical factors (see below). Indeed, purely random distribution of H and R₂Sn moieties within the product mixture would be expected to result in 75% conversion to the two major products Bu₃SnPH₂ and (Bu₃Sn)₂PH, even in the complete absence of any kinetic or thermodynamic biases (which closely matches the combined yields obtained experimentally: ca. 76%).^[9] This conclusion is further supported by calculations on

selected other pathways, which also show similar activation barriers and other energetic changes for each P–P hydrostannylation step (Figures 4.26–4.30).

4.3.2 Experimental Study of Bulkier Hydrostannanes

As noted above, it was not possible to observe P_n reaction intermediates being formed and consumed while monitoring the reaction of P_4 with Bu_3SnH . Nor were intermediates observed during analogous experiments using Ph_3SnH (see Section 4.8.2.4), which previous studies had been shown to also hydrostannylate P_4 , albeit slightly less cleanly.^[9] However, it was speculated that these species might become detectable if significantly bulkier hydrostannanes were employed. Increased steric hindrance should make each addition of an R_3Sn^* moiety progressively more difficult, so could potentially trap out partially functionalized intermediates. Note that, by design this will alter the kinetics and thermodynamics of individual steps and hence is likely to affect selectivity between specific intermediates. Nevertheless, observation of these intermediates should still provide experimental evidence to support the types of intermediate structures identified computationally. The hydrostannylation of P_4 was therefore investigated experimentally using the bulkier tin hydrides iPr_3SnH , $TerSn(Me)_2H$, $Ter^*Sn(Me)_2H$, and $(Fluind)Sn(Me)_2H$, whose full structures are provided in Figure 4.9.

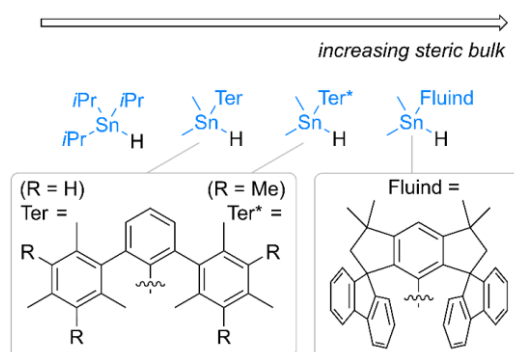
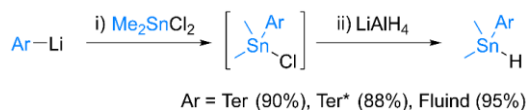


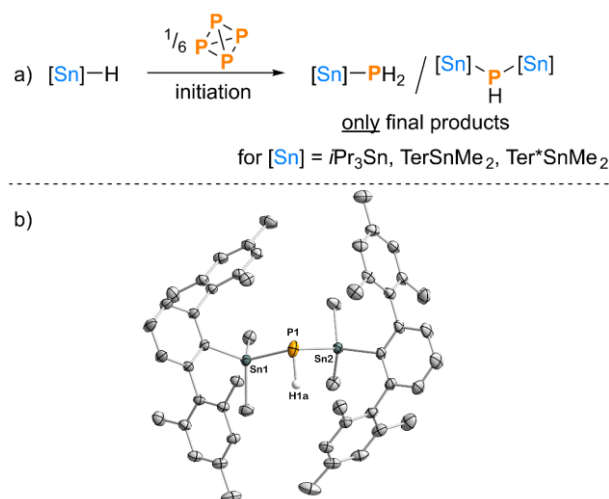
Figure 4.9: Full structures of bulkier hydrostannanes studied for hydrostannylation reactivity towards P_4 .

While iPr_3SnH was prepared in accordance with literature,^[22] $TerSn(Me)_2H$, $Ter^*Sn(Me)_2H$, and $(Fluind)Sn(Me)_2H$ are new compounds and were prepared via reaction of Me_2SnCl_2 with the corresponding aryllithium followed by $LiAlH_4$ reduction, as summarized in Scheme 4.3. These products were isolated in excellent yields (88–95%) and fully characterized by techniques including multinuclear NMR spectroscopy (1H , ^{13}C , ^{119}Sn) and XRD (for full details, see Section 4.8.4.1).



Scheme 4.3: Synthesis of bulky tin hydrides $ArSn(Me)_2H$.

4 Unravelling White Phosphorus



Scheme 4.4: (a) P_4 hydrostannylation using bulky tin hydrides, and (b) single-crystal XRD structure of $[\text{Sn}]_2\text{PH}$ for $[\text{Sn}] = \text{TerSnMe}_2$. Thermal ellipsoids are shown at 50%. For clarity, only one position of the disordered P-bound H atom is shown, and all other H atoms are omitted. C atoms are shown in grey, H is white, P in orange, and Sn in dark grey.

Investigations with even the least bulky of these new hydrostannanes, $i\text{Pr}_3\text{SnH}$, showed that increased steric profile has a marked impact on the P_4 hydrostannylation outcome, with both the light- and AIBN-initiated reactions resulting in exclusive formation of $i\text{Pr}_3\text{SnPH}_2$ and $(i\text{Pr}_3\text{Sn})_2\text{PH}$ without any appreciable PH_3 or $(i\text{Pr}_3\text{Sn})_3\text{P}$ (Scheme 4.4a and Figures 4.42–4.45). This contrasts with the results using Bu_3SnH but is consistent with the bulkier $i\text{Pr}_3\text{Sn}$ moieties needing to be distributed as evenly as possible across the available P atoms in order to minimize steric clash.^[23] It also has significant synthetic implications, as a simpler P_1 mixture could streamline downstream functionalization. Formation and loss of PH_3 has been identified as a possible yield-limiting factor in previous Bu_3SnH -based reactions,^[5,10] which could be sidestepped using bulkier alternatives. Nevertheless, for $i\text{Pr}_3\text{SnH}$ it was still not possible to observe any intermediate P_n species (Figure 4.46).

Gratifyingly, when steric bulk was increased still further, clear observation of intermediate P_n species did become possible. Complete hydrostannylation of P_4 using $\text{TerSn}(\text{Me})_2\text{H}$ or $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ again resulted in clean, exclusive formation of R_3SnPH_2 and $(\text{R}_3\text{Sn})_2\text{PH}$ as the final products (Scheme 4.4a and Sections 4.8.4.2.9 and 4.8.4.2.10), and for the $\text{TerSn}(\text{Me})_2\text{H}$ case it was even possible to obtain an XRD structure of the latter (Scheme 4.4b), further confirming the identity of this product, since previous $(\text{R}_3\text{Sn})_2\text{PH}$ had only been characterized spectroscopically.^[9] However, $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopic monitoring of both reactions also allowed for clear observation of three new species characterized by singlet resonances at -220.0 and -226.5 ppm, and doublets of doublets centered at -251.5, -270.4 and -292.9 ppm (values for $\text{TerSn}(\text{Me})_2\text{H}$; results for $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ were very similar and are shown in Section 4.8.4.2.10).^[24] These resonances can be assigned based on a combination of $^{31}\text{P}\{^1\text{H}\}$, ^{31}P and $^{119}\text{Sn}\{^1\text{H}\}$ -NMR spectroscopy (Figure 4.10; see also Section 4.8.4.2.9).

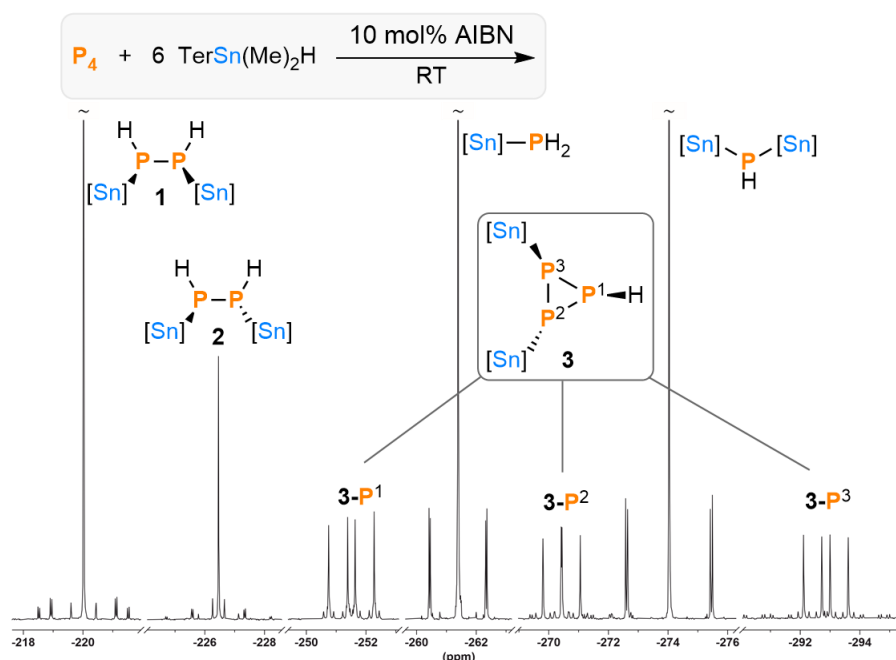


Figure 4.10: $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic observation of reaction intermediates during the hydrostannylation of P_4 using $\text{TerSn}(\text{Me})_2\text{H}$ (6 eq.) initiated by AIBN (10 mol%) in C_6D_6 . $[\text{Sn}] = \text{TerSnMe}_2$. Peaks marked with ~ have been truncated for the sake of clarity. For expanded views of individual $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P resonances, including isotopic satellites, see Figures 4.52–4.55.

The two singlets correspond to the meso and rac isomers of the symmetrical diphosphane $\text{R}_3\text{SnP}(\text{H})\text{--P}(\text{H})\text{SnR}_3$ (**1** and **2**, respectively). Both show AA'XX' splitting patterns in their ^1H -coupled ^{31}P spectra as well as satellites for both 1J and 2J coupling to ^{117}Sn and ^{119}Sn . Their relative assignment is based on comparison with related symmetrical diphosphanes in the literature,^[25] alongside DFT calculations (see Section 4.8.4.3). Meanwhile, the three other signals correspond to a single species (as confirmed by $^{31}\text{P}\text{--}^{31}\text{P}$ COSY): The *cyclo*- P_3 species Sn-*trans*-(R_3Sn) $_2\text{P}_3\text{H}$ (**3**). Due to the relative orientations of the P–H and P–Sn bonds with respect to the P_3 plane this intermediate contains three distinct and mutually-coupled ^{31}P environments, resulting in three doublets in the $^{31}\text{P}\{^1\text{H}\}$ spectrum. For all three it is possible to identify their corresponding 1J and/or 2J couplings to both $^{117/119}\text{Sn}$ and the ring ^1H (the latter being extracted from the proton-coupled ^{31}P spectrum), and thus fully characterize the central $\text{Sn}_2\text{P}_3\text{H}$ spin system.

The observation of the *cyclo*- P_3 species **3** as one of the only observable intermediates is highly interesting, as it is directly equivalent to the calculated structure **Vh'**. This was predicted to be kinetically accessible for less bulky Me_3SnH (Figure 4.4), confirming the ability of steric tuning to stabilize otherwise “invisible” reaction intermediates. Observation of **3** also supports the ability of steric factors to alter the reaction course. It seems clear that with the bulky R_3SnH hydrostannylation proceeds in such a way as to avoid installation of two R_3Sn moieties on a single P atom for as long as possible (leading to **3**), in contrast to the calculated pathways for less bulky Me_3SnH where **Vh'** was a relatively high energy isomer of **V'** (Figure 4.4).^[26] Similarly, the Me_3Sn -substituted analogues of intermediates **1** and **2**, while not shown in Figure 4.8 (cf. $\text{P}_2\text{H}_4 = \text{Xb}$), were also calculated to be kinetically accessible intermediates (**IXi'**, **Xe**; Figures 4.26–4.30). Formation of **1** / **2** can again be justified on steric grounds (for a fuller discussion, see Section 4.8.4.2.9).

4 Unravelling White Phosphorus

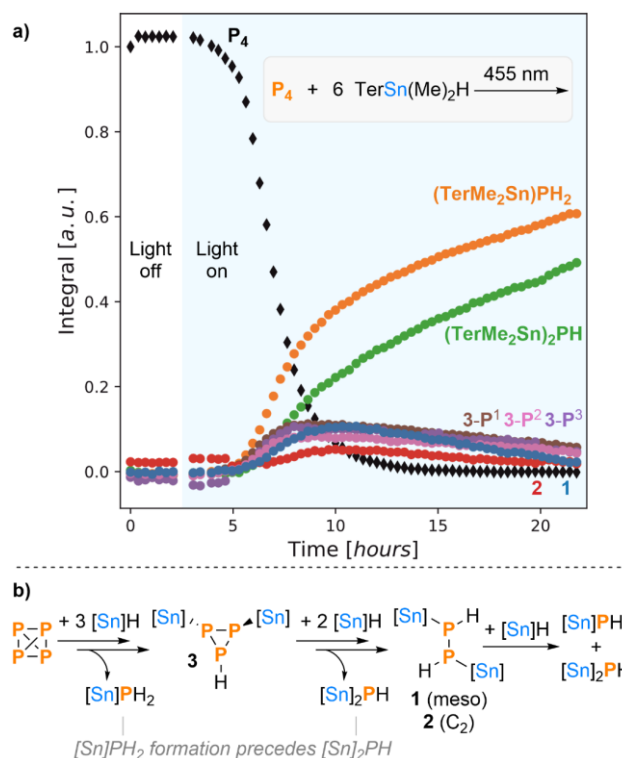


Figure 4.11: (a) Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. $\text{TerSn}(\text{Me})_2\text{H}$ initiated under 455 nm LED irradiation at 298 K in C_6D_6 as monitored by *in situ* $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (irradiation period shaded in light blue); and (b) outline reaction pathway.

The fact that only *specific* intermediates are observed when using $\text{TerSn}(\text{Me})_2\text{H}$ or $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ may imply much greater selectivity between the available pathways than with the less bulky Bu_3SnH (see above). To investigate this further, these reactions were monitored over time. Kinetic profiles were obtained for both light- and AIBN-initiated reactions between P_4 and $\text{TerSn}(\text{Me})_2\text{H}$, which are similar, except for a noticeable induction period for the former. This induction period may be caused by the light induced initiation step,^[15] or simply by low light intensity in the in-situ NMR setup. However, following this induction period the light-driven reaction was found to be slightly faster than that driven by AIBN. It therefore gave a clearer picture of the total reaction course, and so is shown in Figure 4.11a (for the AIBN-driven profile see Figure 4.57 and for the similar profile using $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ see Figure 4.63). Close inspection reveals that **3** is formed fairly rapidly after the induction period of the illuminated reaction before slowly decaying, in line with its role as a reaction intermediate. **1** and **2** follow a qualitatively similar profile, albeit slightly more slowly, indicating that they might be possible downstream products of **3** (although competing pathways cannot be fully excluded). Interestingly, the formation of $(\text{R}_3\text{Sn})_2\text{PH}$ lags noticeably behind that of the other final product R_3SnPH_2 . While an equimolar mixture is observed experimentally after complete hydrostannylation, early on, formation of R_3SnPH_2 significantly outpaces that of $(\text{R}_3\text{Sn})_2\text{PH}$. This is fully consistent with the fact that initial formation of intermediate **3** from $P_4 + 3 \text{ R}_3\text{SnH}$ must be balanced by concomitant formation of R_3SnPH_2 (see Figure 4.11b) and so, synchronous formation of these two species is immediately observed. Only upon subsequent breakdown of **3** does more hindered $(\text{R}_3\text{Sn})_2\text{PH}$ begin to form (for more detailed mechanistic discussion, see Scheme 4.5 and Section 4.8.4.2.9).^[27]

Increasing steric bulk of the tin hydride yet further, beyond $\text{TerSn}(\text{Me})_2\text{H}$ and $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$, was found to completely shut down reactivity. No reaction with P_4 could be observed using $(\text{Fluind})\text{Sn}(\text{Me})_2\text{H}$, revealing an upper limit on the steric bulk range that is tolerated for P_4 hydrostannylation (see Section 4.8.4.2.11).

4.3.3 Discussion and Analysis of Results

From the computational and experimental results described above it is possible to draw several important conclusions:

1. *P₄ hydrostannylation is able to proceed efficiently as a result of activation barriers that are consistently low for each P–P cleavage step.*

These low barriers allow an efficient radical chain reaction to occur even at room temperature and prevent the formation of major thermodynamic sinks that might otherwise hinder reaction progress.

2. *It is possible to identify preferred pathways for P₄ degradation by hydrostannylation using bulky tin hydrides.*

This steric control can also be used to conveniently influence the final product distribution, which should in turn allow for improved onward reactivity.

However:

3. *For less bulky tin hydrides multiple P₄ hydrostannylation pathways are energetically accessible and are likely to operate in parallel.*

Fortunately, each of these pathways is expected to lead to the same eventual set of products, (R₃Sn)_xPH_{3-x}. Thus, the reaction with Bu₃SnH in particular succeeds not by ensuring a single, specific mechanistic pathway but rather by ensuring a specific reaction *outcome*, even if this is achieved via multiple pathways in parallel. This mechanistic flexibility is facilitated by the next conclusion:

4. *Each P–P cleavage step is mechanistically and energetically similar, especially for less bulky tin hydrides.*

While in principle each P–P bond cleavage represents a distinct mechanistic step, in practice each such step is very similar, involving hydrostannylation of a closely comparable P–P single bond via a common sequence of R₃Sn[•] radical attack and H atom transfer, all with similar activation barriers. This near equivalence prevents the formation of intermediate thermodynamic sinks and ensures that each P–P cleavage step can be achieved using the same tin hydride reagent. Crucial to facilitating this is that *each P–P cleavage step has only a small impact on the reactivity of the remaining P–P bonds*.

This is a powerful guideline for the development of future P₄ functionalization chemistry and suggests the targeting of other mechanisms that would break P₄ down “bond by bond”, rather than via fundamental changes to the electronic structure of the overall P_n motif. Indeed, this conclusion may also help to explain the success of the “oxidative onioation” recently reported by the Weigand group, which is another particularly prominent example of recent successful P₄ activation and transformation, and also appears to satisfy this criterion.^[6d] Previous computational studies suggest that this criterion is also satisfied by the well-known reaction of P₄ with I₂ to make PI₃ (these also found the first P–P cleavage step to be the most difficult).^[28] Conversely, this conclusion highlights a potentially significant challenge for the development of “inner sphere” transition metal (TM) mediated processes for P₄ functionalization. These are approaches that have traditionally been heavily emphasized in the field of P₄ chemistry, and reactions of P₄ with TM complexes are by now well known to result in a wide variety of remarkable and academically fascinating TM-bound P_n moieties. However, it is also well known that these different P_n moieties can display markedly different electronic structures (single vs. multiple bonds, π -delocalization, *etc.*) and reactivities, even when bound to the same TM fragment, and can therefore require very different reagents and/or conditions for functionalization. This presents a significant limiting factor that any system seeking to functionalize P₄ via a sequence of TM-bound P_n moieties must overcome (for further discussion see Section 4.8.5).^[6a,g]

4 Unravelling White Phosphorus

4.4 Conclusion

We have described herein the mechanism of the recently reported hydrostannylation of P_4 . This complex reaction can be used to facilitate the convenient transformation of P_4 directly into myriad useful P_1 products, but many aspects of its mechanism had previously remained unclear. Through a combination of computational and experimental study we have been able to identify a preferred sequence of elementary bond cleavage steps through which breakdown of the P_4 tetrahedron can occur, but also demonstrated that many competing pathways are available, all eventually leading to the same set of products $(R_3Sn)_xPH_{3-x}$. These conclusions are supported by DFT calculations and observation of intermediates that have been stabilized by increasing their steric bulk.

From these results it has been possible to identify key, underpinning mechanistic factors that allow the hydrostannylation reaction to proceed so efficiently, and which can act as useful guidelines to aid in the development of future P_4 functionalization reactions. In particular, these studies suggest that it is beneficial for P_4 functionalization reactions to transform their substrate “one P–P bond at a time”, while ensuring that the remaining P–P bonds remain electronically similar (cf. the simplified mechanism in Scheme 4.2). We believe that these insights will help to guide future research towards the goal of practical, direct P_4 functionalization, and we ourselves are currently using them as we continue our efforts to improve and diversify our already-reported strategies.

4.5 Acknowledgements

Daniel J. Scott would like to thank the Alexander von Humboldt foundation for award of a postdoctoral fellowship, and the EPSRC for an Early Career Fellowship (EP/V056069/1). Robert Wolf would like to thank the European Research Council and the Deutsche Forschungsgemeinschaft for funding (ERC CoG 772299 and DFG WO1594/12-1, project number 548830090). Franz F. Westermair and Ruth M. Gschwind would like to thank the Deutsche Forschungsgemeinschaft for funding (DFG, RTG 2620 IonPairs in Reaction Project 426795949). Maria K. Uttendorfer thanks the Fonds der Chemischen Industrie (Kekulé Fellowship) for financial support.

4.6 Conflict of Interest

A patent covering the underlying hydrostannylation chemistry discussed herein has previously been filed (13 February 2020) by the University of Regensburg (EP 20,157,197.3; inventors Daniel J. Scott and Robert Wolf). The authors declare no other competing interests.

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- [19] The calculated barrier for **I**[•]→**II** is compounded by formation of **I**[•] from P₄ being endergonic while formation of the other P-centered radical intermediates via Me₃Sn[•] Arrack is exergonic.
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- b) A. Jupp, J. C. Slootweg, *Angew. Chem. Int. Ed.* **5151**, 59, 10698-10700.
- [21] A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem. Int. Ed.* **2001**, 40, 2834-2838; *Angew. Chem.* **2001**, 113, 891-894.
- [22] J. S. Sapsford, D Csókás, R. C. Turnell-Ritson, L. A. Parkin, A. D. Crawford, I. Pápai, A. E. Ashley, *ACS Catal.* **2021**, 11, 9143-9150.
- [23] This should obviously disfavor (*i*Pr₃Sn)₃P formation, but should also disfavor PH₃ formation, as any ‘unused’ P atoms will force the bulky *i*Pr₃Sn moieties to occupy a smaller number of remaining P atoms increasing steric clash.
- [24] For Ter*Sn(Me)₂H formation of the intermediate singlet signals was only observed at slightly higher temperatures (333 K). For full details see Section 4.8.4.2.10.
- [25] V. Cappello, J. Baumgartner, A. Dransfeld, K. Hassler, *Eur. J. Inorg. Chem.* **2006**, 4589-4599.
- [26] Intuitively, it seems unlikely that increased steric bulk would affect the regiochemical preference for formation of **IVa** shown in Figure 4.2 and 4.3, as the steps up to this point already keep the added R₃Sn moieties as separated as possible. However, subsequent R₃Sn[•] attack to form an analogue of **Va**[•] would force two R₃Sn moieties onto the same P atom. Conversely, formation of an analogue of **Vh**[•], which would then lead to **3**, would minimize steric clash by keeping the R₃Sn moieties as separate as possible. For fuller discussion, see Section 4.8.4.2.9 and Scheme 4.1.
- [27] This can be understood in terms of Sn/H balance, as the total number of P–H and P–Sn bonds should remain equal throughout. This is true for the final equimolar mixture of R₃SnPH₂ and (R₃Sn)₂PH but not for intermediate **3**, which contains more P–Sn than P–H bonds. To compensate for the presence of **3**, more P–H than P–Sn bonds must therefore exist elsewhere in the reaction mixture. Out of intermediates **1** and **2** and the final products, only R₃SnPH₂ can achieve this.
- [28] C. Mealli, A. Ienco, M. Peruzzini, G. Manca, *Dalton Trans.* **2018**, 47, 394-408.

4.8 Supporting Information

4.8.1 General experimental methods

Unless stated otherwise, all reactions and manipulations were performed under an N₂ or Ar atmosphere (< 0.1 ppm O₂, H₂O) through use of MBraun Unilab and GS MEGA Line gloveboxes, and standard Schlenk line techniques. All glassware was oven-dried (160 °C) overnight prior to use. Anhydrous *n*-Hexane and toluene were purified using an MBraun SPS-800 system and stored over molecular sieves (3 Å). Et₂O was dried by distillation from sodium / benzophenone and stored over molecular sieves (3 Å). C₆D₆ was distilled from potassium and stored over molecular sieves (3 Å). *i*Pr₃SnH, Ter-I (Ter = 2,6-*bis*(2,4,6-trimethylphenyl)phenyldimethylstannane), Ter*-Li (Ter* = 2,6-*bis*(2,3,4,5,6-pentamethylphenyl)phenyldimethylstannane) and Fluind-Li(THF)₂ (Fluind = dispiro[fluorene-9,3'-(1',1',7',7'-tetramethyl-s-hydrindacen-4'-yl)]) were prepared in accordance with the literature.^[21,29-32] All other reagents and starting and starting materials were purchased from major suppliers and used as received, including Me₂SnCl₂, LiAlH₄, Ph₃SnH and AIBN. Bu₃SnH was supplied containing 0.05% BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) as stabilizer and was used as received.

Except where noted otherwise below, NMR spectra were recorded at room temperature on Bruker Avance 400 (400 MHz), Bruker Avance III 600 (600 MHz) or Bruker Avance Neo 600 (600 MHz) spectrometers. Chemical

4 Unravelling White Phosphorus

shifts, δ , are reported in parts per million (ppm); ^1H -NMR and ^{13}C -NMR shifts are reported relative to TMS (tetramethylsilane) and were referenced internally to residual solvent peaks (C_6HD_5 : 7.16 ppm for C_6D_6) in the ^1H -NMR spectra, and to the peak of the deuterated solvent (C_6D_6 : 128.06 ppm) in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra,^[33] while ^{31}P -NMR and ^{119}Sn chemical shifts were referenced externally to 85% aqueous H_3PO_4 and TMSn (tetramethylstannane, 90% in C_6D_6), respectively. Except when stated otherwise, integrals for $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P -NMR spectra are provided for the purposes of qualitative comparison only, and should not be considered quantitatively accurate. Assignment of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR resonance signals was made in accordance with the COSY, HSQC and HMBC spectra. The common abbreviations s, d, t, q, m are used to indicate singlets, doublets, triplets, quartets and complex multiplets, respectively.

ESI HRMS spectra were measured on a Bruker Impact II spectrometer. Dichloromethane / acetonitrile or dichloromethane / methanol solutions ($c = 10 \mu\text{mol L}^{-1}$) were injected into the spectrometer at a flow rate of $3 \mu\text{L min}^{-1}$. Nitrogen was used both as drying gas and for nebulization with flow rates of approximately 5 L min^{-1} and a pressure of 344 mbar (5 psi). Pressure in the mass analyzer region was usually about 10^{-5} mbar. Spectra were collected for 1 min and averaged. The nozzle-skimmer voltage was adjusted individually for each measurement. IR spectra were recorded on a Thermo Fisher Scientific Nicolet iS10 spectrometer with a diamond ATR unit. The absorption bands are reported in cm^{-1} with indicated relative intensities: s (strong, 0-33% T); m (medium, 34-66% T), w (weak, 67-100% T), and br (broad).

4.8.2 Initial $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopic monitoring experiments

4.8.2.1 General methods for in situ measurements.

NMR spectroscopic measurement for *in-situ* reaction monitoring were recorded on a Bruker Avance III 600 MHz spectrometer equipped with a 5 mm TBI-P probe (^1H , ^{31}P , X) with z-gradient or a 5 mm TBI-P probe (^1H , ^{19}F , X) with z-gradient or on a Bruker Avance Neo 600 MHz spectrometer equipped with a 5 mm liquid nitrogen cooled BBO-Prodigy probe (X, ^1H) with z-gradient.

^1H -NMR measurements were performed using a standard Bruker pulse program with 90° (zg) or 30° (zg30) excitation pulse.

Quantitative ^{31}P -NMR measurements were typically carried out with a standard Bruker pulse program with inverse-gated ^1H -decoupling and a 30° excitation pulse (zgig30), with a relaxation delay of usually 25 seconds to obtain quantitative spectra, if not stated otherwise.

Two ^{31}P -NMR kinetic experiments were recorded with ^1H -power gated decoupling, using a 90° excitation pulse (zgpg) to enhance sensitivity. These spectra cannot be used for quantitative analysis due to NOE-effects.

Two ^{31}P -NMR kinetic experiments were recorded with ^1H -power gated decoupling, using a 90° excitation pulse (zgpg) to enhance sensitivity. These spectra cannot be used for quantitative analysis due to NOE-effects.

Two ^{31}P -NMR kinetic experiments were recorded with inverse-gated ^1H -decoupling, using an unpublished broadband-excitation pulse kindly provided by Prof. Dr. Burkhard Luy, Karlsruhe Institute of Technology, which allows uniform excitation over the whole spectral width of ^{31}P , for the sake of introducing phase- and integration errors from the long duration of the pulse (0.5 ms) (bulu-zgig). These spectra should also not be treated as quantitative.

^{119}Sn -NMR measurements were performed using a standard Bruker pulse program with power-gated ^1H -decoupling and 90° excitation pulse (zgpg).

Data were processed with the Bruker software TopSpin 4.2.0. Serial integration was done using the “intser” command and the output further analyzed and visualized using self-written Python 3 scripts.

^1H -NMR chemical shifts are reported relative to the residual proton signal of C_6D_6 at 7.16 ppm.

^{31}P -NMR chemical shifts were externally referenced to 85% aqueous H_3PO_4 .

^{119}Sn -NMR chemical shifts were externally referenced to Me_3SnCl in D_2O at 39.3 ppm.

For in situ illumination with 455 nm light, an Osram Osron SSL80 royal-blue LED was used in combination with a 1000 μm high NA glass fiber in a previously described illumination setup.^[34] 365 nm illumination was carried out with a Laser Components LEUVA66X00RV00 UV-LED.

4.8.2.2 AIBN-initiated hydrostannylation using Bu_3SnH

A reaction solution was prepared by combining P_4 (0.01 mmol, as a stock solution in 124.6 μL C_6D_6) and Bu_3SnH (16.2 μL , 0.06 mmol) and AIBN (0.002 mmol as stock solution in 25.8 μL C_6D_6) in C_6D_6 (0.5 mL) inside a glovebox and transferred into an NMR tube with a screw cap. The tube was immediately transferred into a 600 MHz NMR spectrometer and subjected to $^{31}\text{P}\{^1\text{H}\}$ -NMR analysis every 15 minutes. The P_4 starting material and products $(\text{Bu}_3\text{Sn})_x\text{PH}_{3-x}$ ($x = 0-3$) could be identified based on their known chemical shifts.^[9] The resulting reaction profile is shown in Figure 4.1 and below in Figure 4.12.

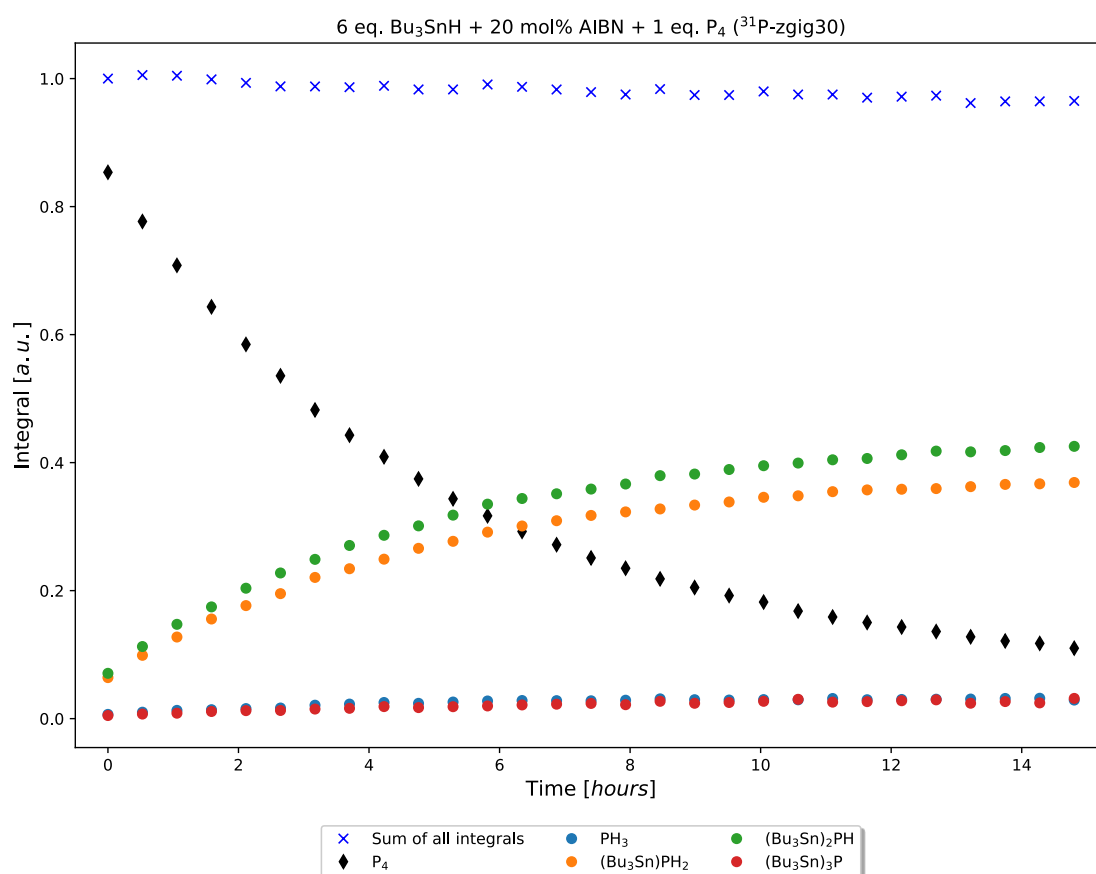


Figure 4.12: Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. Bu_3SnH initiated by 20 mol% AIBN in C_6D_6 at room temperature.

4 Unravelling White Phosphorus

No other transient ^{31}P -containing species could be observed during this experiment. In addition, no overall loss of ^{31}P integral was observed, which would have indicated the formation of polymeric side-products that would either be insoluble, or yield signals too broad to be observed with high resolution NMR spectroscopy.

A detailed kinetic analysis of this reaction is beyond the scope of this work and – given the multitude of available pathways and the similarity of many of the activation barriers involved (e.g. initial Bu_3Sn^* formation from Bu_3SnH and $^*\text{C}(\text{CN})\text{Me}_2$, initial Bu_3Sn^* attack on P_4 , *etc.*) – potentially rather complex. Nevertheless, during the course of this study several different iterations of the above reaction were monitored using different initial concentrations of Bu_3SnH and/or AIBN as part of the unsuccessful effort to observe well-defined intermediates. From the analysis of these experiments several relevant observations can be made.

Plots of the integral of Bu_3SnH against reaction time, t , reveal a clear, consistent exponential decay, indicating net first-order (or pseudo-first order) kinetics (Figure 4.13). Likewise, plots of the integral of P_4 against reaction time, t , show equivalent exponential decay, within error, consistent with 6 equivalents of tin hydride reacting overall with one equivalent of P_4 (Figure 4.14). Since no internal standard was employed, the reaction rates given in Table 4.1 were normalized relative to the reaction where 6 equivalents Bu_3SnH and 10 mol% AIBN were employed.

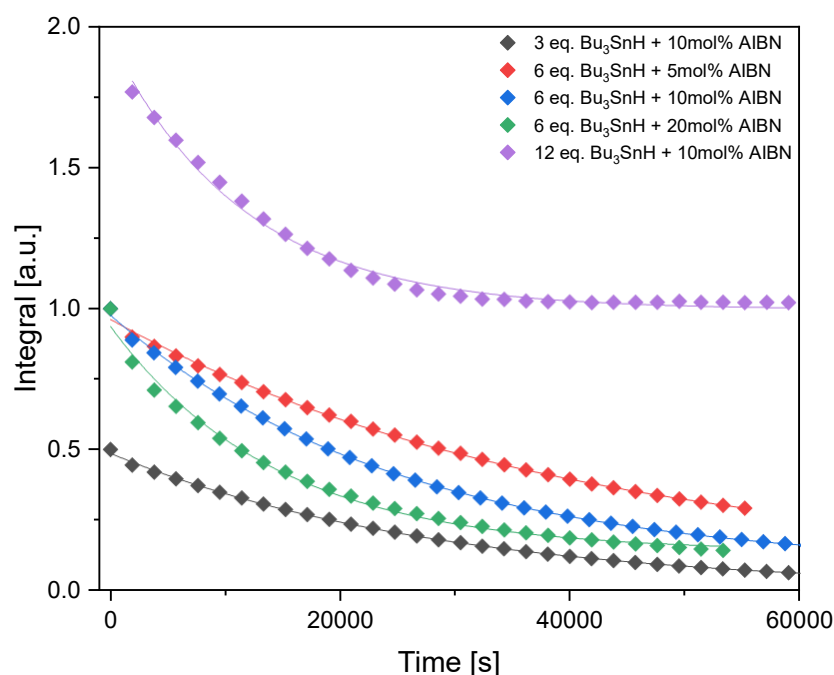


Figure 4.13: Plots of $[\text{Bu}_3\text{SnH}]$ (measured by integration of the SnH ^1H NMR resonance) against t for reactions of P_4 with various concentrations of Bu_3SnH and AIBN at room temperature in C_6D_6 . Aside from scaling the amounts of Bu_3SnH and AIBN, experimental procedures are as outlined above.

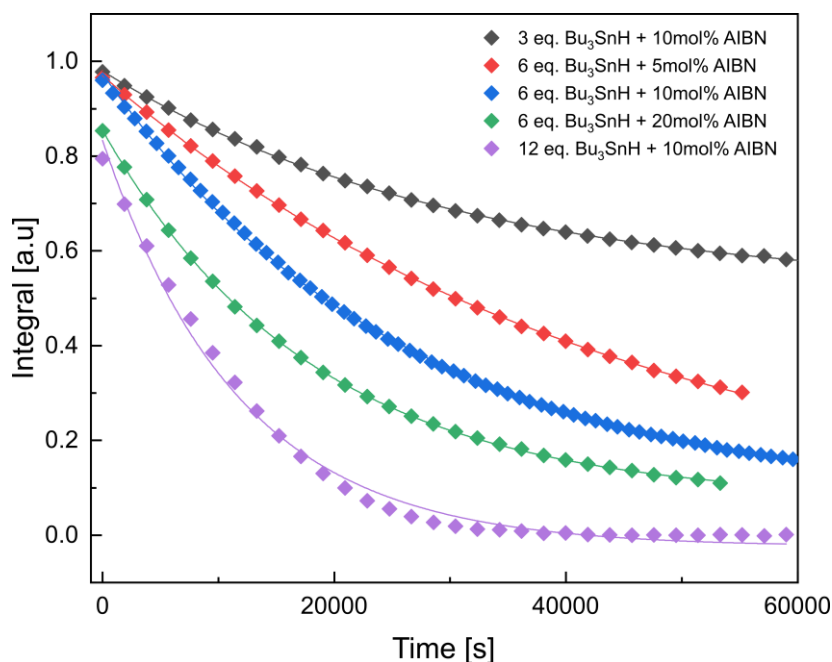


Figure 4.14: Plots of $[P_4]$ (measured by integration of the ^{31}P NMR resonance) against t for reactions of P_4 with various concentrations of Bu_3SnH and AIBN at room temperature in C_6D_6 . Aside from scaling the amounts of Bu_3SnH and AIBN, experimental procedures are as outlined above.

Table 4.1: Relative pseudo-first order rates constants, k , obtained *via* least-squares fitting of the data in Figures 4.13 and 4.14. Relative rates are given, since no internal standard was used.

Bu_3SnH loading / eq.	AIBN loading / mol%	P_4 : relative k / s^{-1}	$\text{Bu}_3\text{Sn-H}$: relative k / s^{-1}
6	10	1.0	1.0
6	20	1.4	1.9
6	5	0.7	0.6
12	10	2.2	2.2
3	10	0.9	0.9

4.8.2.3 Light-initiated hydrostannylation using Bu_3SnH

A reaction solution was prepared by combining P_4 (0.01 mmol, as a stock solution in 124.6 μL C_6D_6) and Bu_3SnH (16.2 μL , 0.06 mmol) in C_6D_6 (0.3 mL) inside a glovebox and transferred into an NMR tube fitted with an insert and glass fiber for in situ illumination, using a setup described previously.^[34] The tube was immediately transferred into a 600 MHz NMR spectrometer and subjected to $^{31}\text{P}\{^1\text{H}\}$ NMR analysis every 15-30 minutes. The P_4 starting material and products $(\text{Bu}_3\text{Sn})_x\text{PH}_{3-x}$ ($x = 0-3$) could be identified based on their known chemical shifts,^[9] and the resulting reaction profile is shown in Figure 4.15, below.

4 Unravelling White Phosphorus

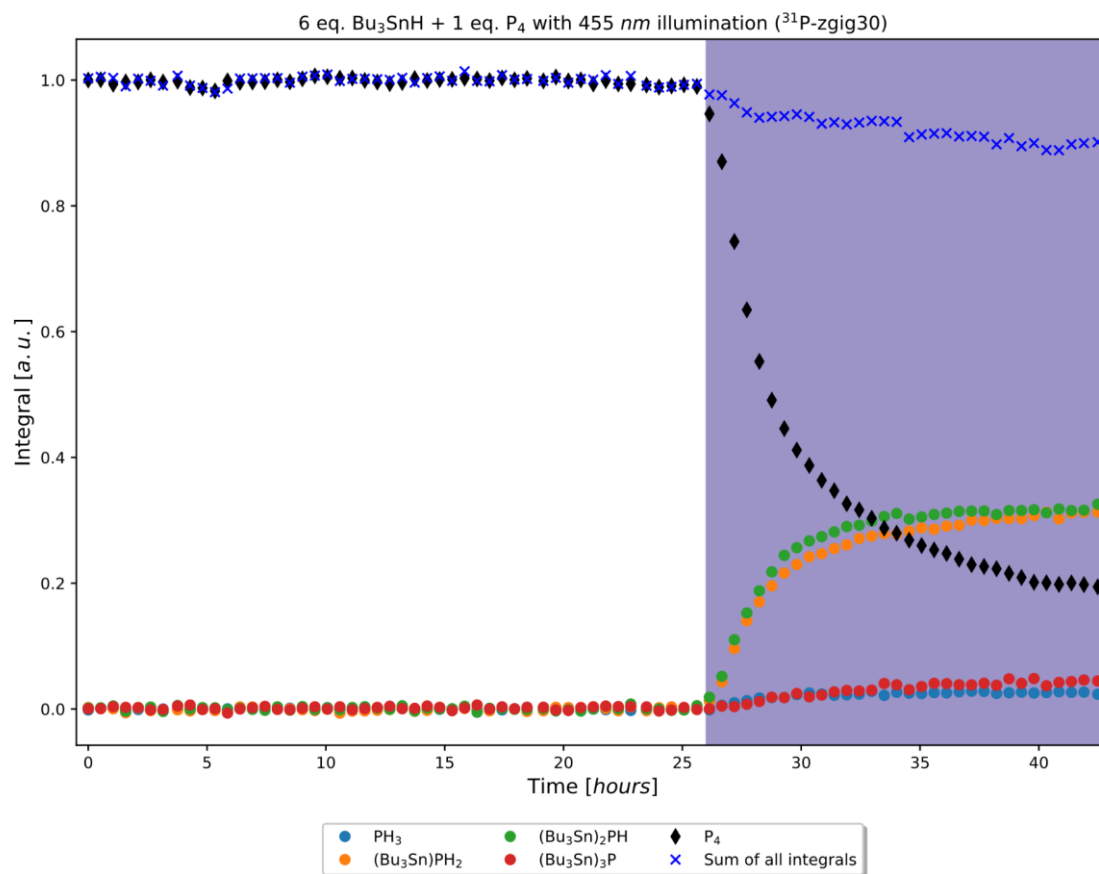


Figure 4.15: Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. Bu_3SnH initiated by in situ 455 nm LED irradiation (starting after 26 h, illumination period indicated by blue shading) in C_6D_6 at room temperature.

The results confirmed that there is negligible reactivity in the dark. However, upon irradiation consumption of P_4 and formation of the expected products immediately began to be observed. This light-dependence was further illustrated by an “on/off” experiment in which the reaction was cycled between 2 h periods of darkness and irradiation, with progress being observed only during the latter (Figure 4.16).

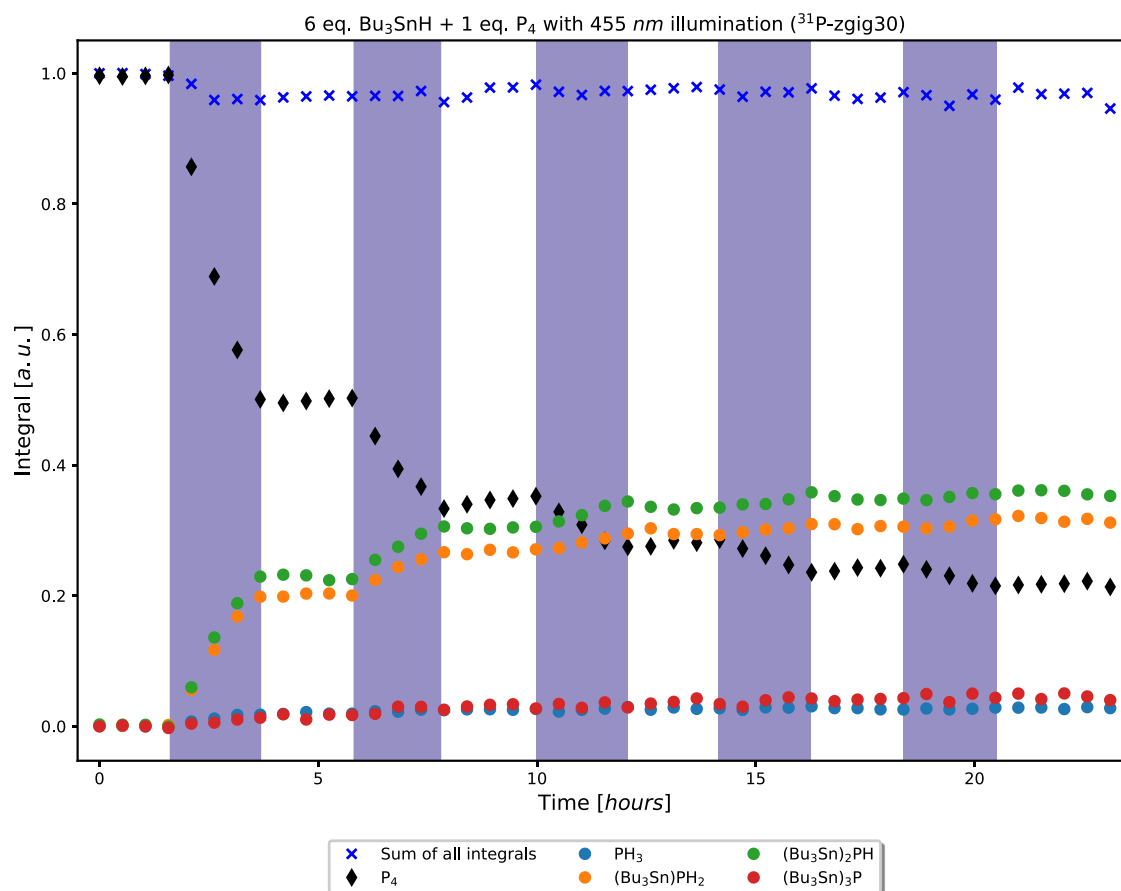


Figure 4.16: Evolution over time of P atom speciation in the reaction between P₄ and 6 eq. Bu₃SnH initiated by *in situ* 455 nm LED irradiation in C₆D₆ at room temperature. The reaction was cycled between light and darkness over time, with periods of illumination indicated by blue shading.

4.8.2.4 Hydrostannylation using Ph₃SnH

In a previous report, it was noted that as well as Bu₃SnH, Ph₃SnH can also be used for the hydrostannylation of P₄, achieving very similar net results (albeit with some competing formation of the distannane Ph₃SnSnPh₃).^[9]

As such, efforts were made to monitor this reaction over time, as well. Unfortunately, initial attempts using AIBN initiation led to reactions that had reached completion during the time needed for sample preparation, transfer from the glovebox to the spectrometer and shimming (ca. 20 minutes). As such it was not possible to obtain a reaction profile for these experiments (although the results do indicate significantly faster kinetics for Ph₃SnH than Bu₃SnH). Instead, a light-initiated reaction was monitored, following a procedure equivalent to that described in Section 4.8.2.3, but using Ph₃SnH in place of Bu₃SnH (Figure 4.17). A very similar outcome was observed, with P₄ consumption and final product formation beginning immediately upon the start of 455 nm irradiation (traces of product observed prior to illumination are attributed to minor light exposure during sample preparation). As with Bu₃SnH, no intermediate resonances attributable to reaction intermediates were detected.

4 Unravelling White Phosphorus

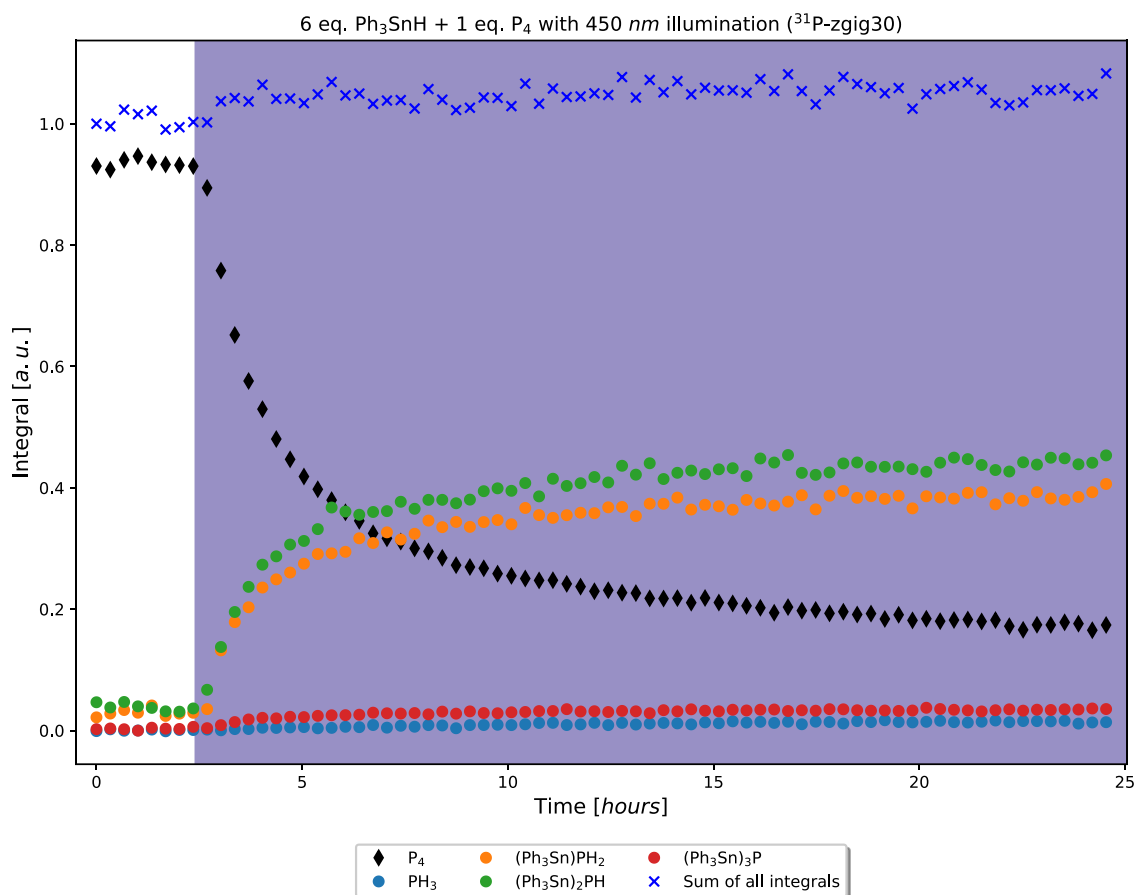


Figure 4.17: Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. Ph_3SnH initiated by in situ 455 nm LED irradiation (starting after 3 h, illumination period indicated by blue shading) in C_6D_6 at room temperature.

4.8.3 Computational Investigations

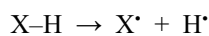
4.8.3.1 General Methods

All calculations were carried out with the ORCA program package.^[35,36] Unless stated otherwise, all calculations were carried out on isolated molecules (in the gas phase) at 298 K. Density fitting techniques, also called resolution-of-identity approximation (RI)^[37], were used for GGA calculations and the RIJCOSX^[38] approximation was used for hybrid-GGA DFT calculations. Atom-pairwise dispersion corrections with the Becke-Johnson damping (D3BJ)^[39,40] were used for all DFT calculations. Pictures were rendered with the software Avogadro.^[41] All geometries were obtained at the PBE-D3BJ/def2-TZVP level of theory.

Bond dissociation energies were calculated according the following equation

$$\text{Bond dissociation energy} = H(\text{X}^\bullet) + H(\text{H}^\bullet) - H(\text{X-H})$$

which corresponds to the enthalpy of the homolysis reaction



$H(\text{H}^\bullet) = -0.49584461$ Eh. Enthalpy values for all other relevant molecules (X-H and $\text{X}^\bullet$) are given in Section 4.8.7.

4.8.3.2 Radical hydrostannylation of P₄

4.8.3.2.1 Mechanisms of Initiation

In our initial report,^[9] initiation was proposed to proceed *via* fragmentation of AIBN followed by H atom abstraction from Me₃SnH. The former step has not been calculated as it is well established experimentally,^[14] but the latter step was calculated, to allow for direct comparison with an alternative mechanism for initiation via attack of the initially-formed radical [•]C(CN)Me₂ on P₄ rather than Me₃SnH. As expected, H atom transfer from Me₃SnH to [•]C(CN)Me₂ is calculated to proceed over only a modest activation barrier of 15.1 kcal mol⁻¹ (Figure 4.18a), which is only slightly higher than the largest activation barrier identified during the subsequent P–P cleavage steps (13.7 kcal mol⁻¹, *en route* to **II**; Figure 4.2). This elementary step is also exergonic by 8.4 kcal mol⁻¹. In contrast, [•]C(CN)Me₂ attack on P₄ is calculated to be significantly uphill (by 13.3 kcal mol⁻¹), with an activation barrier of 15.9 kcal mol⁻¹ (Figure 4.18b). Not only is this larger than the activation barrier for H atom transfer from Me₃SnH to [•]C(CN)Me₂, it is also much higher than the low barrier to P₄ attack by Me₃Sn[•], clearly supporting initiation occurring via the latter mechanism. These calculations are consistent with experimental investigations that show no appreciable reaction between AIBN and P₄ even under considerably more forcing conditions (Section 4.8.3.2.2), which further supports this conclusion.

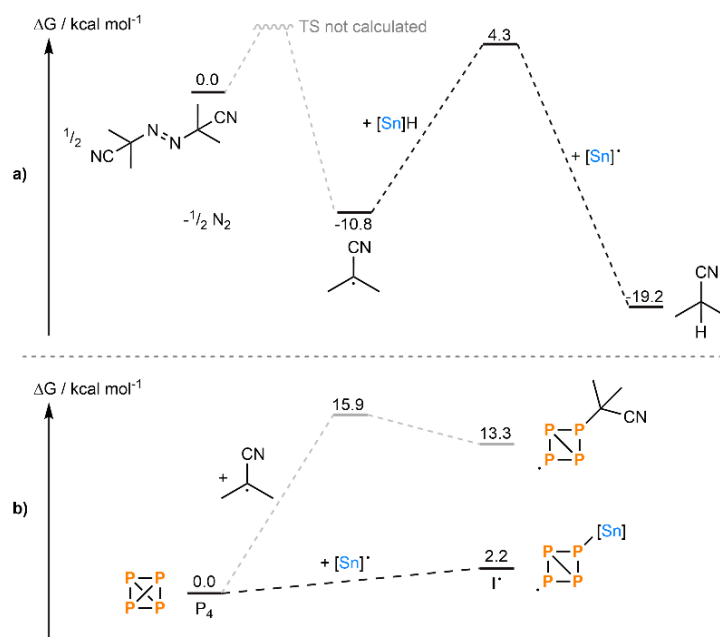


Figure 4.18: Calculated mechanisms for initiation *via* AIBN fragmentation and subsequent (a) H atom abstraction from Me₃SnH or (b) addition to P₄ (also shown for ease of comparison is Me₃Sn[•] addition to P₄). [Sn] = Me₃Sn.

4.8.3.2.2 Experimental Investigation of AIBN Reactivity towards P₄

To a 10 mL, flat-bottomed, stoppered tube were added toluene (500 μ L), P₄ (0.01 mmol, as a stock solution in 97.6 μ L benzene) and AIBN (10.7 mg, 0.065 mmol). The tube was sealed and heated to 80 $^{\circ}$ C for 18 hours. The resulting mixture was analyzed by ³¹P{¹H}-NMR spectroscopy, as shown in Figure 4.19, below.

The resulting ³¹P{¹H}-spectrum indicates retention of the P₄ starting material and no significant reaction with AIBN, despite the use of stoichiometric quantities and elevated temperatures sufficient to ensure (near)-complete AIBN fragmentation within the reaction timeframe.^[14] An equivalent lack of reaction is also observed in reactions at lower temperatures (60 $^{\circ}$ C or room temperature) or with higher AIBN loadings (13.5 eq.). This observation is

4 Unravelling White Phosphorus

interesting not only due to its mechanistic relevance (effectively excluding AIBN activation of P_4 as a means of initiation) but also because of the apparent contrast with previous reports in which addition of organic radicals to P_4 is proposed to be a key step.^[6b,6c,6f,6h,6i,8,42] One possible explanation for this seeming discrepancy could be the relatively electrophilic character of the AIBN-derived radical, which may discourage reaction with P_4 (which also generally shows electrophilic rather than nucleophilic behavior).

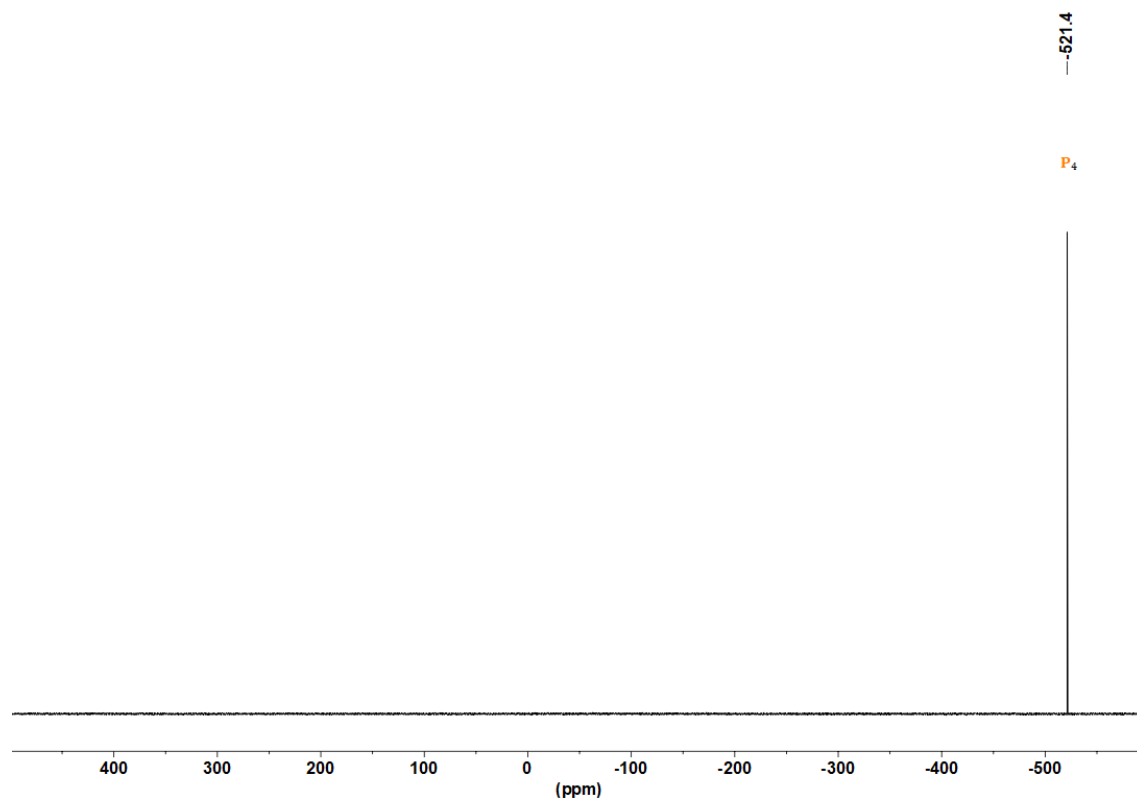


Figure 4.19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the reaction of P_4 (0.01 mmol) with AIBN (0.065 mmol in PhMe, heated to 80 °C for 18 h).

4.8.3.2.3 Mechanisms of P_4 hydrostannylation by Me_3SnH

Given the sheer number of pathways that are available, an exhaustive calculation of every possible sequence of P–P cleavage steps during the hydrostannylation of P_4 is impractical. Attention was therefore focused on a more specific, representative subset. To achieve this, the sequence described below was carried out. In order to limit this study to a manageable number of calculations the possibility of intermediates isomerizing between steps was not considered, and nor was *aggregation* of P_4 to larger P_n moieties (for example by addition of P_4 to intermediates such as **I'**). However, based on the consistent similarities between P–P cleavage steps noted in the main manuscript it seems very unlikely that such processes would impact the overall conclusion: that multiple pathways are able to compete in parallel to generate the same set of final products. Indeed, intuitively, the possibility of yet further pathways being available would only seem to reinforce the likelihood of this conclusion.

First P–P cleavage:

Addition of $\text{Me}_3\text{Sn}^\bullet$ to P_4 was calculated to occur most favorably via an *exo* attack to generate the *exo*-butterfly radical intermediate **I'**, as shown in Figure 4.20 (and Figure 4.2). This was found to be slightly uphill, with relaxed surface scans revealing no identifiable transition state.

Due to P_4 's symmetrical structure, only one regiochemical possibility exists for this first step. However, an alternative stereochemical option does exist. *Endo* attack of $Me_3Sn^\bullet$ would give the alternative *endo* isomer I' , and this option was also calculated. $endo I'$ was actually found to be slightly lower in energy than I' ; however its barrier for formation was much higher (and higher than any of the downstream steps calculated), and so this pathway was not considered further.

H atom abstraction from Me_3SnH by the radical I' was then calculated and found to be slightly endergonic with a modest activation barrier, as discussed in the previous sections. *Exo* addition of the H atom was found to be slightly preferable to the *endo* alternative on both thermodynamic and kinetic grounds, and so this option was carried forward for calculation of the second P–P cleavage step.

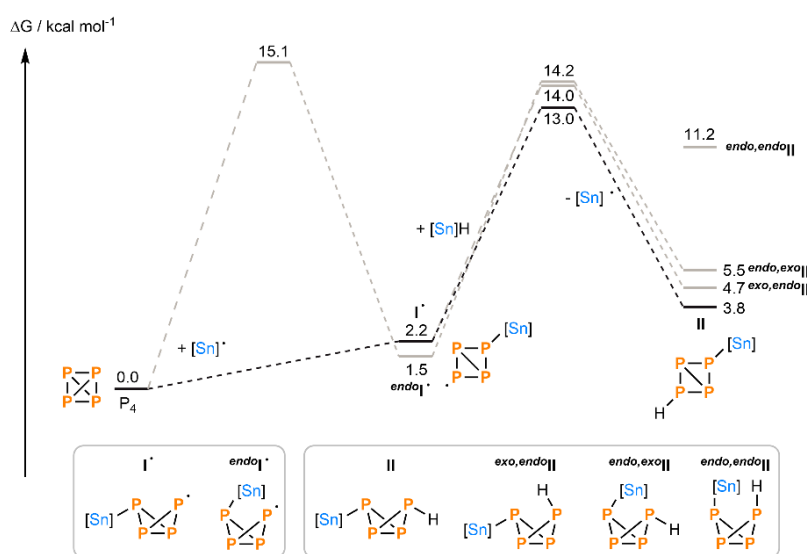


Figure 4.20: Calculated mechanism for hydrostannylation of the first P–P bond in P_4 by Me_3SnH , including stereochemistry, with relative free energies in $kcal\ mol^{-1}$. $[Sn] = Me_3Sn$.

Second P–P cleavage:

For the resulting intermediate II , $Me_3Sn^\bullet$ attack could occur on any of the three chemically distinct P–P bonds, two of which are unsymmetrical and so can each be attacked with two possible regiochemical outcomes, resulting in five possible intermediate constitutional isomers III , as shown in Figure 4.21 and 4.3).

All five options were calculated and found to be exergonic and essentially barrierless, with no transition states identified by relaxed surface scans. In principle, more than one diastereochemical option is available for each of these steps (*cf.* the 1st step, above). However, to limit the number of calculations required to a reasonable level, only one specific option was calculated in each case. This was done by initially locating the $Me_3Sn^\bullet$ at a chemically reasonable position (based on sterics, expected reaction geometry, *etc.*) and optimizing without restriction, in line with standard practice. (This treatment was repeated for steps 3–6.)

The apparent lack of kinetic barriers suggests formation of all five isomers, III , should be kinetically feasible.

For each of the isomers of III H atom abstraction from Me_3SnH was then calculated. The process with the lowest *overall* barrier was found to be reaction *via* the lowest-energy isomer $IIIa'$, to give the closed-shell intermediate IVa . However, it should be emphasized that if there is any kinetic preference for IVa over IVb it is extremely modest (likely within the margin of error), and both pathways are likely to be kinetically competitive. Assigning a formal kinetic product is also complicated by the lack of apparent kinetic barriers for the formation of III . A

4 Unravelling White Phosphorus

possible kinetic argument in favor of **IVa** over **IVb** can be made if an equilibrium between **IIIa*** and **IIIb*** is assumed (i.e. if formation of **IIIa*** or **IIIb*** is reversible), since in this case **IIIa*** provides the lowest energy onward transition state (albeit only by a very small margin as already noted). However, starting from **IIIb***, the barrier for this equilibrium (via reversion of **IIIb*** to **II**) is essentially identical to that of the forward reaction (**IIIb*** → **IVb**), suggesting only partial reversibility at most, and in the absence of reversibility the barrier for **IIIb*** → **IVb** is in fact slightly lower than for **IIIa*** → **IVa**. Again, this implies that formation of **IVb** is likely to be kinetically competitive with formation of **IVa**.

In contrast, H atom abstraction by any of the other isomers (**IIIc***-**IIIe***) involves transition state energies that are appreciably higher than for reversion to **II**, suggesting that they should react preferentially via reversion to **II** and equilibration to the thermodynamically preferred isomers **IVa** or **IVb**, which provide lower energy onward transition states.

Based on these arguments, both **IVa** and **IVb** could reasonably be taken forward for further calculations. However, for the sake of practicality, and to minimize the number of possible downstream steps requiring investigation, it was decided to investigate only a single isomer, with **IVa** being arbitrarily chosen (see below).

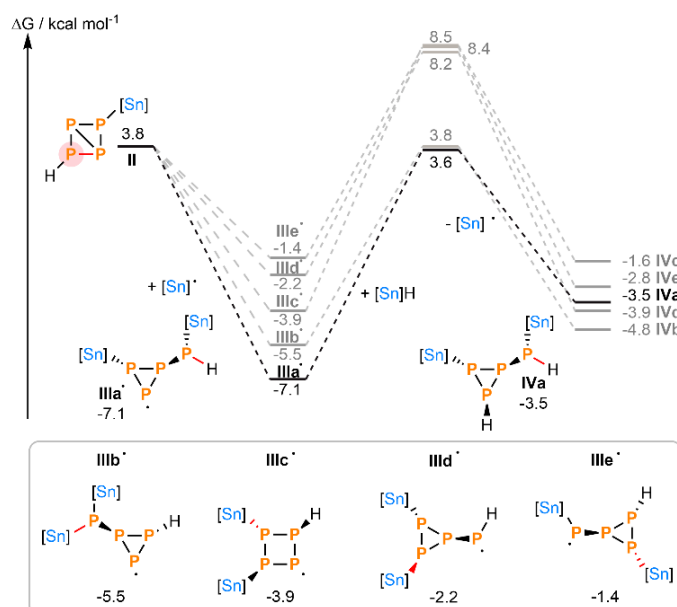


Figure 4.21: Calculated mechanism for hydrostannylation of the second P–P bond in P₄ by Me₃SnH, including relative stereochemistry, with relative free energies in kcal mol⁻¹. [Sn] = Me₃Sn.

Third P–P cleavage:

The addition of Me₃Sn* to **IVa** was calculated using the same strategy as for addition to **II** discussed above. In this case, eight constitutional isomers of the intermediate **V*** are available, and formation of each was calculated to be essentially barrierless (Figure 4.22 and Figure 4.4). The energies of the subsequent product isomers **VI**, derived upon H atom transfer to **V***, were also calculated. However, for the sake of computational efficiency (particularly because the conformational flexibility of most of the isomers of **V*** complicates the calculation of transition states), activation barriers were only calculated for the two lowest energy isomers, i.e. for **Va*** → **VIa** and **Vb*** → **VIb**. Of these, **Va*** → **VIa** was found to be kinetically preferred (note that equilibration of **Va*** and **Vb*** via reversion to **IVa** is more accessible than either forward reaction, making the argument for kinetic preference more clear cut than in step 2), and so this option was taken forward to provide the starting point for the fourth P–P cleavage step (see

below). However, it should be emphasized that the possibility of other pathways (i.e. H atom transfer to **Vc'**-**Vh'**) being kinetically competitive cannot be excluded, especially given that reversion of any of the isomers of **V'** to **IVa** is calculated to have a lower barrier than **Va'** → **VIa** (i.e. interconversion between the isomers of **V'** should be more facile than onward reactivity). However, the existence of any extra pathways would reinforce the overall conclusion of this study (i.e. that the observed reaction outcome is likely due to an ensemble of pathways operating in parallel).

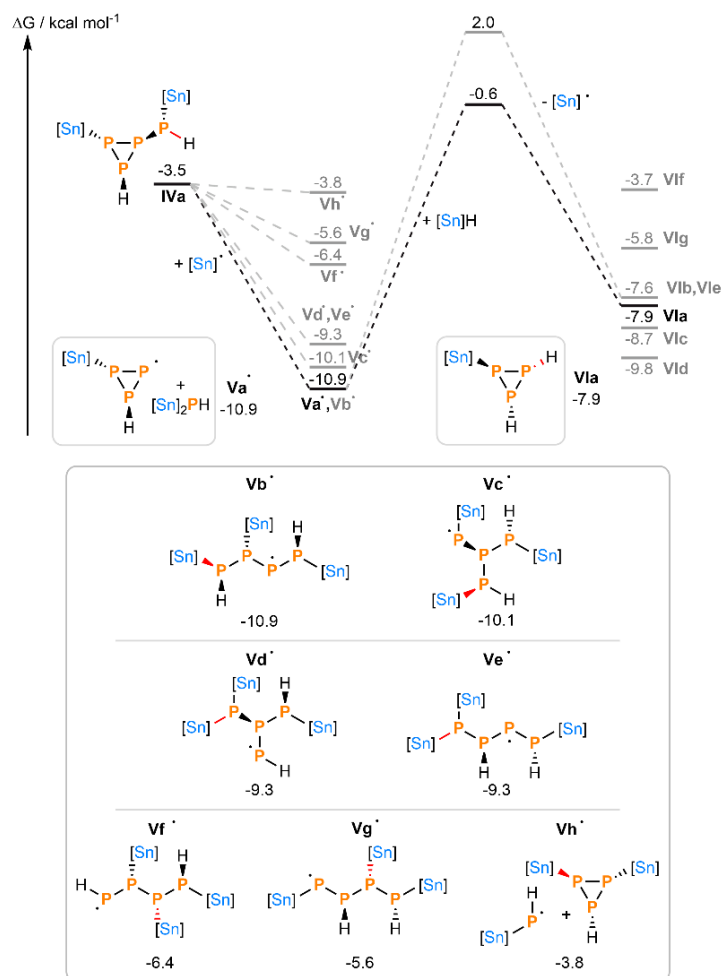


Figure 4.22: Calculated mechanism for hydrostannylation of the third P–P bond in P₄ by Me₃SnH, including relative stereochemistry, with relative free energies in kcal mol⁻¹. [Sn] = Me₃Sn.

Fourth P–P cleavage:

Three regiochemical options for Me₃Sn' attack on **VIa** are available, all of which were calculated using the same strategy as in the second and third steps and found to be effectively barrierless (Figure 4.23 and Figure 4.5). The reduced size of this system relative to the previous step (P₃ vs. P₄ fragments, fewer isomers) allowed transition states for all three onward H atom transfer steps (**VII'** → **VIII**) to be calculated. Of these options, **VIIc'** → **VIIIc** was found to be both kinetically and thermodynamically preferred, so **VIIIc** was taken forward for calculation of the fifth P–P cleavage step (see below). Notably, for both **VIIa'** and **VIIb'** reversion to **VI** followed by conversion to **VIIIc** via **VIIc'** should be lower in energy than direct H atom transfer.

4 Unravelling White Phosphorus

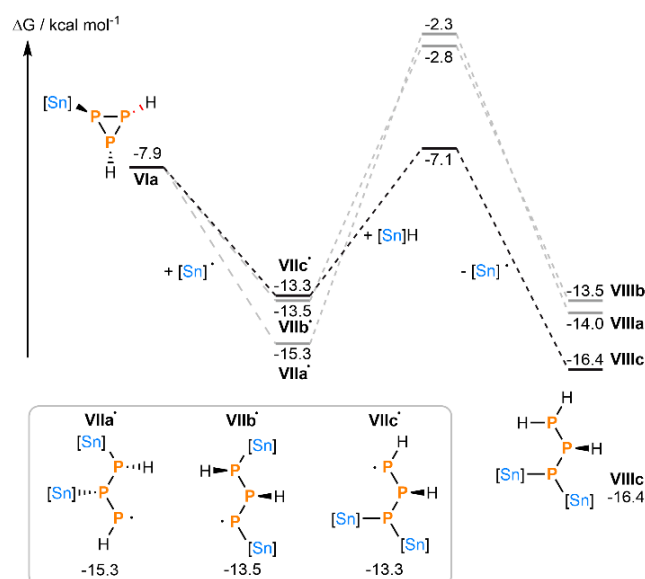


Figure 4.23: Calculated mechanism for hydrostannylation of the fourth P–P bond in P_4 by Me_3SnH , including relative stereochemistry, with relative free energies in $kcal\ mol^{-1}$. $[Sn] = Me_3Sn$.

Fifth P–P cleavage:

Starting from **VIIIc**, the fifth step offers four options for $Me_3Sn^\bullet$ attack, which were again calculated using the same strategy as for the second–fourth steps, and again found to be effectively barrierless (Figure 4.24 and Figure 4.6). Two of these options were calculated to be downhill (leading to **IXa'** and **IXb'**), but two were calculated to be slightly uphill (leading to **IXc'** and **IXd'**). For simplicity, onward H atom transfer reactivity was calculated only for the former pair, with **IXb'** found to lead to the lower activation barrier, *en route* to product **Xb**, which was then taken forward for the final P–P cleavage step. Again, it can be noted that H atom transfer to **IXa'** to form **Xa** has a higher activation barrier than transformation to **Xb** *via* reversion to **VIIIc** and formation of **IXb'**, making **Xb** the kinetically preferred product.

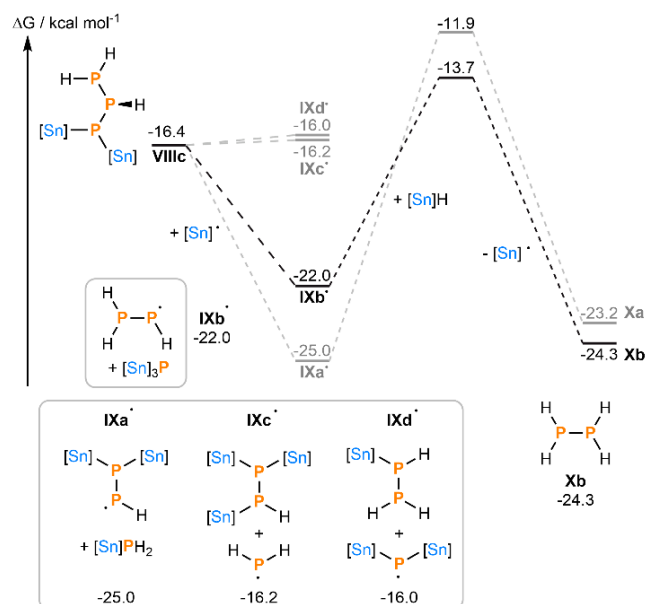


Figure 4.24: Calculated mechanism for hydrostannylation of the fifth P–P bond in P_4 by Me_3SnH , including relative stereochemistry, with relative free energies in $kcal\ mol^{-1}$. $[Sn] = Me_3Sn$.

Sixth P–P cleavage:

Starting from **Xb**, only one option is available for the final $\text{Me}_3\text{Sn}^\bullet$ attack, which was again calculated using the same strategy as for the second-fifth steps (Figure 4.7 and repeated for convenience in Figure 4.25). This was again calculated to be essentially barrierless, generating intermediate **XI'** that can engage in a final H atom transfer step to generate the final product PH_3 .

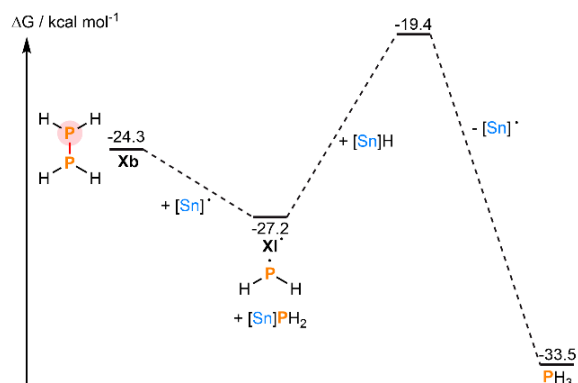


Figure 4.25: Calculated mechanism for hydrostannylation of the final P–P bond in P_4 by Me_3SnH , with relative free energies in kcal mol $^{-1}$. $[\text{Sn}] = \text{Me}_3\text{Sn}$.

Alternative P–P cleavage steps:

During the course of this study, a handful of other possible P–P bond cleavage steps were also calculated, in addition to the primary sequence summarized above. For completeness, these are summarized in Figures 4.26–4.30. Notably, all show similar patterns of reactivity (i.e. similar activation barriers, *etc.*) to the steps that make up the main pathway, further supporting the conclusion that multiple competing pathways are likely to be energetically accessible.

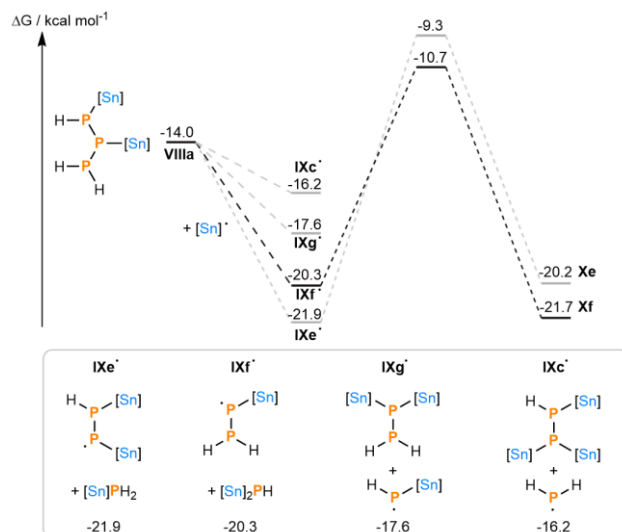


Figure 4.26: Calculated mechanism for an alternative hydrostannylation of the fifth P–P bond in P_4 by Me_3SnH , starting from **VIIIa** instead of **VIIIc**, with relative free energies in kcal mol $^{-1}$. $[\text{Sn}] = \text{Me}_3\text{Sn}$.

4 Unravelling White Phosphorus

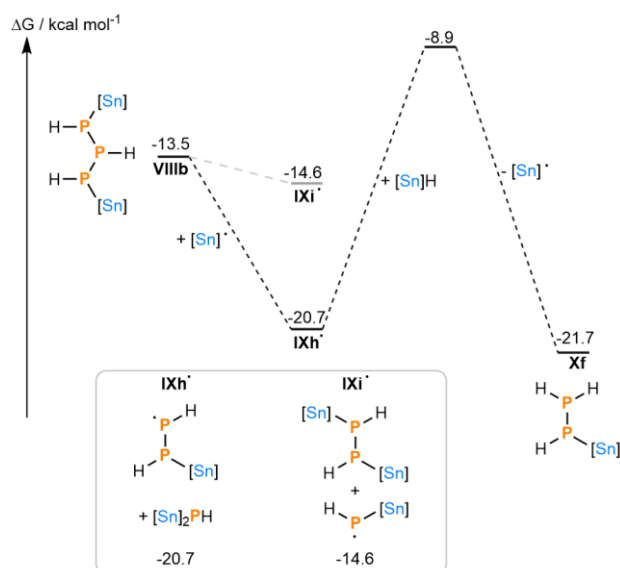


Figure 4.27: Calculated mechanism for an alternative hydrostannylation of the fifth P–P bond in P_4 by Me_3SnH , starting from **VIIIb** instead of **VIIIc**, with relative free energies in kcal mol^{-1} . $[Sn] = Me_3Sn$.

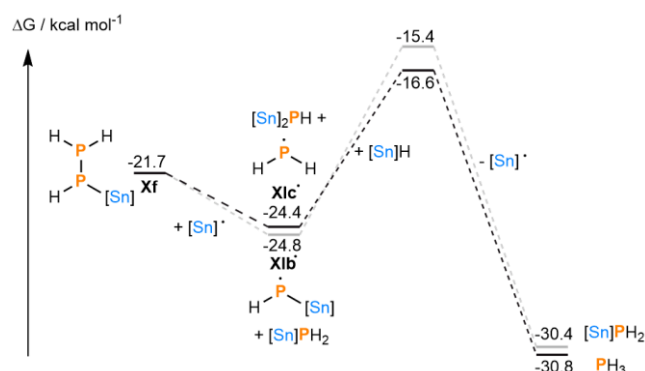


Figure 4.28: Calculated mechanism for an alternative hydrostannylation of the final P–P bond in P_4 by Me_3SnH , starting from **Xf** (which would be derived from H atom transfer to **IXf** or **IXh**) instead of **Xb**, with relative free energies in kcal mol^{-1} . $[Sn] = Me_3Sn$.

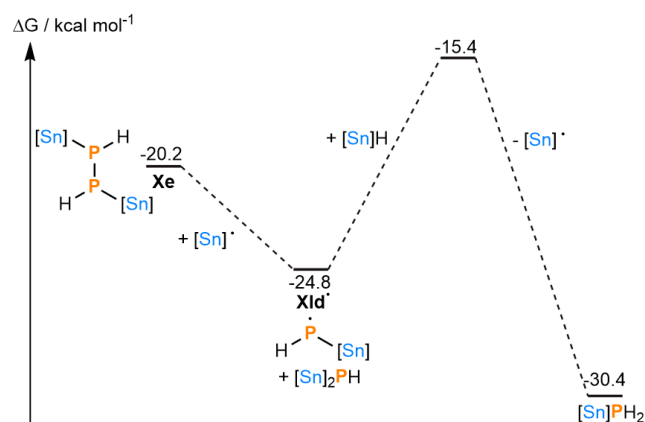


Figure 4.29: Calculated mechanism for an alternative hydrostannylation of the final P–P bond in P_4 by Me_3SnH , starting from **Xe** (which would be derived from H atom transfer to **IXe**) instead of **Xb**, with relative free energies in kcal mol^{-1} . $[Sn] = Me_3Sn$.

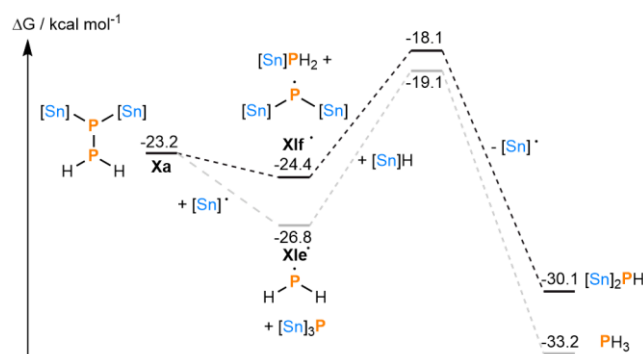


Figure 4.30: Calculated mechanism for an alternative hydrostannylation of the final P–P bond in P_4 by Me_3SnH , starting from **Xa** (which would be derived from H atom transfer to **IXa**) instead of **Xb**, with relative free energies in kcal mol^{-1} . $[Sn] = Me_3Sn$.

4.8.4 Investigation of bulkier Hydrostannanes

4.8.4.1 Synthesis and characterization of new hydrostannanes

4.8.4.1.4 $TerSn(Me)_2H$ (2,6-Mes₂C₆H₃Sn(CH₃)₂H)

Ter-I (5.00 g, 11.3 mmol, 1.00 eq.) was suspended in a Schlenk tube in Et_2O (80 mL) and cooled to 0 °C, to which *n*-butyllithium (2.5 M in *n*-hexane, 5.00 mL, 12.5 mmol, 1.10 eq.) was added dropwise over the course of 5 minutes. After stirring for one hour the solution was transferred dropwise to a cooled suspension of dimethyltin dichloride (2.50 g, 11.3 mmol, 1.00 eq.) in Et_2O . The reaction mixture was stirred for an additional hour at 0 °C and then for two hours at room temperature. The solvent was removed under reduced pressure to remove butyl iodide. Afterwards it was suspended in Et_2O (50 mL) and cooled to -20 °C. To this $LiAlH_4$ (0.429 g, 11.3 mmol, 1.00 eq.) was added as a solid. The reaction mixture was stirred for 2 hours at -20 °C and then the solvent was removed under reduced pressure. The residual solid was extracted with toluene (50 mL) and filtered through a pad of celite to remove any insoluble material. The solvent was removed in vacuum to afford the target compound as a crystalline solid (4.70 g, 10.1 mmol, 90%).

Crystals suitable for X-ray structure determination were grown from a hot toluene solution.

1H -NMR (600 MHz, C_6D_6): δ = 7.25 (t, $^3J(^1H-^1H)$ = 7.6 Hz, 1H, H4), 6.96 (d, $^3J(^1H-^1H)$ = 7.6 Hz, 2H, H3 and H5), 6.84 (s, 4H, H9 and H11), 4.81 (hept, 1H, $^3J(^1H-^1H)$ = 2.6 Hz, $^1J(^1H-^{119}Sn)$ = 1796.8 Hz, SnH), 2.18 (s, 6H, H14), 2.08 (s, 12H, H13 and H15), -0.24 (d, $^3J(^1H-^1H)$ = 2.6 Hz, 6H, $SnCH_3$) ppm.

$^{13}C\{^1H\}$ -NMR (151 MHz, C_6D_6): δ = 150.01 (s, C2 and C6), 141.13 (s, C8), 140.19 (s, C1), 136.59 (s, C10), 135.84 (s, C8 and C12), 129.44 (s, C3), 128.26 (s, C9 and C11), 127.25 (s, C3 and C5), 20.85 (s, C14) 20.77 (s, C13 and C15), -10.16 (s, $SnCH_3$) ppm.

^{119}Sn -NMR (C_6D_6 , 224 MHz): δ = -145.60 (dp, $^2J(^{119}Sn-^1H)$ = 57.1 Hz, $^1J(^{119}Sn-^1H)$ = 1793.76 Hz) ppm.

HRMS ESI (m/z): $[M-H]^+$ calculated. for $C_{26}H_{31}Sn$, 463.14470; found, 463.14441. **IR** (ATR, neat): $\tilde{\nu}$ = 1833 cm^{-1} (s, Sn-H). Melting Point: 104 °C.

4 Unravelling White Phosphorus

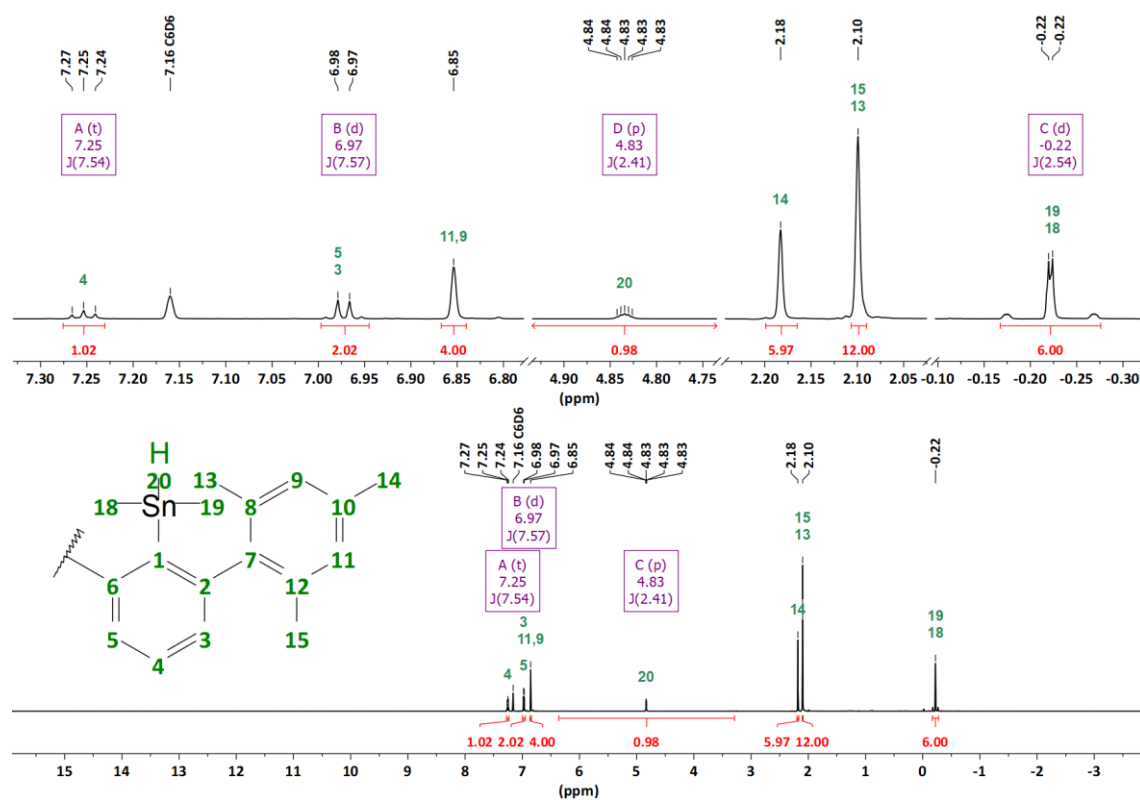


Figure 4.31: ^1H NMR (C_6D_6 , 600 MHz) spectrum of $\text{TerSn}(\text{Me})_2\text{H}$.

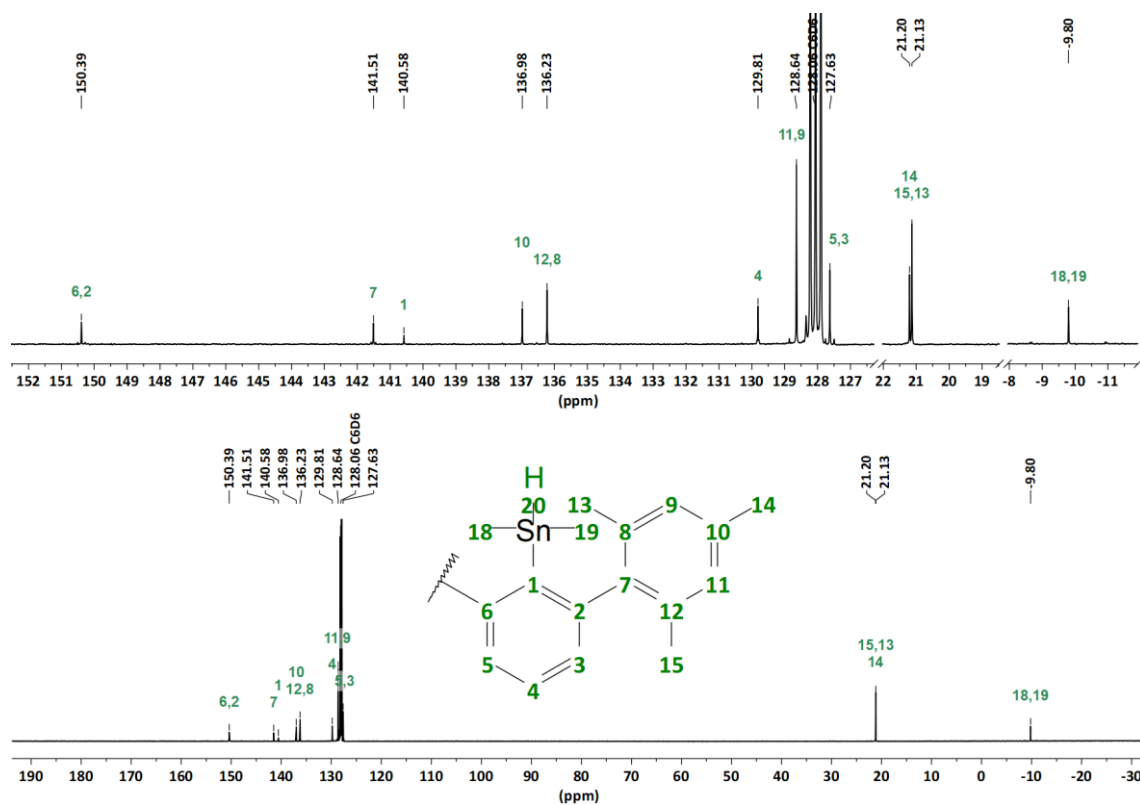


Figure 4.32: $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 151 MHz) spectrum of $\text{TerSn}(\text{Me})_2\text{H}$.

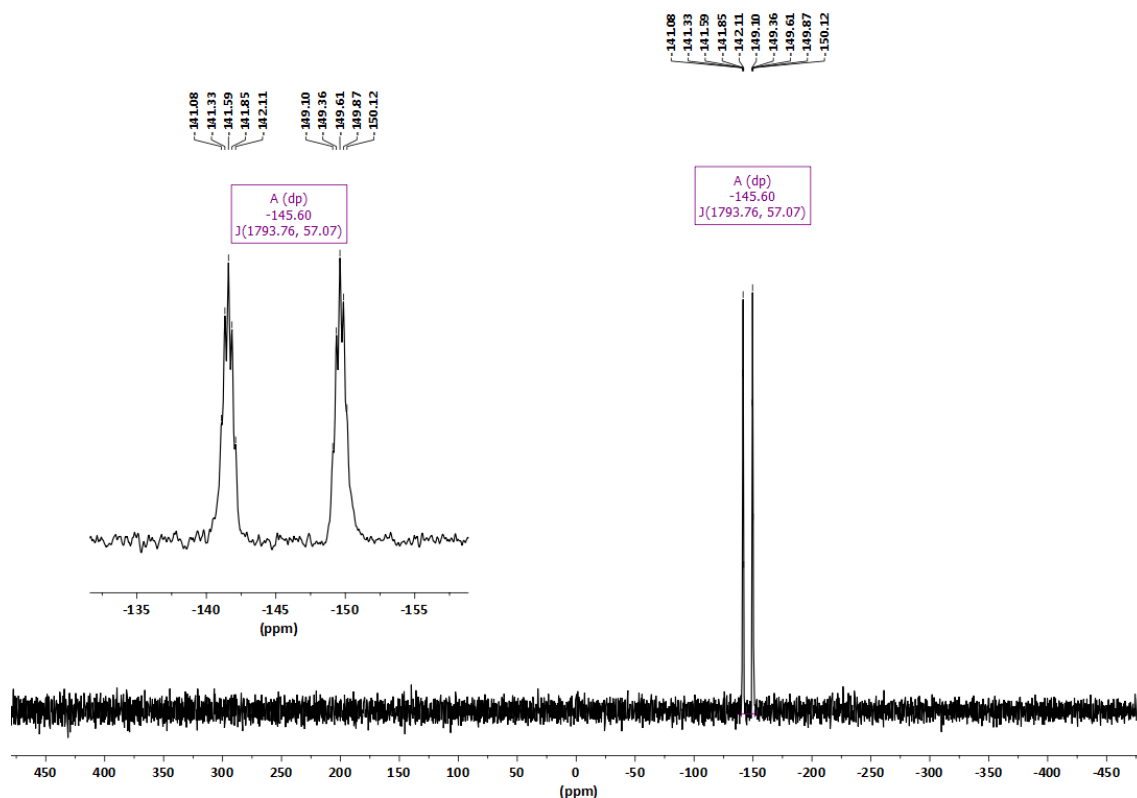


Figure 4.33: ^{119}Sn NMR (C_6D_6 , 224 MHz) spectrum of $\text{TerSn}(\text{Me})_2\text{H}$.

4.8.4.1.5 $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ (2,6-(C_6Me_5) $_2\text{C}_6\text{H}_3\text{Sn}(\text{CH}_3)_2\text{H}$)

Me_2SnCl_2 (0.219 g, 1.00 mmol, 1.00 eq.) was placed in a Schlenk tube and dissolved in Et_2O (5 mL) and cooled to 0 °C. Separately $\text{Ter}^*\text{-Li}$ (0.376 g, 1.00 mmol, 1.00 eq.) was dissolved in Et_2O (5 mL) and added dropwise to the Me_2SnCl_2 solution over the course of ten minutes. After two hours the solvent was removed under vacuum and the residual solid was dissolved in fresh Et_2O . This solution was cooled to -60 °C and LiAlH_4 (0.107 g, 2.8 mmol, 2.8 eq.) was added as a solid. The reaction mixture was stirred for an additional four hours at -20 °C. After this, the solvent was removed under reduced pressure and the product was dried at 60 °C for 18 hours. The residual solid was suspended in toluene (16 mL) and filtered through a PTFE syringe filter. The solvent of the filtrate was removed under reduced pressure and the solid was dissolved in hot *n*-hexane (2 mL) and cooled to 0 °C, during which the product crystallized. The residual solution was decanted off and the solid was dried under reduced pressure to obtain the title compound as a colorless solid (457 mg, 0.879 mmol, 88%).

Crystals suitable for X-ray structure determination were grown from a hot *n*-hexane solution.

^1H -NMR (600 MHz, C_6D_6): δ = 7.33 (t, $^3J(\text{H-H})$ = 7.5 Hz, 1H, H4), 7.09 (d, $^3J(\text{H-H})$ = 7.6 Hz, 2H, H3 and H5), 4.78 (hept, 1H, $^3J(\text{H-H})$ = 2.4 Hz, H20), 2.14 (s, 12H, H13 and H17), 2.13 (s, 6H, H15), 2.13 (s, 12H, H14 and H16), -0.31 (d, $^3J(\text{H-H})$ = 2.5 Hz, 6H, H18 and H19) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (151 MHz, C_6D_6): δ = 152.32 (s, C2 and C6), 142.14 (s, C7), 141.85 (s, C1), 134.00 (s, C10), 132.45 (s, C8 and C12), 131.79 (s, C9 and C11), 129.55 (s, C4), 127.62 (s, C3 and C5), 18.86 (s, C13 and C17), 16.83 (s, C15), 16.69 (s, C14 and C16), -9.90 (s, C18 and C19) ppm.

^{119}Sn -NMR (C_6D_6 , 224 MHz): δ = -147.88 (dp, $^2J(^{119}\text{Sn-H})$ = 57.7 Hz, $^1J(^{119}\text{Sn-H})$ = 1791.8 Hz) ppm.

HRMS ESI (m/z): $[\text{M-H}]^+$ calculated. for $\text{C}_{26}\text{H}_{31}\text{Sn}$, 519.20740; found, 519.20696. **IR** (ATR, neat): $\tilde{\nu}$ = 1827 cm^{-1} (s, Sn-H). Melting Point: 167 °C.

4 Unravelling White Phosphorus

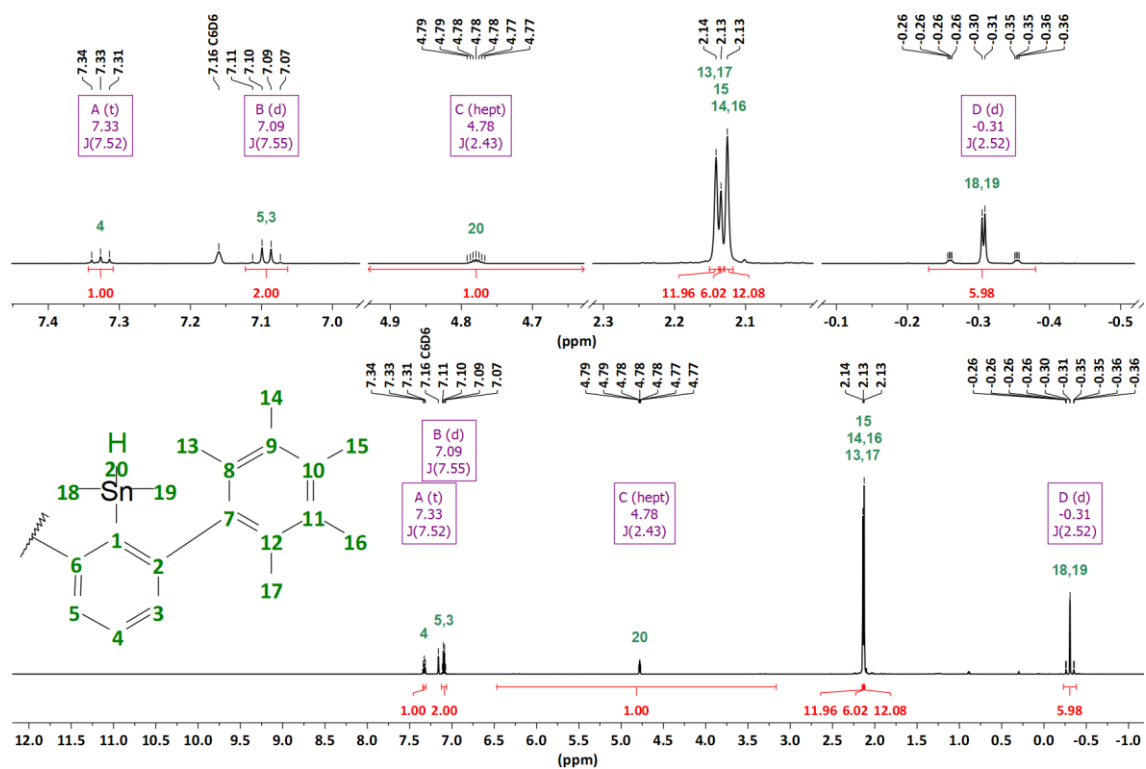


Figure 4.34: ^1H NMR (C_6D_6 , 600 MHz) spectrum of $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$.

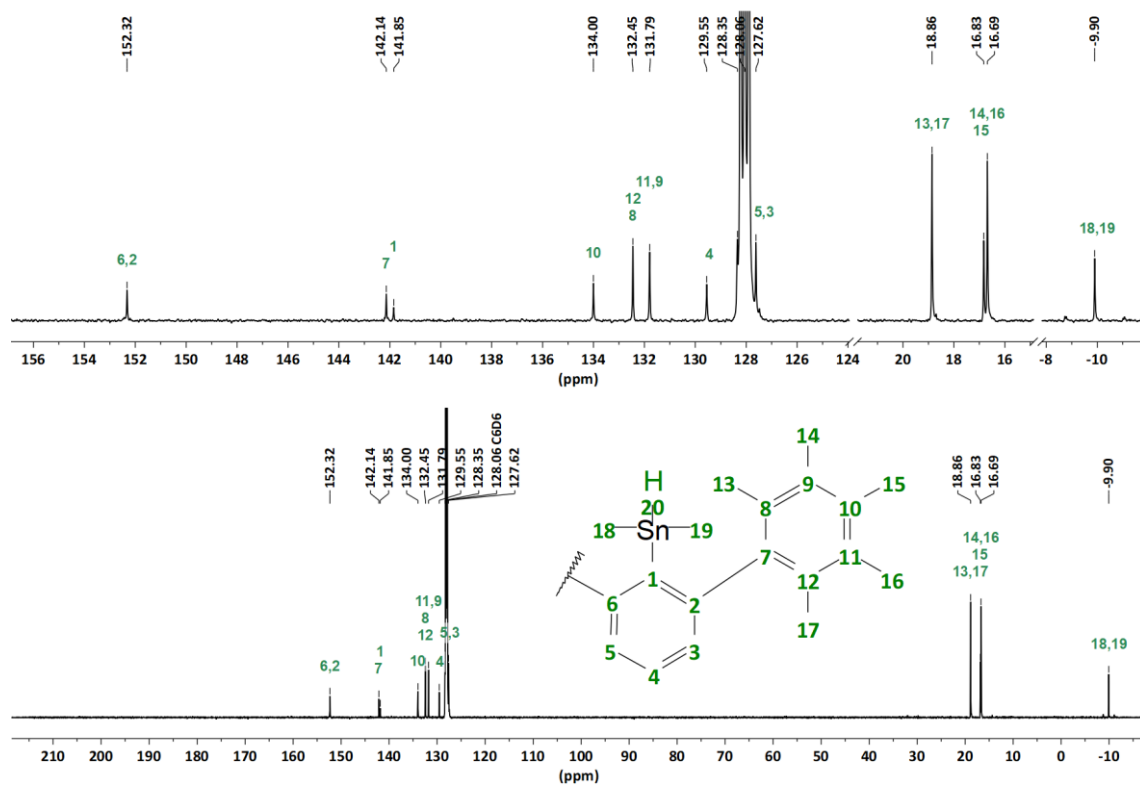


Figure 4.35: $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 151 MHz) spectrum of $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$.

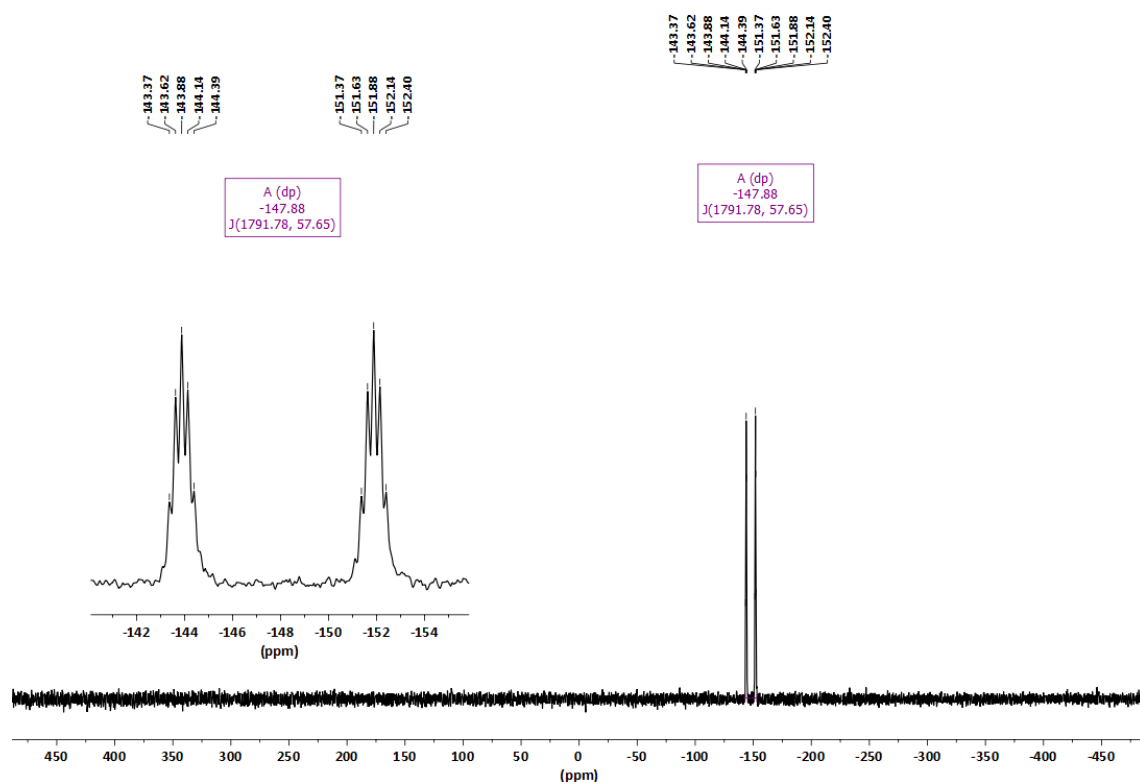


Figure 4.36: ^{119}Sn NMR (C_6D_6 , 224 MHz) spectrum of $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$.

4.8.4.1.6 (Fluid) $\text{Sn}(\text{Me})_2\text{H}$

This synthesis is modified from a known literature procedure for the synthesis of $\text{FluidSn}(\text{CH}_3)_2\text{Cl}$.^[43]

Me_2SnCl_2 (0.219 g, 1.00 mmol, 1.00 eq.) was placed in a Schlenk tube and dissolved in toluene (5 mL) and cooled to 0 °C. Separately $\text{FluidLi}(\text{THF})_2$ (0.665 g, 1.00 mmol, 1.00 eq.) was suspended in toluene (5 mL) and added dropwise to the Me_2SnCl_2 solution over the course of ten minutes. After two hours the solvent was removed under vacuum and the residual solid was suspended in Et_2O (10 mL). This suspension was cooled to -60 °C and LiAlH_4 (0.114 g, 3.00 mmol, 3.00 eq.) was added as a solid. The reaction mixture was stirred for an additional four hours at -20 °C. After this, the solvent was removed under reduced pressure and the product was dried at 60 °C. The residual solid was dissolved in toluene (10 mL) and filtered through a PTFE syringe filter. The solvent was removed under vacuum to obtain the target compound as a colorless solid (629 mg, 0.948 mmol, 95%).

Crystals suitable for X-ray structure determination were grown from a hot toluene/*n*-hexane (1:4) solution.

^1H -NMR (600 MHz, C_6D_6): δ = 7.49 (d, $^3J(^1\text{H}-^1\text{H})$ = 7.2 Hz, 4H, H14 and H21), 7.40 (s, H4), 7.19 (d, $^3J(^1\text{H}-^1\text{H})$ = 7.5 Hz, 4H, H11 and H18), 7.10 (td, $^3J(^1\text{H}-^1\text{H})$ = 7.5 Hz, $^4J(^1\text{H}-^1\text{H})$ = 1.2 Hz, 4H, H13 and H20), 7.03 (td, $^3J(^1\text{H}-^1\text{H})$ = 7.5 Hz, $^4J(^1\text{H}-^1\text{H})$ = 1.2 Hz, 4H, H12 and H19), 3.91 (hept, $^3J(^1\text{H}-^1\text{H})$ = 2.8 Hz, 1H, H24), 2.32 (s, 4H, H6), 1.46 (s, 12H, H8 and H9), -1.04 (d, $^3J(^1\text{H}-^1\text{H})$ = 2.8 Hz, 6H, H22 and H23) ppm. **$^{13}\text{C}\{^1\text{H}\}$ -NMR (151 MHz, C_6D_6):** δ = 156.45 (s, C10 and C17), 155.58 (s, C3), 151.67 (s, C2), 141.02 (s, C15 and C16), 137.50 (s, C1), 128.35 (s, C12 and C19), 127.35 (s, C13 and C20), 124.76 (s, C11 and C18), 120.67 (s, C14 and C21), 118.12 (s, C4), 66.57 (s, C5), 59.95 (s, C6), 42.49 (s, C7), 32.62 (s, C8 and C9), -9.95 (s, C22 and C23) ppm. **^{119}Sn -NMR (C_6D_6 , 224 MHz):** δ = -161.41 (dp, $^2J(^{119}\text{Sn}-^1\text{H})$ = 57.7 Hz, $^1J(^{119}\text{Sn}-^1\text{H})$ = 1806.9 Hz) ppm. **HRMS ESI (m/z):** $[\text{M}-\text{H}]^+$ calculated. for $\text{C}_{42}\text{H}_{39}\text{Sn}$, 663.20771; found, 663.20749. **IR** (ATR, neat): $\tilde{\nu}$ = 1927 cm^{-1} (m, br, Sn-H). Melting Point: 248 (decomp.) °C.

4 Unravelling White Phosphorus

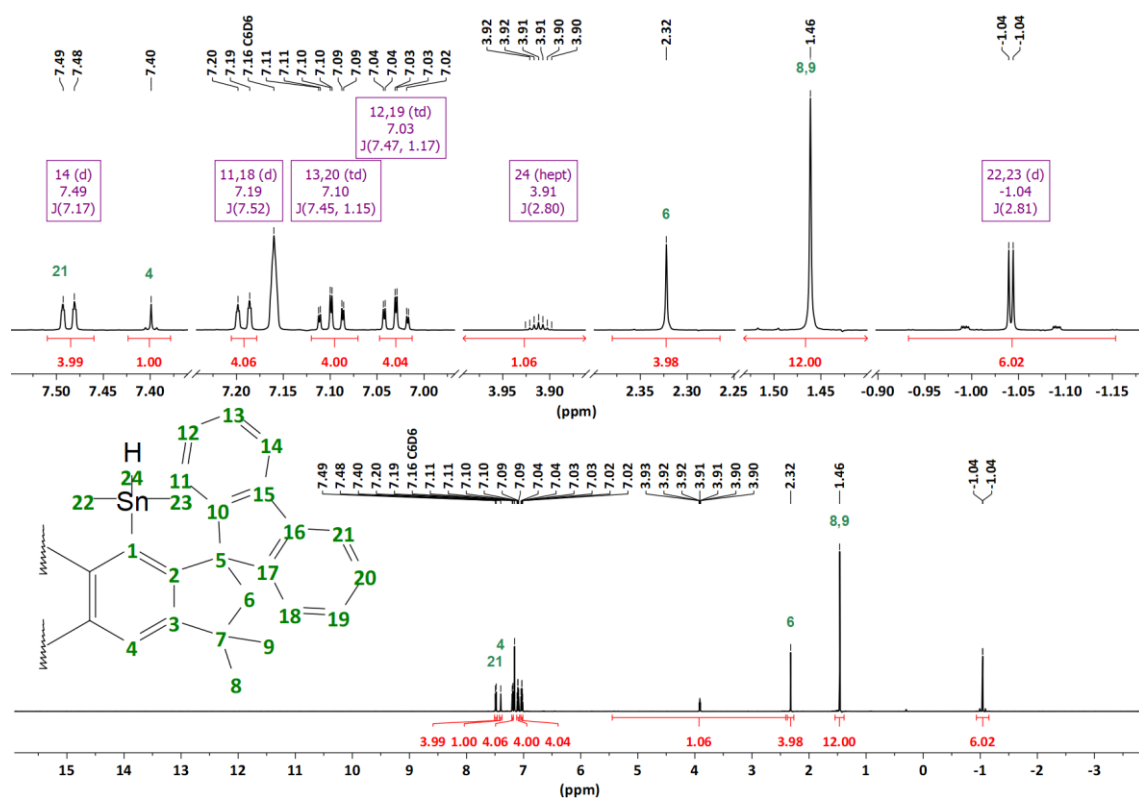


Figure 4.37: ^1H NMR (C_6D_6 , 600 MHz) spectrum of $\text{FluidSn}(\text{Me})_2\text{H}$.

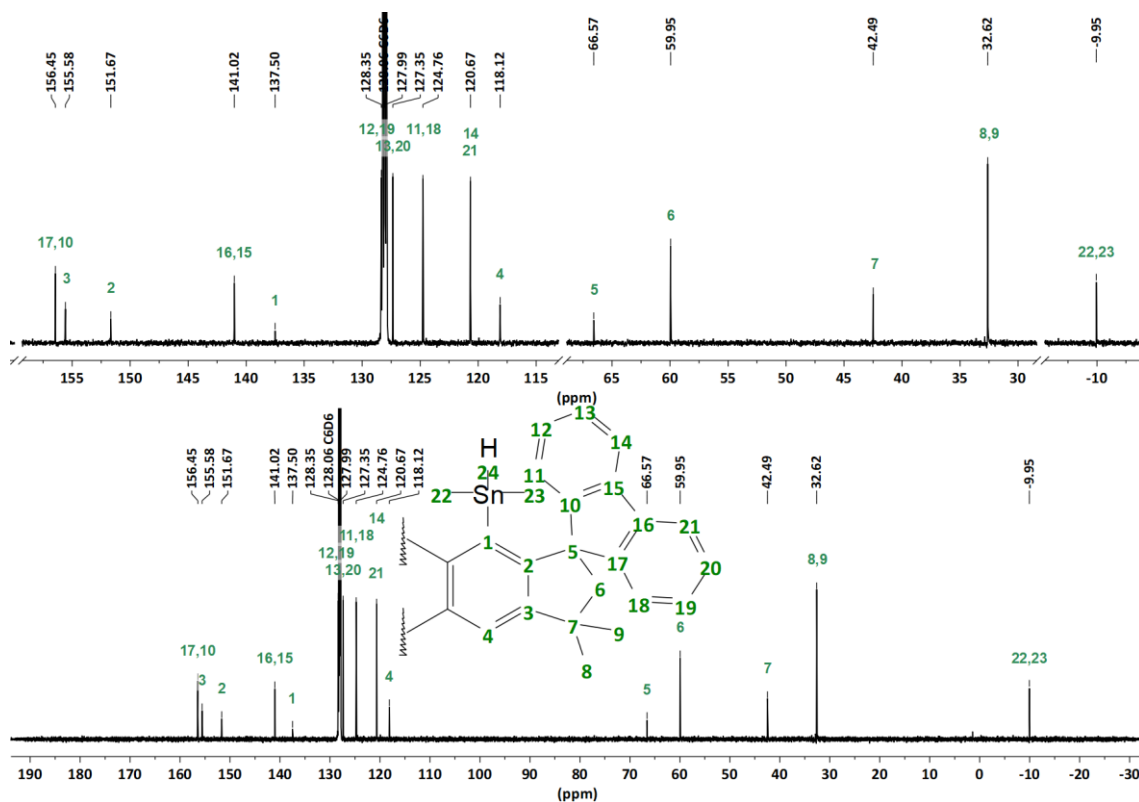


Figure 4.38: $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 151 MHz) spectrum of $\text{FluidSn}(\text{Me})_2\text{H}$.

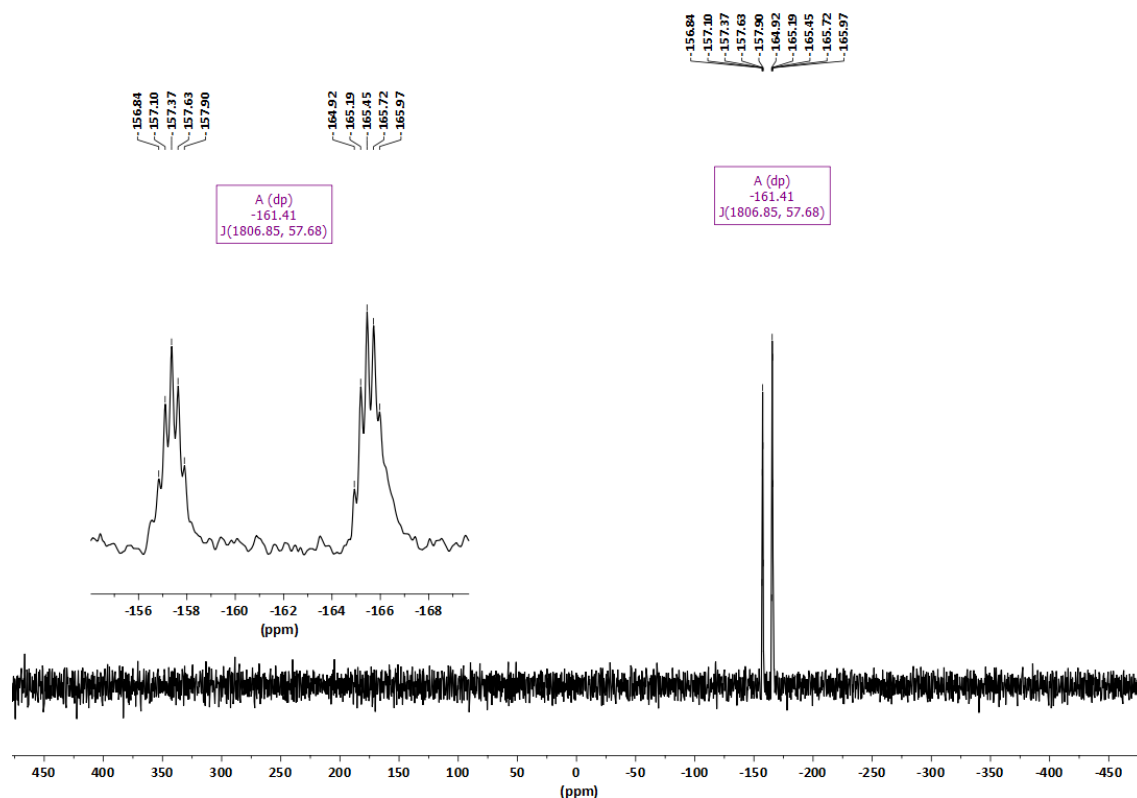


Figure 4.39: ^{119}Sn NMR (C_6D_6 , 224 MHz) spectrum of $\text{FluidSn}(\text{Me})_2\text{H}$.

4.8.4.1.7 Crystallographic Characterization of new hydrostannanes

Single crystal X-ray diffraction data for $\text{TerSn}(\text{Me})_2\text{H}$ was collected at 150 K due to a phase transition at 140 K and for $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ and $\text{FluidSn}(\text{Me})_2\text{H}$ at 100 K using an open flow nitrogen stream on a Bruker Venture D8 diffractometer with a Photon 100 detector in shutterless mode using a microfocus source ($\text{Mo}_{\text{K}\alpha} = 0.71073 \text{ \AA}$). All structures were solved by the SHELXT structure solution program using Intrinsic phasing and refined with the SHELX program package using Least Squares minimization as implemented in Olex2.^[44,45] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms at the Sn atoms were located from the Fourier difference map and had their positions and isotropic displacement parameter refined freely. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are collected in Table 4.2, and the structures themselves are illustrated in Figure 4.40. Crystallographic data for these structures has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of this data can be obtained free of charge on quoting the depository numbers: 2315115, 2315154, 2315177; E-mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>.

4 Unravelling White Phosphorus

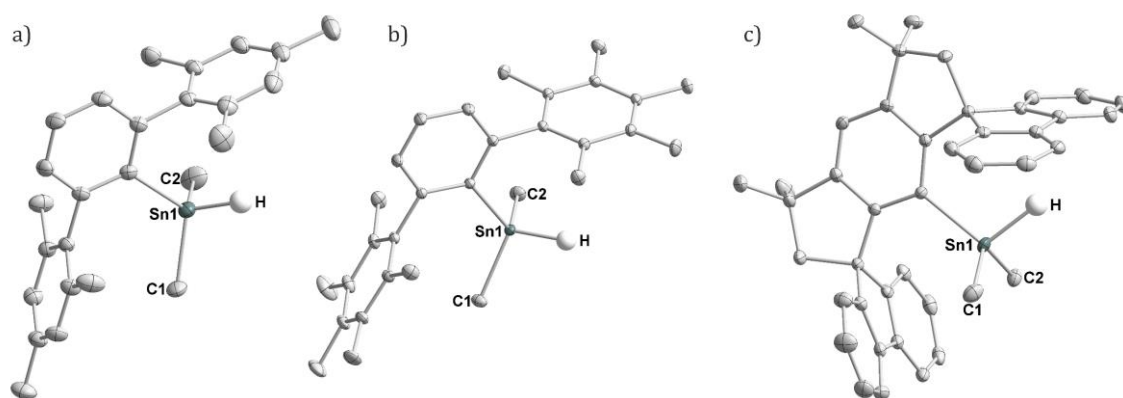


Figure 4.40: Single-crystal XRD structures of (a) $\text{TerSn}(\text{Me})_2\text{H}$, (b) $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$, (c) $\text{FluidSn}(\text{Me})_2\text{H}$. Thermal ellipsoids are shown at 50%. H atoms, except for those bound directly to Sn, are omitted for clarity. For (c) $\text{FluidSn}(\text{Me})_2\text{H}$ the less occupied position of the disorder is omitted for clarity. C atoms are shown in grey, H in white, and Sn in dark grey.

Table 4.2: Crystal data and structure refinement of $\text{TerSn}(\text{Me})_2\text{H}$, $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ and $\text{FluidSn}(\text{Me})_2\text{H}$.

	$\text{TerSn}(\text{Me})_2\text{H}$	$\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$	$\text{FluidSn}(\text{Me})_2\text{H}$
Formula	$\text{C}_{26}\text{H}_{32}\text{Sn}$	$\text{C}_{30}\text{H}_{40}\text{Sn}$	$\text{C}_{42}\text{H}_{40}\text{Sn}$
Formula weight, g mol^{-1}	463.20	519.31	663.43
Crystal system	Monoclinic	Triclinic	Triclinic
Crystal size, mm	$0.18 \times 0.18 \times 0.14$	$0.32 \times 0.14 \times 0.10$	$0.26 \times 0.26 \times 0.10$
Space group	$P2_1/c$	P-1	P-1
a , Å	17.9790(8)	8.9780(7)	9.6930(5)
b , Å	8.5727(4)	9.0895(7)	11.5749(7)
c , Å	15.9417(7)	18.2993(15)	15.9229(9)
α , °	90	78.754(3)	70.426(3)
β , °	106.5900(10)	89.042(3)	82.300(3)
γ , °	90	60.517(3)	73.912(3)
V , Å ³	2354.79(18)	1269.47(18)	1615.65(16)
Z	4	2	2
ρ_{calcd} , Mg m^{-3}	1.307	1.359	1.364
μ (Mo $K\alpha$), mm^{-1}	1.092	1.021	0.819
$F(000)$	952.0	540.0	684.0
2θ range, deg	4.728 to 56.556	5.272 to 73.206	5.368 to 54.206
Index ranges	$-23 \leq h \leq 23$ $-11 \leq k \leq 11$ $-20 \leq l \leq 21$	$-14 \leq h \leq 14$ $-15 \leq k \leq 15$ $-30 \leq l \leq 30$	$-12 \leq h \leq 12$ $-14 \leq k \leq 14$ $-20 \leq l \leq 20$
No. of reflns collected	100484	94845	44401
No. indep. Reflns	14937	12450	7116
No. refined params	256	296	422
GooF (F^2)	1.141	1.063	1.049
R_1 (F) ($I > 2\sigma(I)$)	0.0264	0.0217	0.0302

$wR_2 (F^2)$ (all data)	0.0551	0.0534	0.0726
Largest diff peak/hole, $e \text{ \AA}^{-3}$	0.40 / -0.64	0.63 / -0.38	0.74 / -0.77
CCDC number	2315115	2315154	2315177

4.8.4.2 $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic monitoring experiments

4.8.4.2.8 $i\text{Pr}_3\text{SnH}$

Ex situ under LED irradiation (455 nm)

To a 10 mL, flat-bottomed, stoppered tube were added C_6D_6 (500 μL), P_4 (0.01 mmol, as a stock solution in 124.6 μL C_6D_6) and $i\text{Pr}_3\text{SnH}$ (15.0 mg, 0.06 mmol). The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 3.2 V, 700 mA, Osram OSOLON SSL 80) for 24 hours. The resulting mixture was analyzed by ^1H , $^{31}\text{P}\{^1\text{H}\}$, and ^{31}P -NMR spectroscopy, as shown in Figures 4.41-4.43, below.

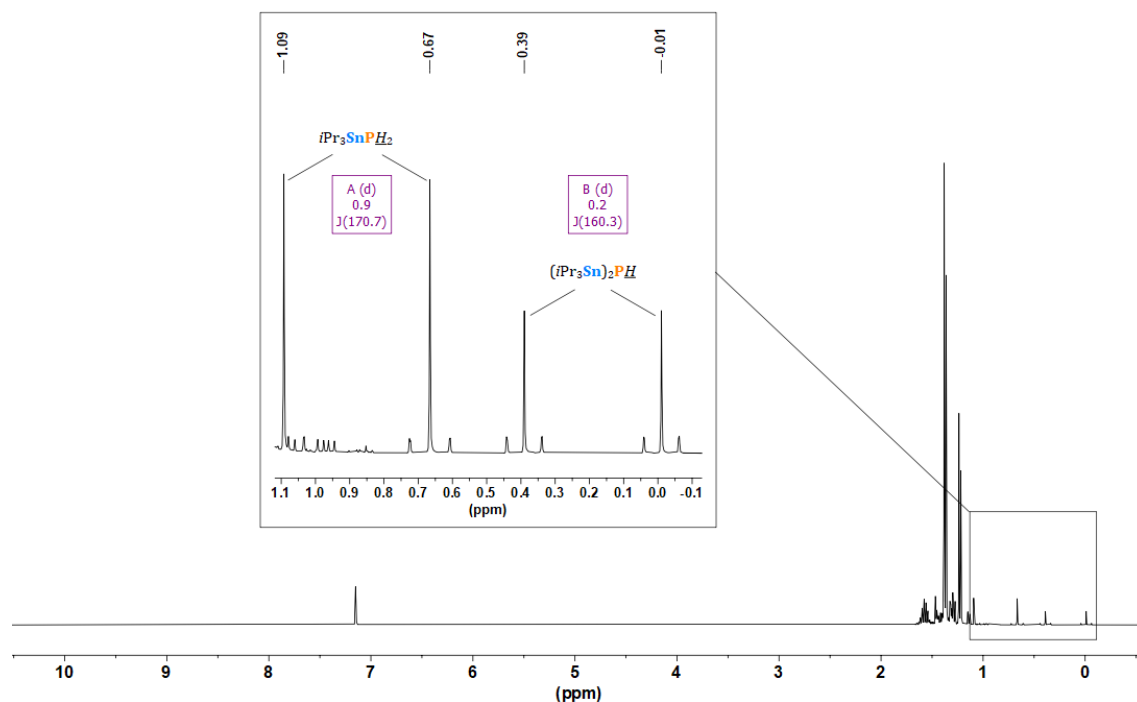


Figure 4.41: ^1H NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $i\text{Pr}_3\text{SnH}$ (0.06 mmol) in C_6D_6 and driven by 455 nm LED irradiation for 24 h. The inset shows expansions of the doublet resonance with $^{117/119}\text{Sn}$ satellites attributed to the PH_2 and PH moieties of $i\text{Pr}_3\text{SnPH}_2$ and $(i\text{Pr}_3\text{Sn})_2\text{PH}$, respectively.

4 Unravelling White Phosphorus

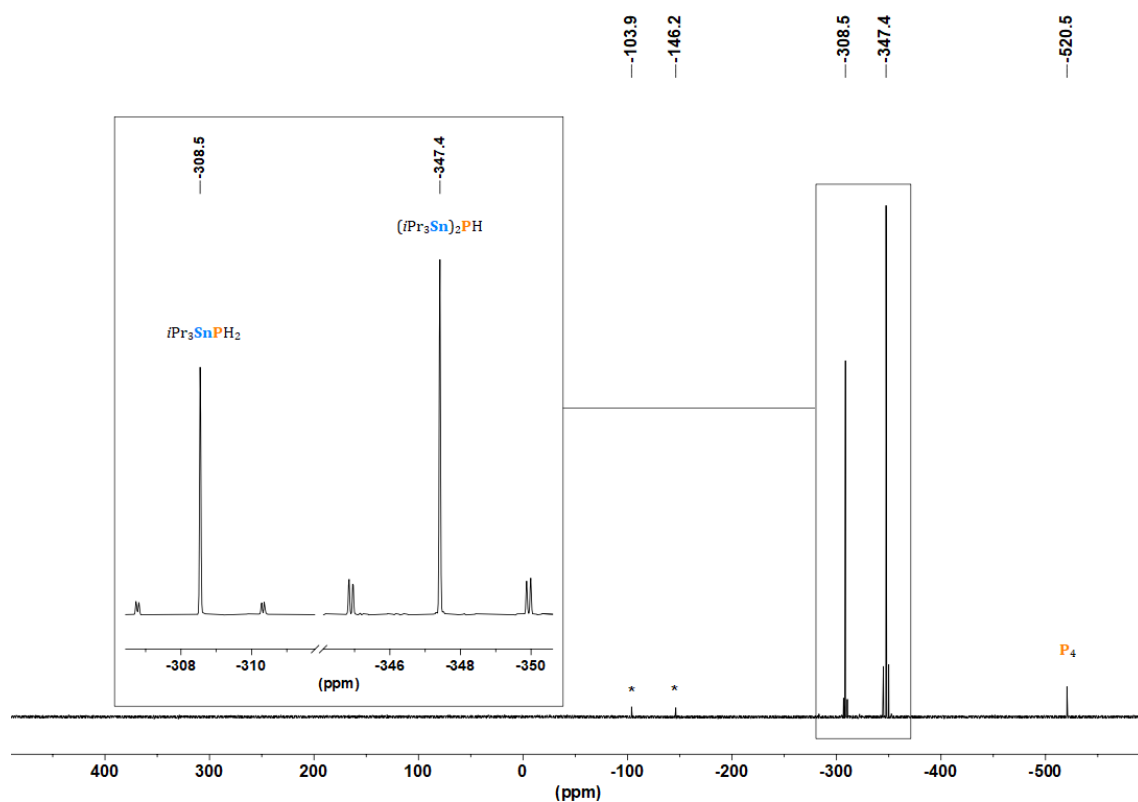


Figure 4.42: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $i\text{Pr}_3\text{SnH}$ (0.06 mmol) in C_6D_6 and driven by 455 nm LED irradiation for 24 h. The inset shows expansions of the signals attributed to $i\text{Pr}_3\text{SnPH}_2$ and $(i\text{Pr}_3\text{Sn})_2\text{PH}$, highlighting the presence of $^{117}/^{119}\text{Sn}$ satellites. * marks minor, unknown side products.

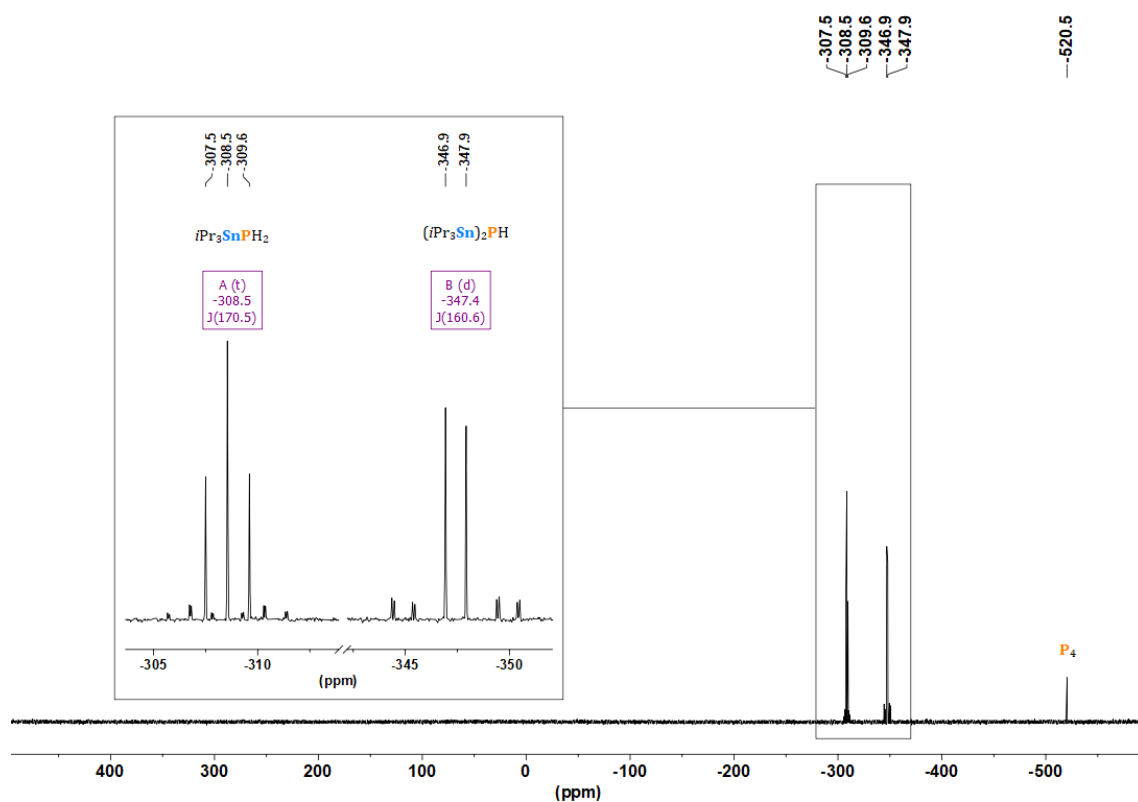


Figure 4.43: ^{31}P spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $i\text{Pr}_3\text{SnH}$ (0.06 mmol) in C_6D_6 and driven by 455 nm LED irradiation for 24 h. The inset shows expansions of the signals attributed to $i\text{Pr}_3\text{SnPH}_2$ and $(i\text{Pr}_3\text{Sn})_2\text{PH}$, highlighting their multiplicity due to $^1J(^{31}\text{P}\text{-}^1\text{H})$ couplings.

Ex situ, with AIBN

To a 10 mL, flat-bottomed, stoppered tube were added C_6D_6 (500 μL), P_4 (0.01 mmol, as a stock solution in 124.6 μL C_6D_6), $i\text{Pr}_3\text{SnH}$ (15.0 mg, 0.06 mmol) and AIBN (0.001 mmol, as a stock solution in 12.9 μL C_6D_6). The tube was sealed, wrapped in Al foil to exclude light, and heated to 60 $^\circ\text{C}$ for 24 hours. The resulting mixture was analyzed by $^{31}\text{P}\{^1\text{H}\}$, and ^{31}P -NMR spectroscopy, as shown in Figures 4.44 and 4.45, below.

4 Unravelling White Phosphorus

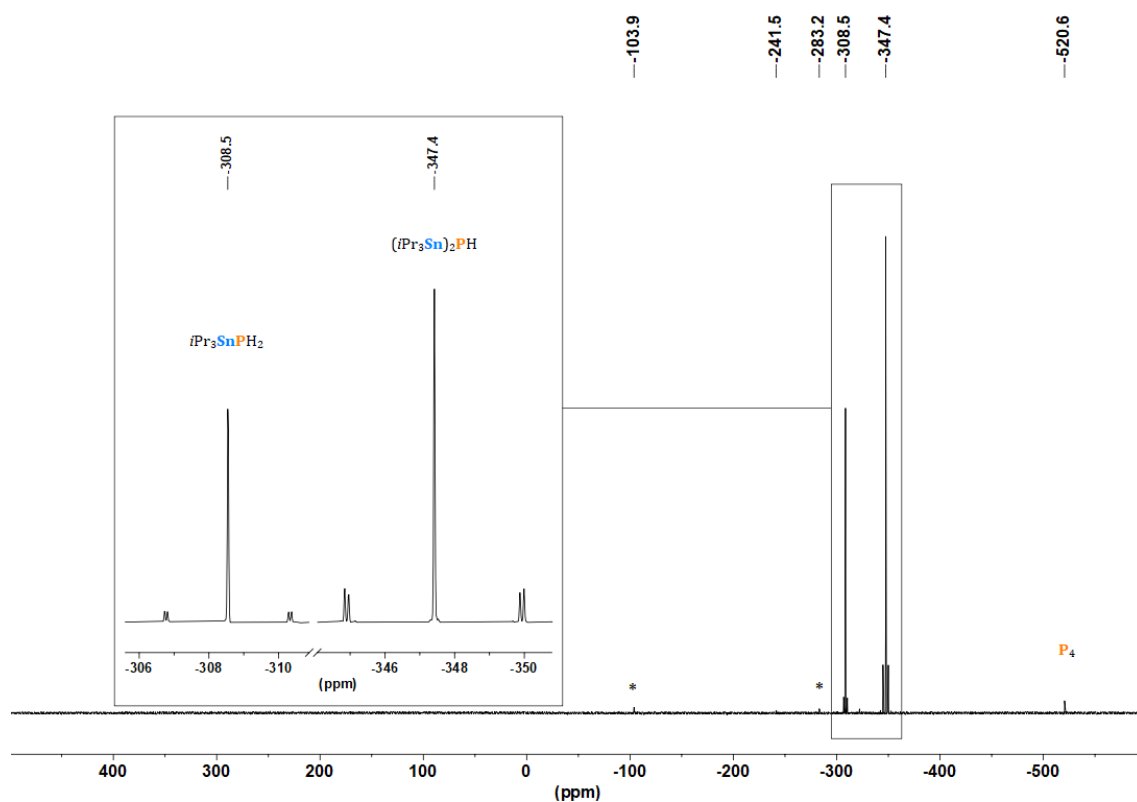


Figure 4.44: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $i\text{Pr}_3\text{SnH}$ (0.06 mmol) and AIBN (0.001 mmol) in C_6D_6 , heated to 60 °C for 24 h in the dark. The inset shows expansions of the signals attributed to $i\text{Pr}_3\text{SnPH}_2$ and $(i\text{Pr}_3\text{Sn})_2\text{PH}$, highlighting the presence of $^{117/119}\text{Sn}$ satellites. *marks minor, unknown side products.

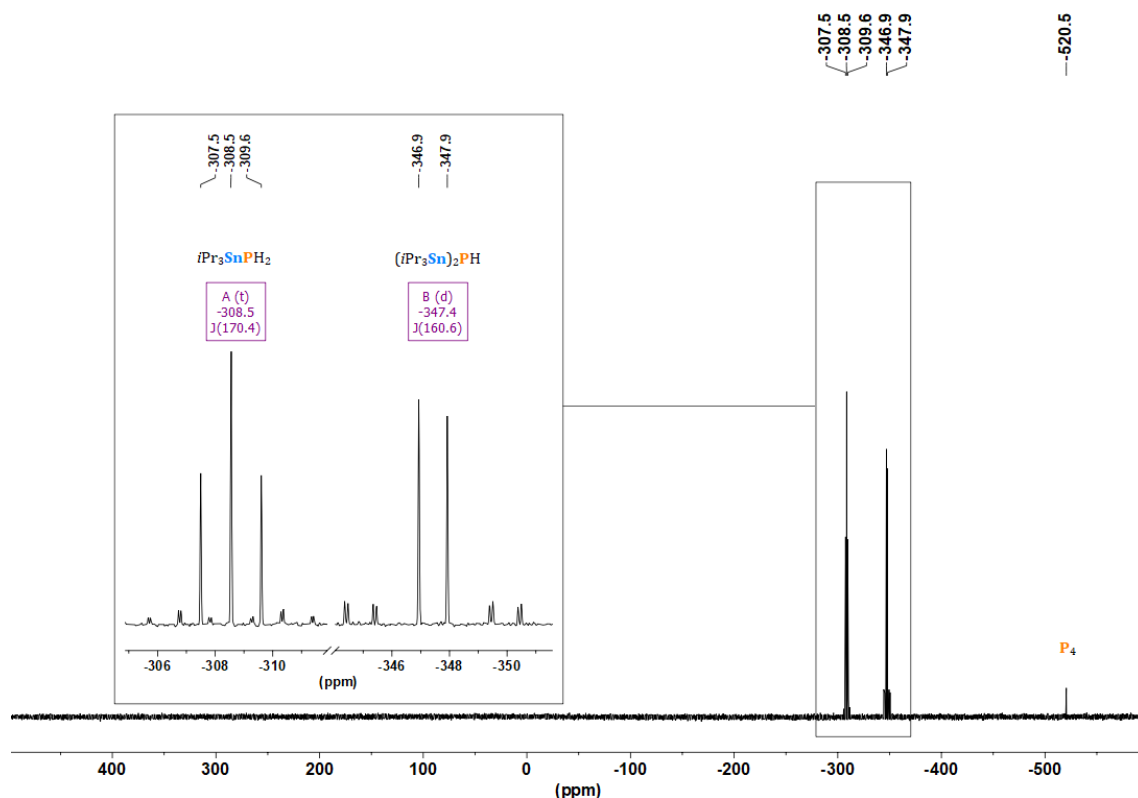


Figure 4.45: ^{31}P NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $i\text{Pr}_3\text{SnH}$ (0.06 mmol) and AIBN (0.001 mmol) in C_6D_6 , heated to 60°C for 24 h in the dark. The inset shows expansions of the signals attributed to $i\text{Pr}_3\text{SnPH}_2$ and $(i\text{Pr}_3\text{Sn})_2\text{PH}$, highlighting their multiplicity due to $^1J(^{31}\text{P}-^1\text{H})$ couplings.

In situ, with AIBN

This reaction was prepared in the same manner as the *ex-situ* experiment described immediately above, but was transferred to a screw-cap NMR tube and monitored by *in situ* $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy (for general details, see Section 4.8.2.1) at room temperature. As in the equivalent reaction with Bu_3SnH steady consumption of P_4 and concomitant product formation were observed, with no intermediates being detected. However, unlike for Bu_3SnH , only two products were observed to form: $i\text{Pr}_3\text{SnPH}_2$ and $(i\text{Pr}_3\text{Sn})_2\text{PH}$, in an approximately 1:1 ratio (Figure 4.46).

4 Unravelling White Phosphorus

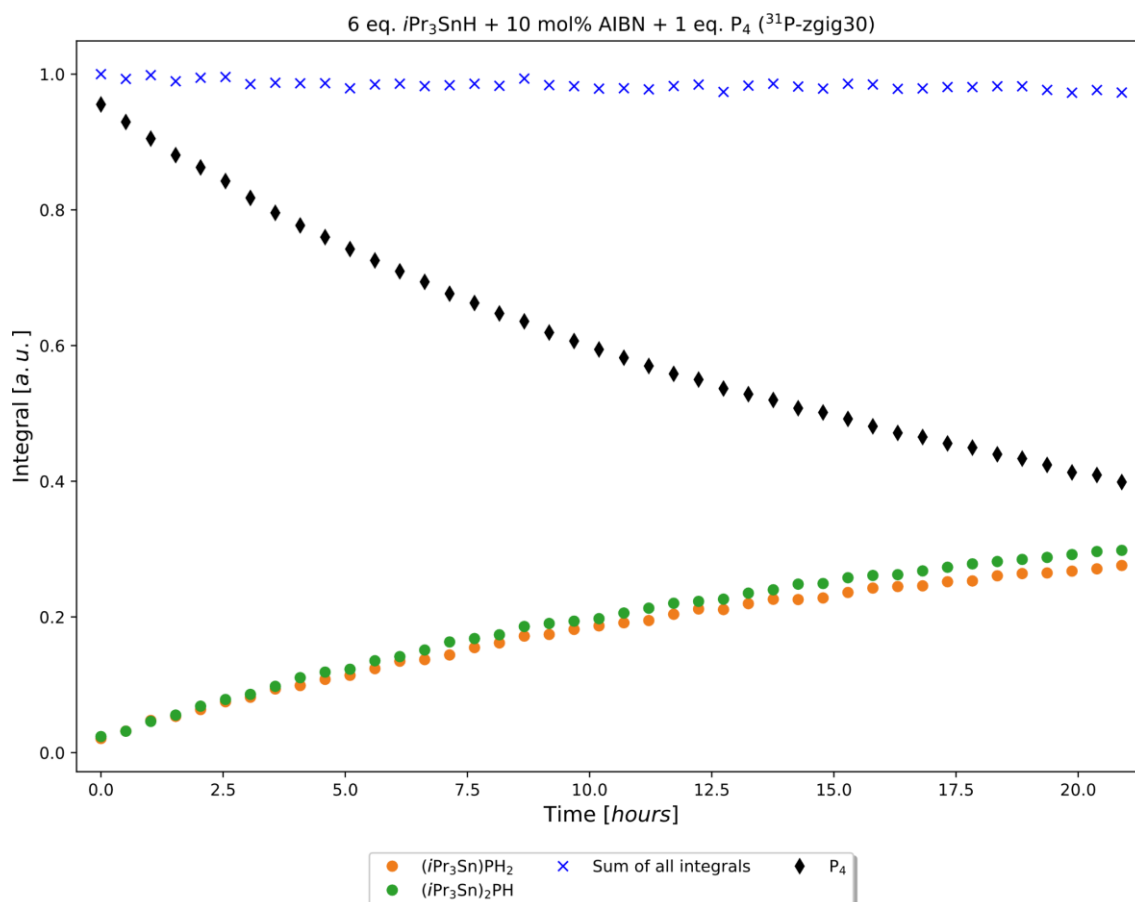


Figure 4.46: Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. $i\text{Pr}_3\text{SnH}$ initiated by 10 mol% AIBN in C_6D_6 at room temperature.

4.8.4.2.9 $\text{TerSn}(\text{Me})_2\text{H}$

Ex situ, under LED irradiation (455 nm)

To a 10 mL, flat-bottomed, stoppered tube were added benzene (non-deuterated, 500 μL), P_4 (0.01 mmol, as a stock solution in 88.6 μL benzene) and $\text{TerSn}(\text{Me})_2\text{H}$ (27.8 mg, 0.06 mmol). The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 3.2 V, 700 mA, Osram OSOLON SSL 80) for 18 hours. The resulting mixture was analyzed by $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P -NMR spectroscopy, as shown in Figures 4.47 and 4.48, below.

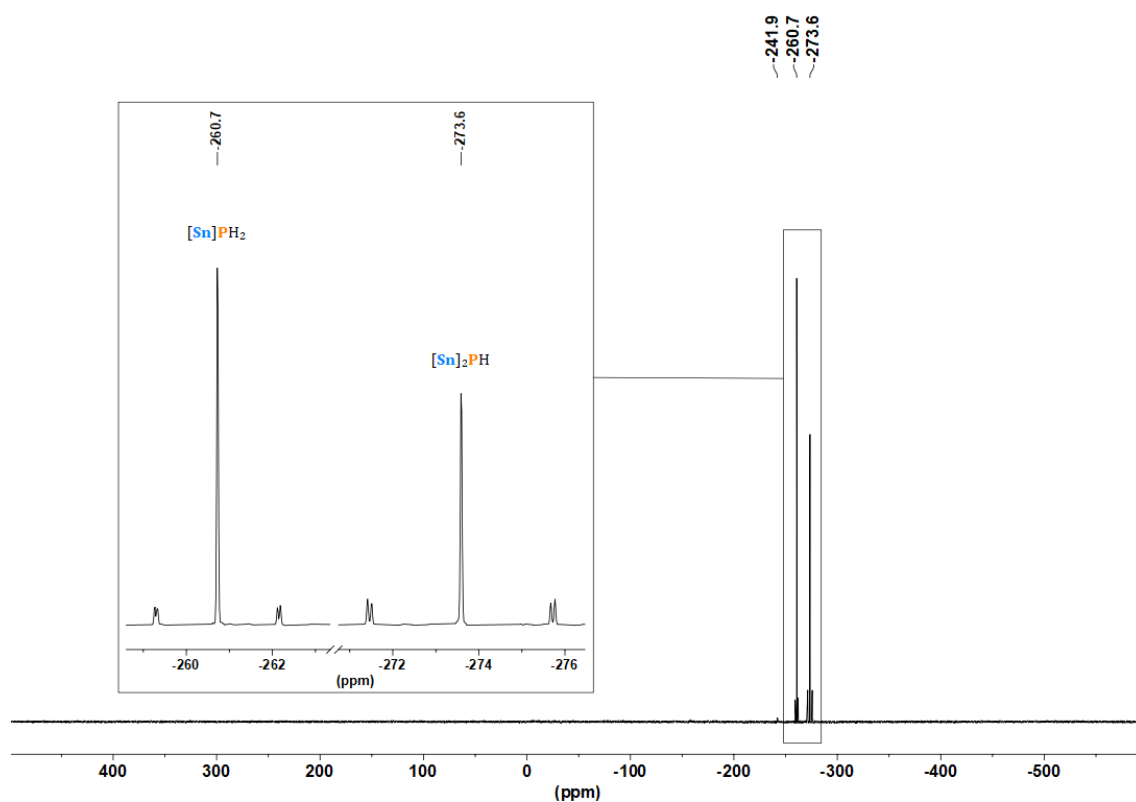


Figure 4.47: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $\text{TerSn}(\text{Me})_2\text{H}$ (0.06 mmol) in PhMe and driven by 455 nm LED irradiation for 18 h. The inset shows expansions of the signals attributed to $[\text{Sn}]\text{PH}_2$ and $[\text{Sn}]_2\text{PH}$ ($[\text{Sn}] = \text{TerSn}(\text{Me})_2$), highlighting the presence of $^{117}/^{119}\text{Sn}$ satellites.

4 Unravelling White Phosphorus

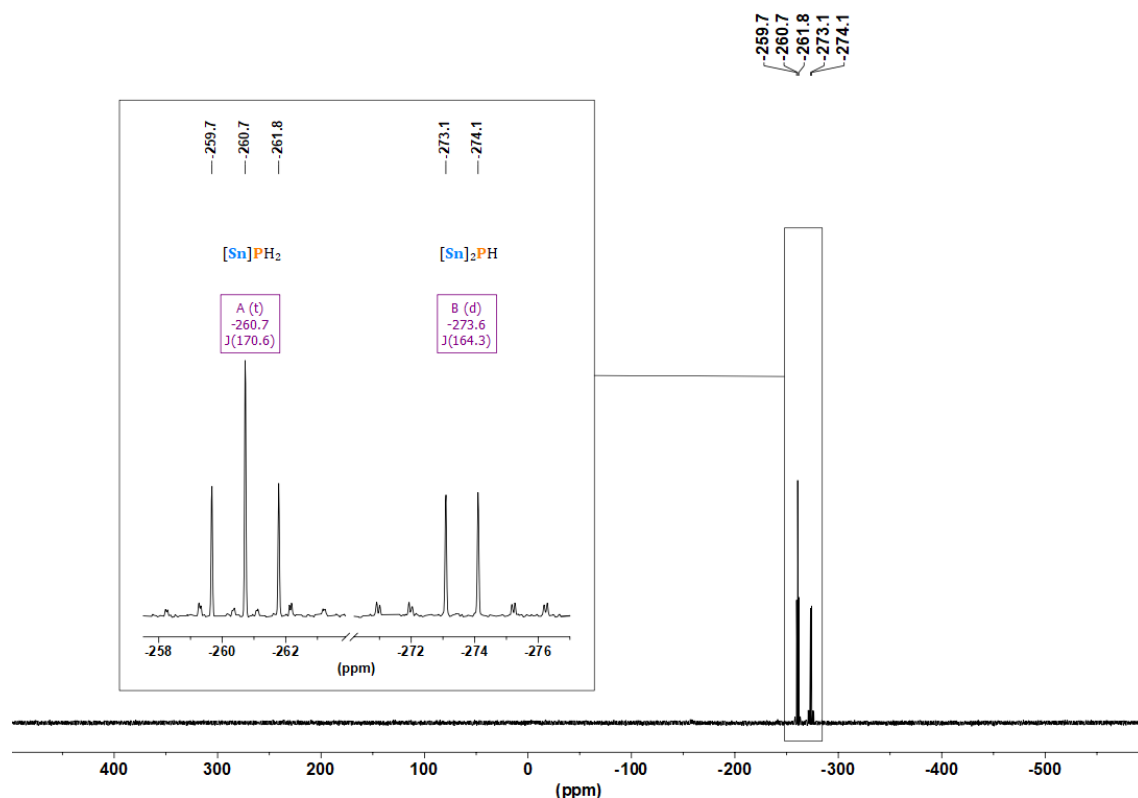


Figure 4.48: ^{31}P NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $\text{TerSn}(\text{Me})_2\text{H}$ (0.06 mmol) in PhMe and driven by 455 nm LED irradiation for 18 h. The inset shows expansions of the signals attributed to $[\text{Sn}]\text{PH}_2$ and $[\text{Sn}]_2\text{PH}$ ($[\text{Sn}] = \text{TerSn}(\text{Me})_2$), highlighting their multiplicity due to $^1J(^{31}\text{P}-^1\text{H})$ couplings.

Ex situ, with AIBN

To a 10 mL, flat-bottomed, stoppered tube were added C_6D_6 (500 μL), P_4 (0.01 mmol, as a stock solution in 124.6 μL C_6D_6), $\text{TerSn}(\text{Me})_2\text{H}$ (27.8 mg, 0.06 mmol) and AIBN (0.001 mmol, as a stock solution in 12.9 μL C_6D_6). The tube was sealed, wrapped in Al foil to exclude light, and heated to 60 $^\circ\text{C}$ for 24 hours. The resulting mixture was analyzed by $^{31}\text{P}\{^1\text{H}\}$, and ^{31}P NMR-spectroscopy, as shown in Figures 4.49 and 4.50, below.

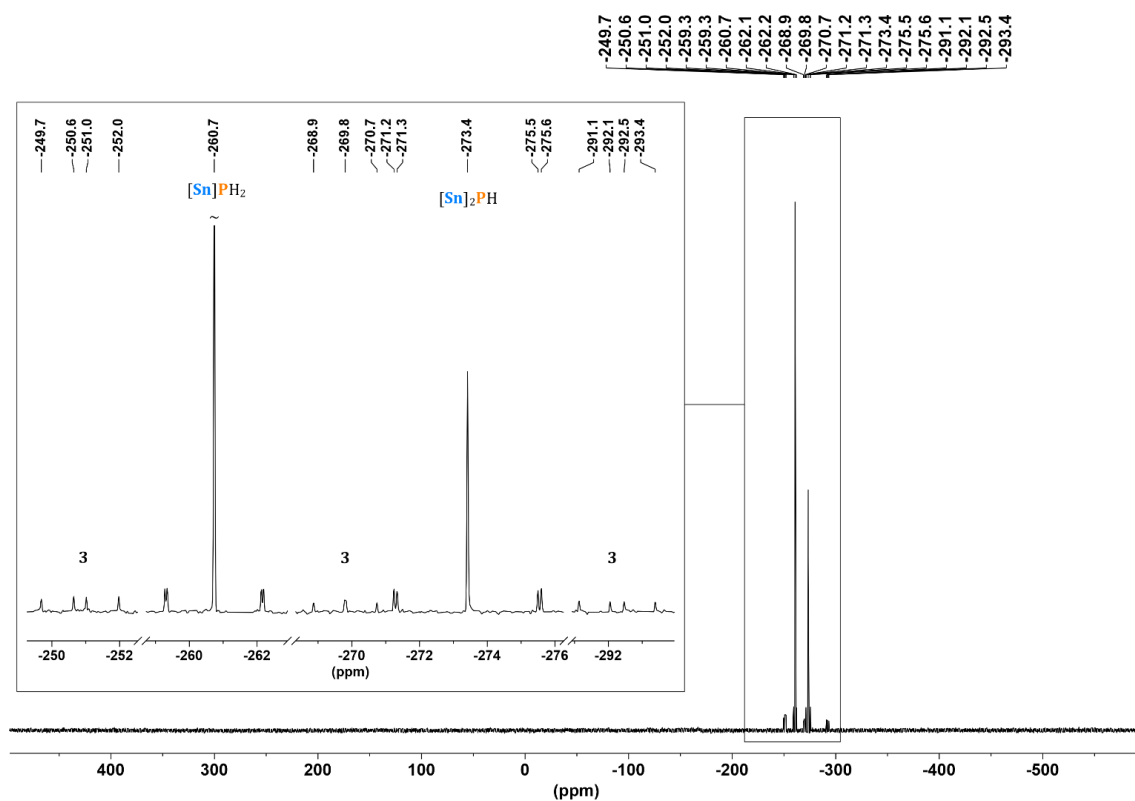


Figure 4.49: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $\text{TerSn}(\text{Me})_2\text{H}$ (0.06 mmol) in C_6D_6 and AIBN (0.001 mmol) in C_6D_6 , heated to 60 °C for 24 h in the dark. The inset shows expansions of the signals attributed to $[\text{Sn}]\text{PH}_2$ and $[\text{Sn}]_2\text{PH}$ ($[\text{Sn}] = \text{TerSn}(\text{Me})_2$), highlighting the presence of $^{117}/^{119}\text{Sn}$ satellites. Peak marked with ~ has been truncated for the sake of clarity.

4 Unravelling White Phosphorus

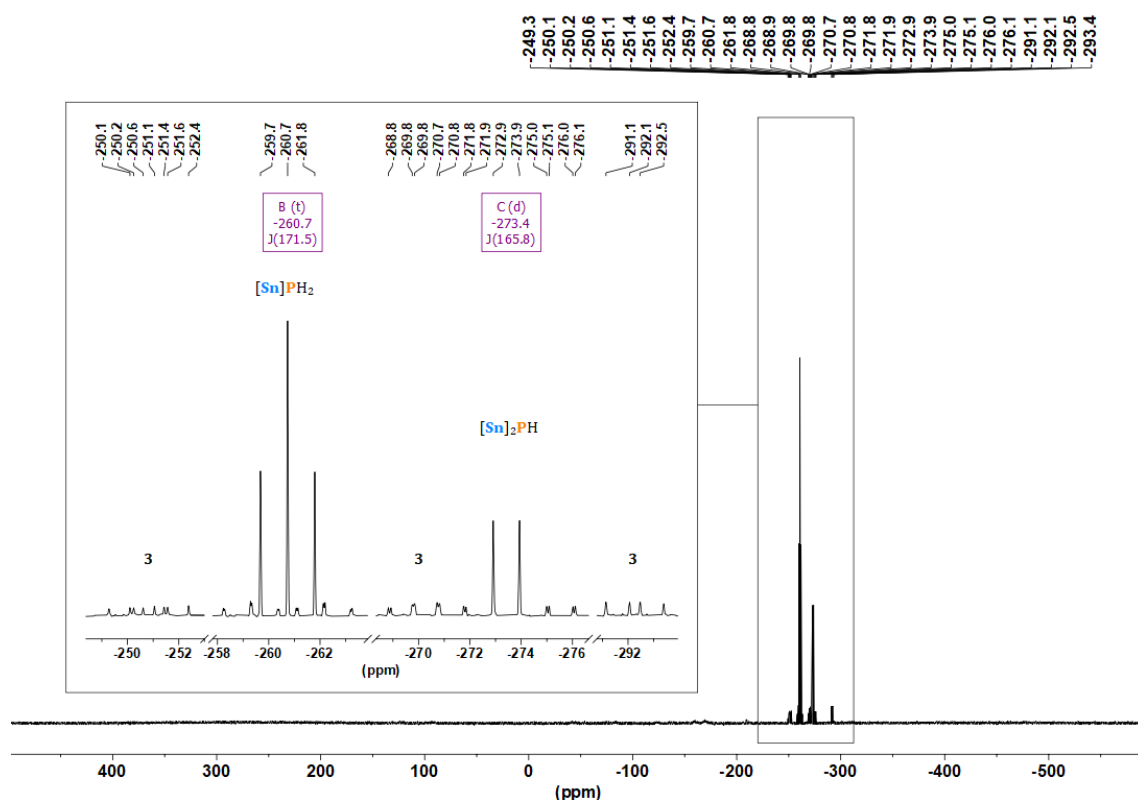


Figure 4.50: ^{31}P NMR spectrum for the *ex situ* reaction of P_4 (0.01 mmol) with $\text{TerSn}(\text{Me})_2\text{H}$ (0.06 mmol) in C_6D_6 and AIBN (0.001 mmol) in C_6D_6 , heated to 60 °C for 24 h in the dark. The inset shows expansions of the signals attributed to $[\text{Sn}]\text{PH}_2$ and $[\text{Sn}]_2\text{PH}$ ($[\text{Sn}] = \text{TerSn}(\text{Me})_2$), highlighting the presence of $^{117/119}\text{Sn}$ satellites.

In situ, with AIBN

To a screw-capped NMR tube were added C_6D_6 (500 μL), P_4 (0.01 mmol, as a stock solution in 124.6 μL C_6D_6), $\text{TerSn}(\text{Me})_2\text{H}$ (27.8 mg, 0.06 mmol), and AIBN (0.001 mmol, as a stock solution in 12.9 μL C_6D_6). The resulting solution was monitored by in situ $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy (for general details, see Section 4.8.2.1) at room temperature.

In addition to resonances for the P_4 starting material and the final products $[\text{Sn}]\text{PH}_2$ and $[\text{Sn}]_2\text{PH}$ (where $[\text{Sn}] = \text{TerSnMe}_2$), five further resonances were observed as the reaction progressed, which can be assigned to reaction intermediates. A representative spectrum showing all detected resonances is shown in Figure 4.10 and in Figure 4.51, below.

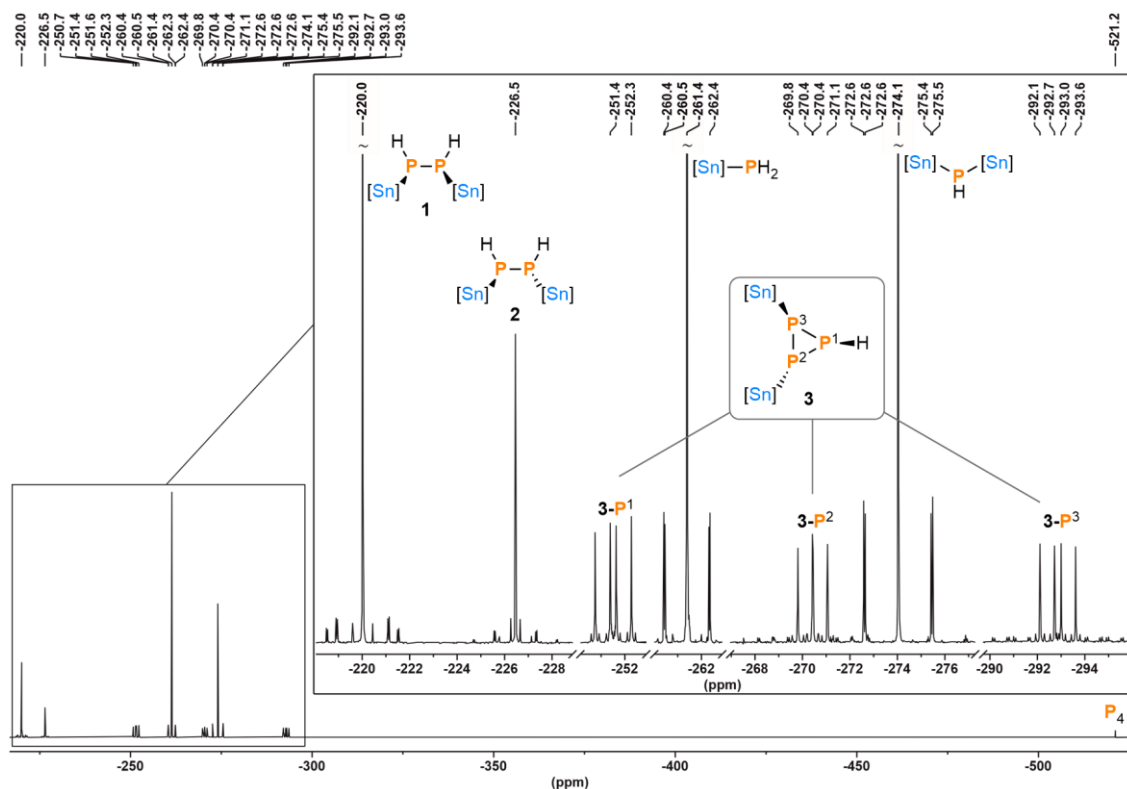


Figure 4.51: $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic observation of reaction intermediates during the hydrostannylation of P_4 using $\text{TerSn}(\text{Me})_2\text{H}$ (6 eq.) initiated by AIBN (10 mol%) in C_6D_6 at room temperature. $[\text{Sn}] = \text{TerSnMe}_2$. Peaks marked with ~ have been truncated for the sake of clarity.

Of the five signals assigned to intermediates, the two singlets -220.0 ppm and -226.5 ppm can be attributed to the meso and C_2 isomers of the symmetrical diphosphane $[\text{Sn}]\text{P}(\text{H})\text{--P}(\text{H})[\text{Sn}]$ (**1** and **2**, respectively). The presence of a higher-order spin system is evident both from the pattern of the $^{117/119}\text{Sn}$ satellites and the corresponding ^1H -coupled ^{31}P spectra (Figures 4.52 and 4.53), with very similar patterns having been reported for silylated diphosphanes, $\text{HypP}(\text{H})\text{--P}(\text{H})\text{Hyp}$ ($\text{Hyp} = \text{Si}(\text{SiMe}_3)_3$).^[46] Note that ^{119}Sn and $^1\text{H}(\text{PH})$ resonances for these intermediates could not be resolved.

4 Unravelling White Phosphorus

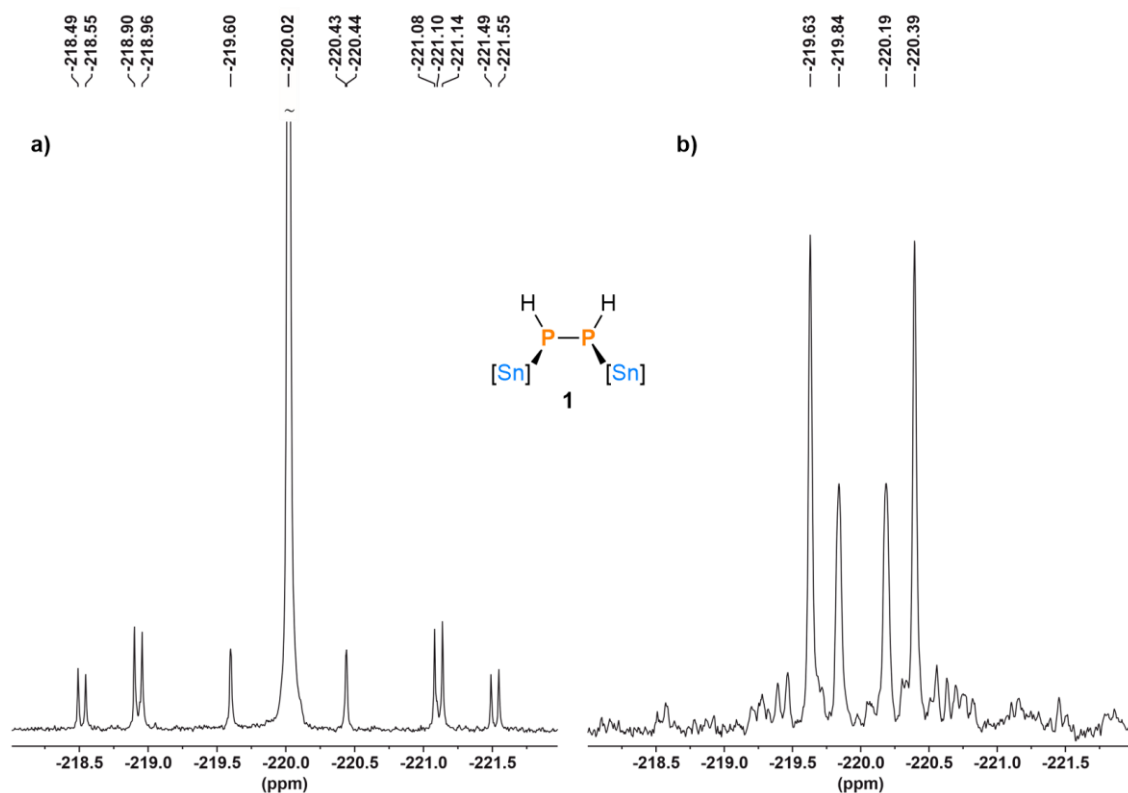


Figure 4.52: (a) $^{31}\text{P}\{^1\text{H}\}$ and (b) ^{31}P NMR resonances of **1** (meso-[Sn]P(H)-P(H)[Sn]), as observed during *in situ* experiments. [Sn] = TerSnMe₂. Peak marked with ~ has been truncated for the sake of clarity.

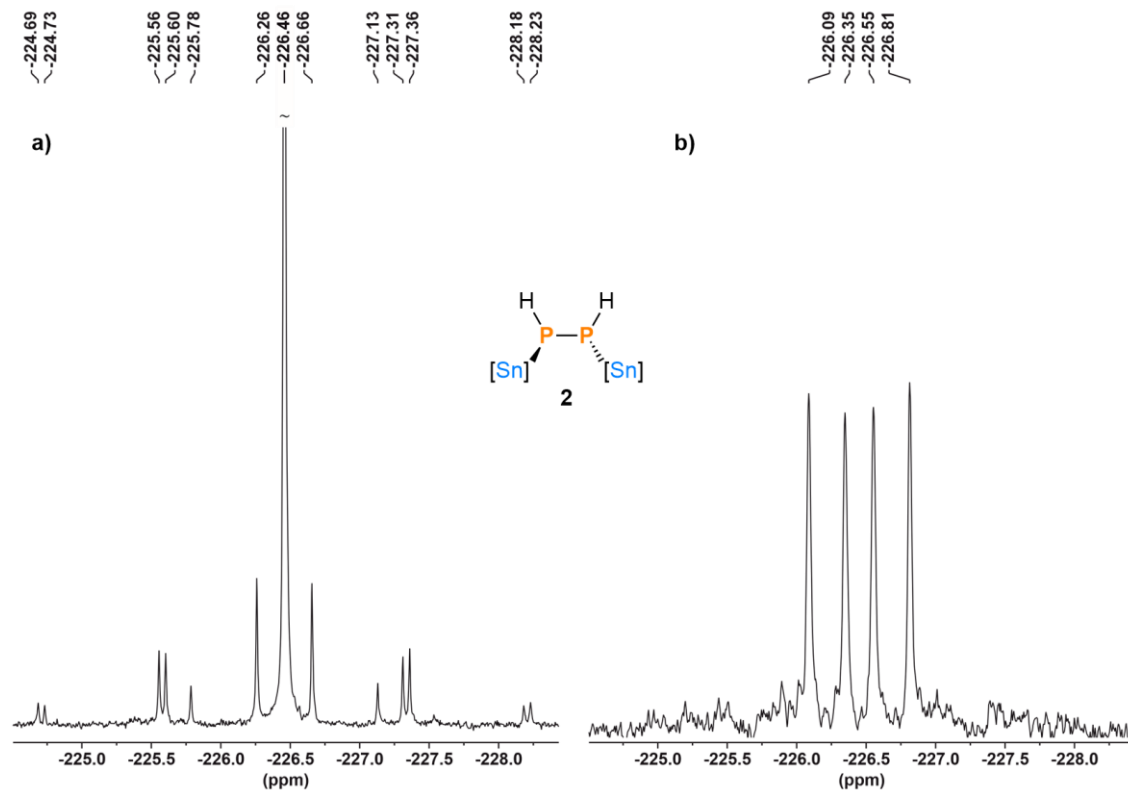


Figure 4.53: (a) $^{31}\text{P}\{^1\text{H}\}$ and (b) ^{31}P NMR resonances of **2** (C₂-[Sn]P(H)-P(H)[Sn]), as observed during *in situ* experiments. [Sn] = TerSnMe₂. Peak marked with ~ has been truncated for the sake of clarity.

The remaining three doublet of doublet signals show mutual coupling constants, suggesting they can be assigned to a single species. This was confirmed by ^{31}P -COSY (Figure 4.54), and based on the observation of ^{31}P - ^{31}P , ^{31}P - ^1H and ^{31}P - $^{117/119}\text{Sn}$ scalar couplings (Figure 4.55) as well as ^{119}Sn -NMR spectra (Figure 4.56) this species is assigned as the *cyclo*- P_3 structure $[\text{Sn}]_2\text{P}_3\text{H}$, **3**, whose P_3 ring is substituted by two $[\text{Sn}]$ moieties in a trans arrangement, and one H atom. The H atom is trans to one $[\text{Sn}]$ group and cis to the other, resulting in three distinct ^{31}P environments and hence the three observed signals.

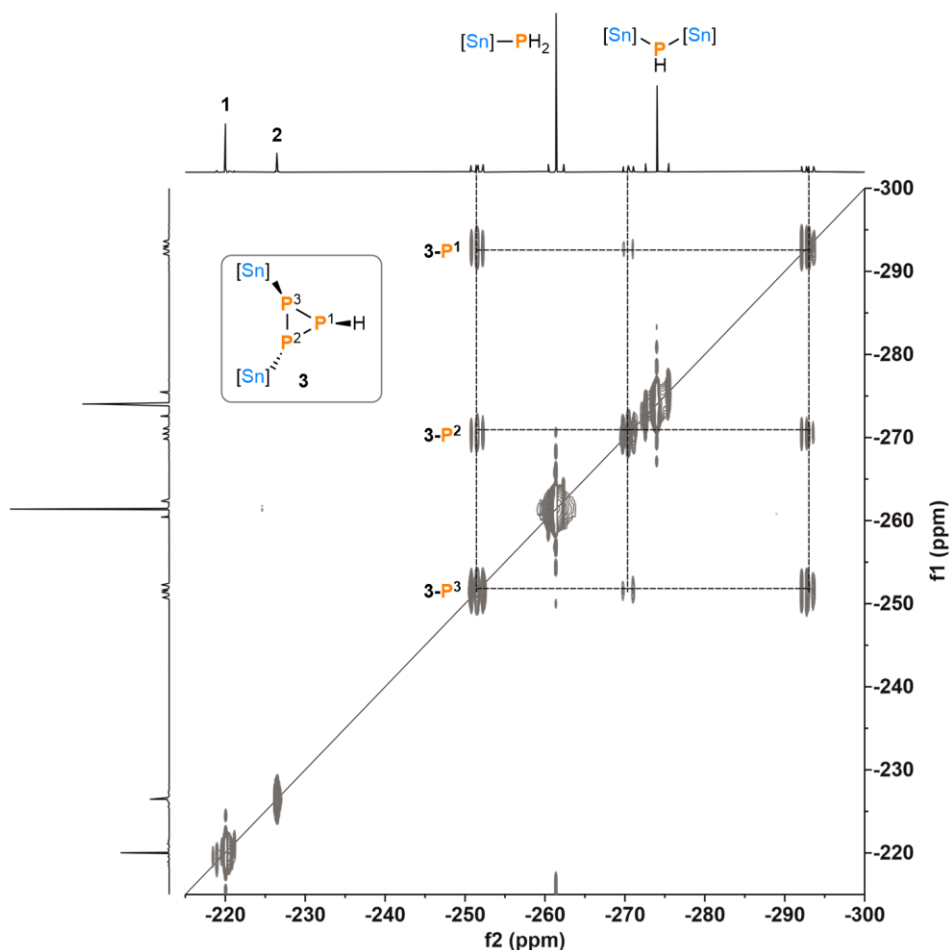


Figure 4.54: ^{31}P COSY spectrum showing coupling between the three resonances attributed to intermediate **3** ($[\text{Sn}]_2\text{P}_3\text{H}$), as observed during *in situ* experiments. $[\text{Sn}] = \text{TerSnMe}_2$.

4 Unravelling White Phosphorus

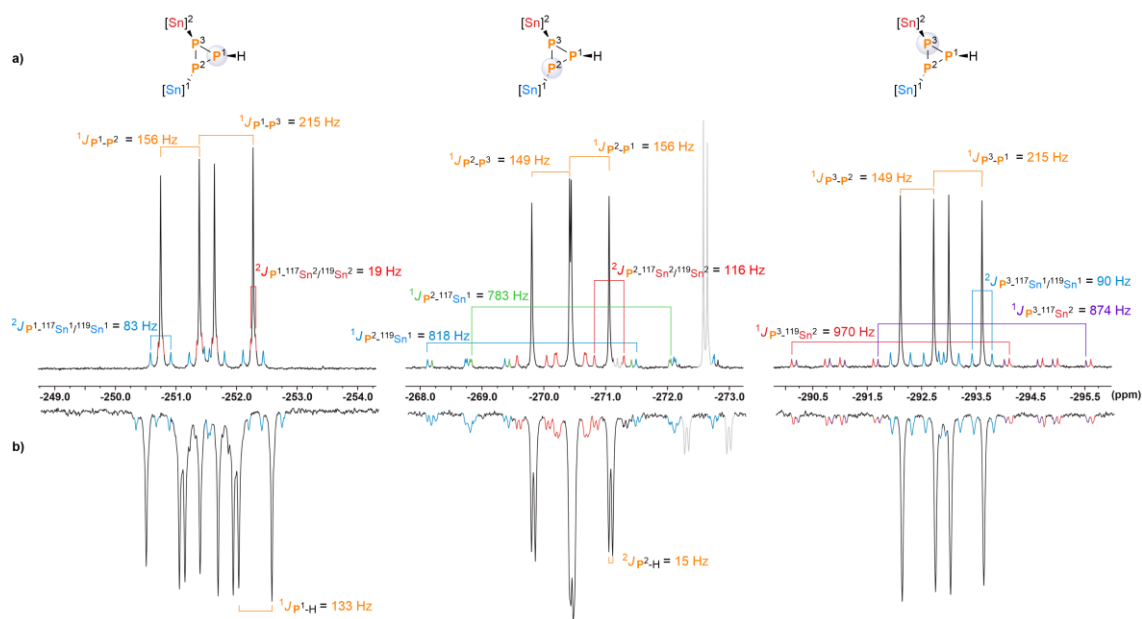


Figure 4.55: (a) $^{31}\text{P}\{^1\text{H}\}$ and (b) ^{31}P NMR resonances of **3** ($[\text{Sn}]_2\text{P}_3\text{H}$), as observed during *in situ* experiments. $[\text{Sn}] = \text{TerSnMe}_2$.

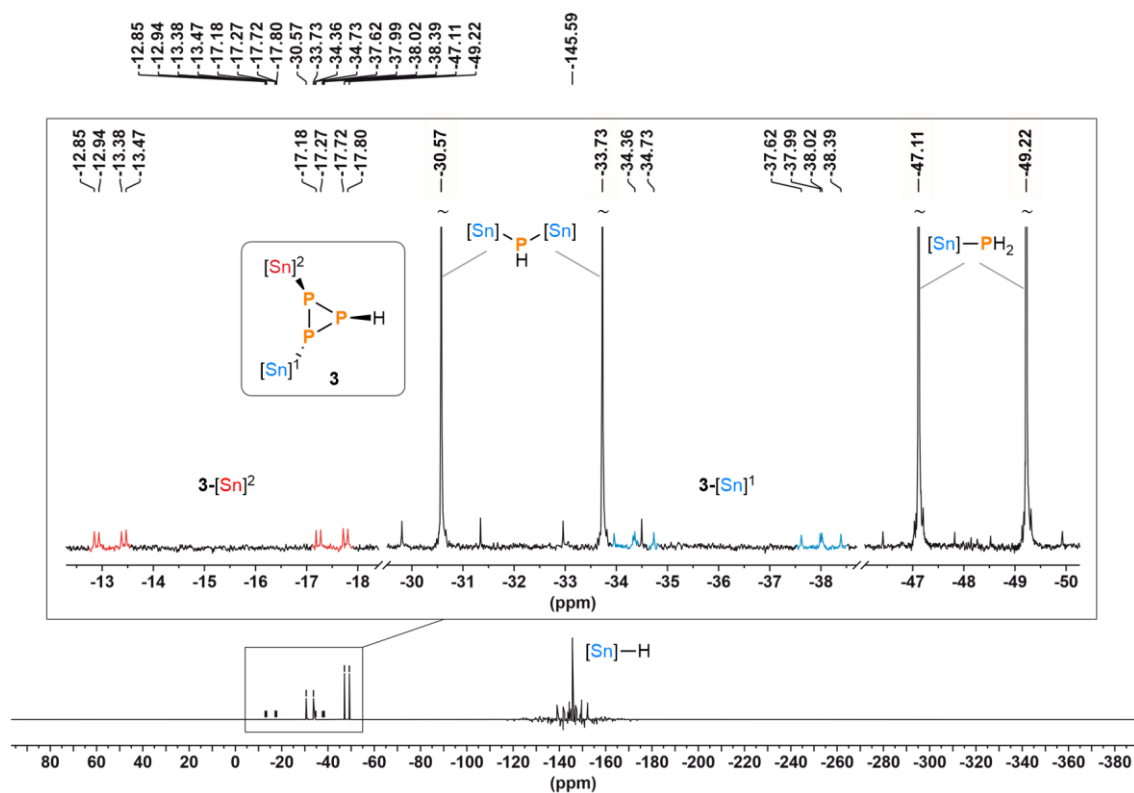


Figure 4.56: $^{119}\text{Sn}\{^1\text{H}\}$ NMR resonances of **3** ($[\text{Sn}]_2\text{P}_3\text{H}$), as observed during *in situ* experiments. $[\text{Sn}] = \text{TerSnMe}_2$. The ^{119}Sn -NMR signal of $[\text{Sn}]\text{H}$ is strongly distorted due to artifacts from proton decoupling. Peaks marked with $\sim$ have been truncated for the sake of clarity.

These structural assignments were further confirmed by DFT calculations (see Section 4.8.4.3), which were also used as the basis for distinguishing between **1** and **2** (although this should be viewed as a tentative assignment only).

The evolution of ^{31}P speciation in the in-situ experiment is shown in Figure 4.57, below. P_4 has an unusually long T_1 relaxation time (*ca.* 40 s). However, to avoid undesirably long acquisition times, this experiment used a D_1 delay of just 2.0 s between scans. As a result, the P_4 concentration is underestimated by these measurements, leading to an apparent increase in overall integral intensity as P_4 is converted into other species.

It can be seen qualitatively that formation of $[\text{Sn}]\text{PH}_2$ begins immediately. Similarly, **3** appears to form immediately before plateauing, as expected for an intermediate. In contrast, formation of $[\text{Sn}]_2\text{PH}$ seems to lag behind formation of $[\text{Sn}]\text{PH}_2$ by an amount that appears fixed once **3** reaches its plateau (notably, a fixed difference rather than a fixed *ratio*). Formation of **1** and **2** also appears to plateau, albeit more slowly than for **3**, which would be consistent with **1** and **2** being downstream intermediates from **3**.

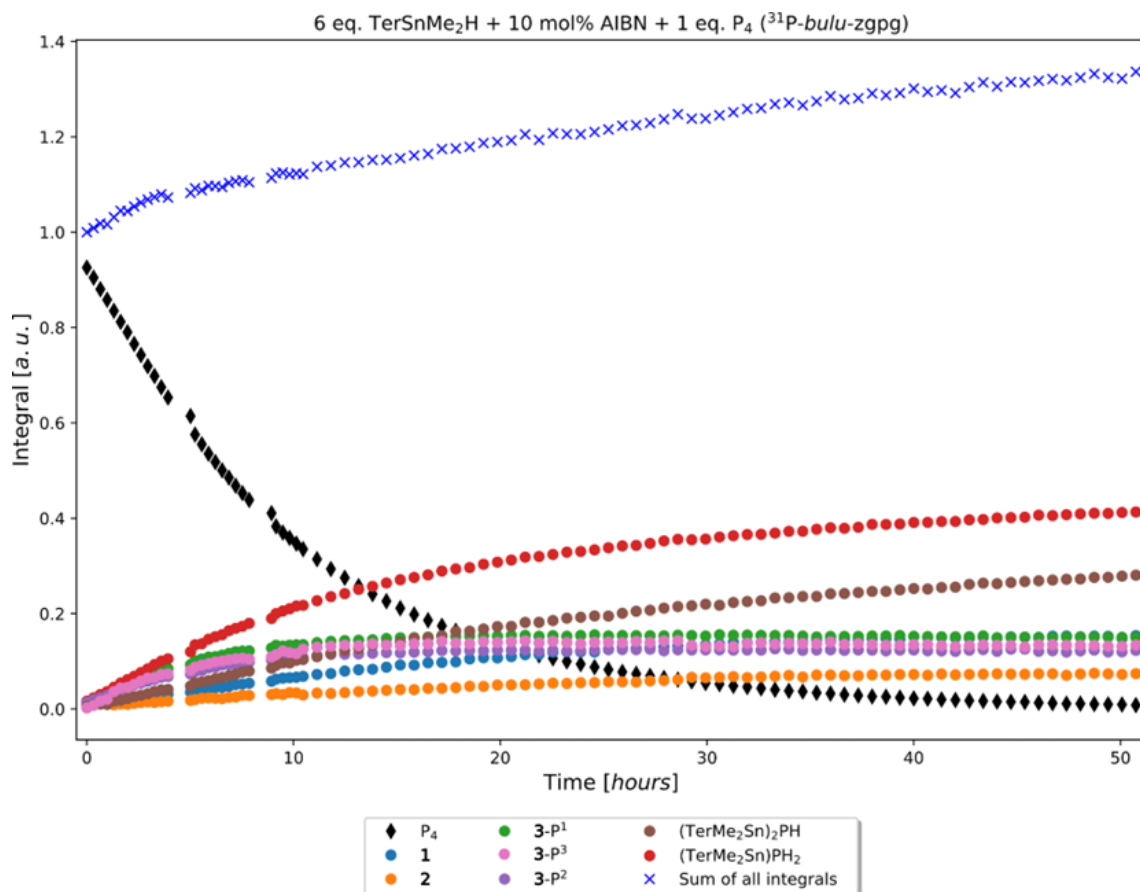


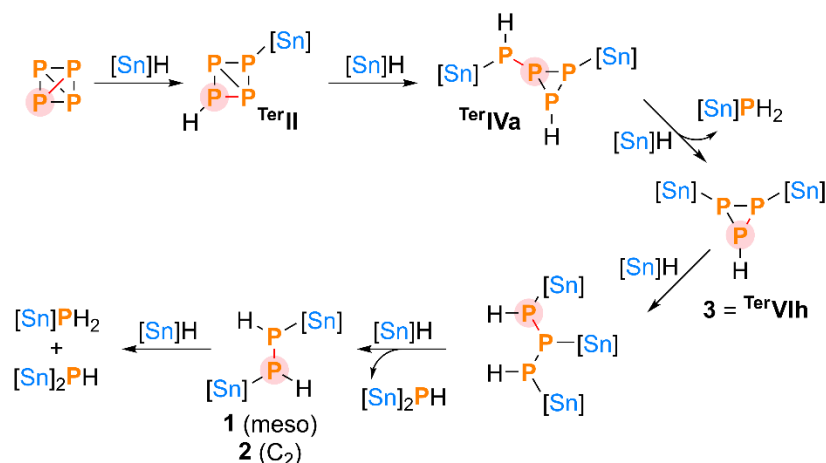
Figure 4.57: Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. $\text{TerSn}(\text{Me})_2\text{H}$ initiated by 10 mol% AIBN at 298 K in C_6D_6 as monitored by *in situ* $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Based on these observations, hydrostannylation of P_4 using $\text{TerSn}(\text{Me})_2\text{H}$ appears to follow the same general mechanism as using smaller $\text{Bu}_3\text{SnH}/\text{Me}_3\text{SnH}$ (Scheme 4.2). However, it is proposed that the increased steric bulk of the more hindered TerSnMe_2 moiety significantly affects the preferred sequence of P–P cleavage steps and biases the overall mechanism towards a single sterically-preferred pathway, in contrast to the “ensemble mechanism” suggested for $\text{Bu}_3\text{SnH}/\text{Me}_3\text{SnH}$. (Note, however, that the continued existence of other, competing pathways whose intermediates remain “invisible” cannot be fully excluded.)

This pathway is summarized in Scheme 4.5. The first P–P addition must still furnish the butterfly-type structure **TerII**, and the second is expected to occur without any change in regioselectivity since the (modest) preference for **IIIa’/IVa** calculated for Me_3SnH already keeps the two R_3Sn moieties as separated as possible (and, notably, much further apart than in **IIIb’/IVb**, the closest kinetic competitor). This would give **TerIVa**. Based on the experimental

4 Unravelling White Phosphorus

observation of **3** (= **TerVIh**) as an intermediate, the third addition is proposed to occur at the *exo* P–P bond of **TerIV**. This is a divergence with the mechanism calculated for Me₃SnH, but attack on the unstannylated P atom (trans to the existing ring-bound [Sn] group) would plausibly help to minimize steric clash. The fourth addition is then presumed to occur at the least hindered position on the *cyclo*-P₃ ring (PH). Similarly, the fifth addition is proposed to occur at one of the less hindered, terminal positions of the P₃ chain (generating the observed symmetrical isomers **1** and **2**). The final addition then has only one possible regiochemical outcome. Notably, this pathway readily accounts for immediate formation of [Sn]PH₂ and an initial observable intermediate **3**, followed by further transformation of **3** into [Sn]PH₂ + 2 [Sn]₂PH, via downstream intermediate **1** or **2**.



Scheme 4.5: Sequence of P–P cleavage steps proposed to occur preferentially during hydrostannylation of P₄ using TerSn(Me)₂H. [Sn] = TerSnMe₂. Bonds cleaved are highlighted in red.

In situ, under LED irradiation (455 nm)

A reaction solution was prepared by combining P₄ (0.01 mmol, as a stock solution in 124.6 μL C₆D₆) and TerSn(Me)₂H (27.8 mg, 0.06 mmol) in C₆D₆ (0.3 mL) inside a glovebox and transferred into an NMR tube incorporating our apparatus for in situ illumination.^[34] The tube was immediately transferred into a 600 MHz NMR spectrometer and subjected to ³¹P{¹H}-NMR analysis every 15–30 minutes. The resulting reaction profile is shown in Figure 4.11 and below in Figure 4.58.

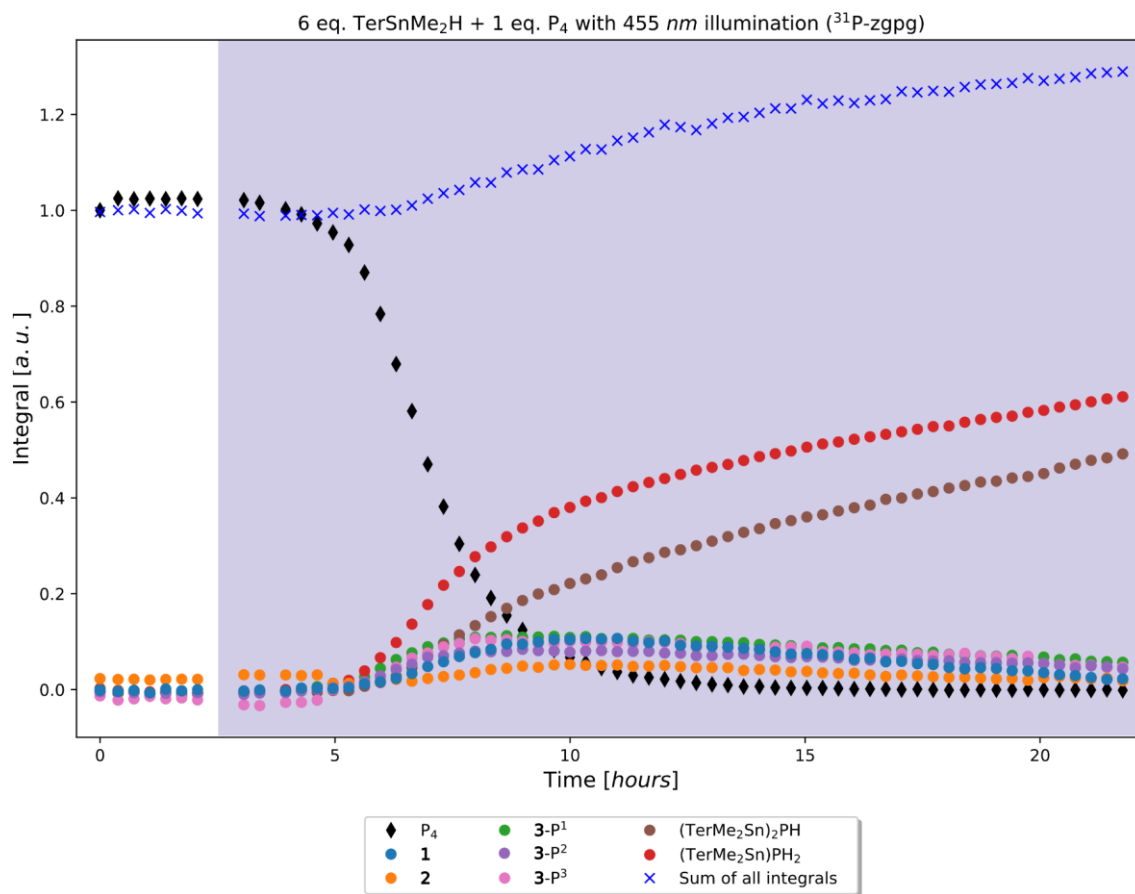


Figure 4.58: Evolution over time of P atom speciation in the reaction between P_4 and 6 eq. $\text{TerSn}(\text{Me})_2\text{H}$ initiated by *in situ* 455 nm LED irradiation (starting after 3 h, illumination period indicated by blue shading) in C_6D_6 at room temperature.

4.8.4.2.10 $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$

Ex situ, under LED irradiation (455 nm)

To a 10 mL, flat-bottomed, stoppered tube were added C_6D_6 (500 μL), P_4 (0.005 mmol, as a stock solution in 62.3 μL C_6D_6), $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ (15.6 mg, 0.03 mmol). The tube was sealed, placed in a water-cooled block to maintain near-ambient temperature, and irradiated with blue light (455 nm (± 15 nm), 3.2 V, 700 mA, Osram OSOLON SSL 80) for 24 hours. The resulting mixture was analyzed by $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P -NMR spectroscopy, as shown in Figures 4.59, and 4.60, below.

4 Unravelling White Phosphorus

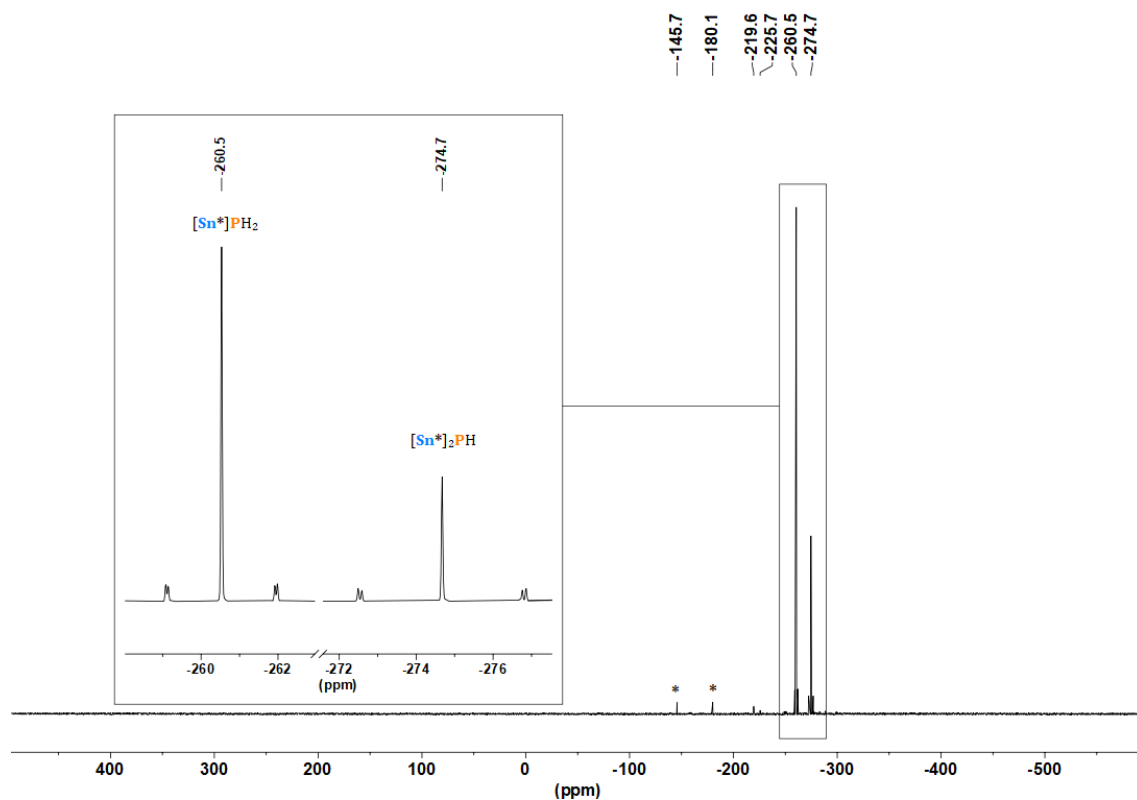


Figure 4.59: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the *ex situ* reaction of P_4 (0.005 mmol) with $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ (0.03 mmol) and AIBN (0.0005 mmol) in C_6D_6 , and driven by 455 nm LED irradiation for 24 h. The $[\text{Sn}^*] = \text{Ter}^*\text{Sn}(\text{Me})_2$. *marks minor, unknown side products.

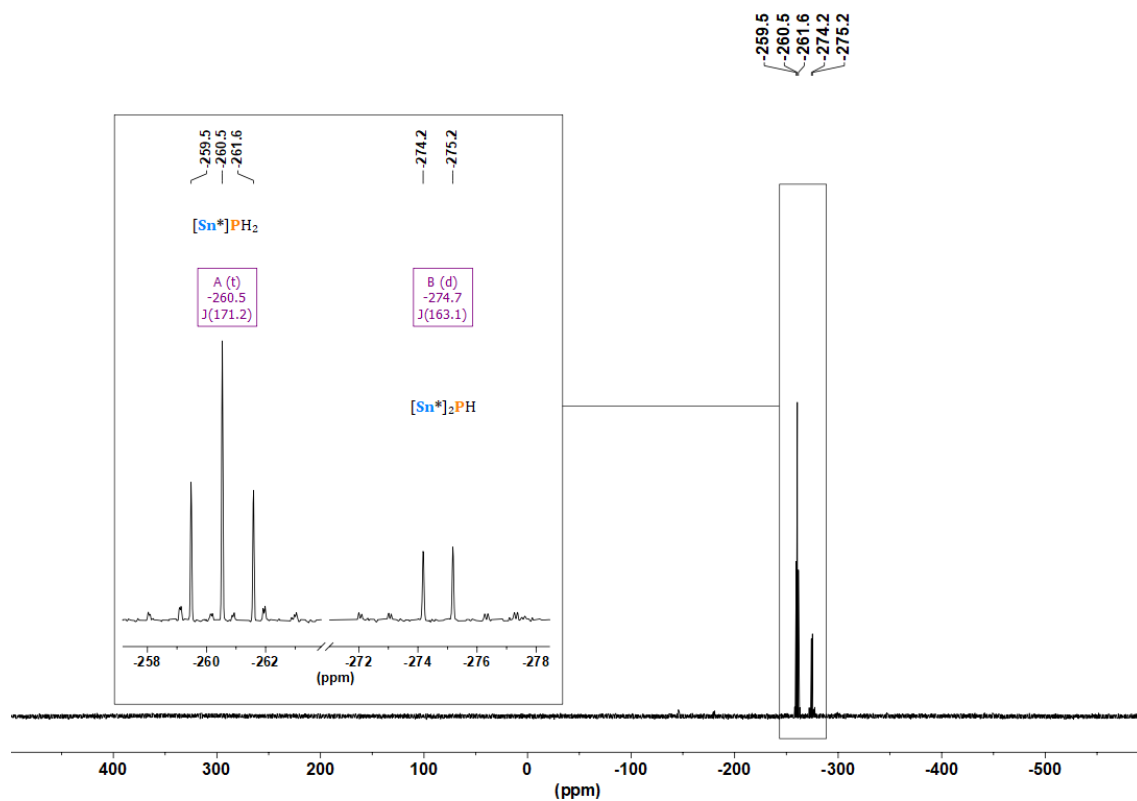


Figure 4.60: ^{31}P NMR spectrum for the *ex situ* reaction of P_4 (0.005 mmol) with $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ (0.03 mmol) and AIBN (0.0005 mmol) in C_6D_6 , and driven by 455 nm LED irradiation for 24 h. The $[\text{Sn}^*] = \text{Ter}^*\text{Sn}(\text{Me})_2$.

Ex situ, with AIBN

To a 10 mL, flat-bottomed, stoppered tube were added C_6D_6 (500 μL), P_4 (0.005 mmol, as a stock solution in 62.3 μL C_6D_6), $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ (15.6 mg, 0.03 mmol) and AIBN (0.0005 mmol, as a stock solution in 6.5 μL C_6D_6). The tube was sealed, wrapped in Al foil to exclude light, and heated to 60 $^\circ\text{C}$ for 24 hours. The resulting mixture was analyzed by $^{31}\text{P}\{^1\text{H}\}$, and ^{31}P -NMR spectroscopy, as shown in Figures 4.61 and 4.62, below.

In addition to the expected products $[\text{Sn}^*]\text{PH}_2$ and $[\text{Sn}^*]_2\text{PH}$ ($[\text{Sn}^*] = \text{Ter}^*\text{Sn}(\text{Me})_2$), a major set of three coupled doublets of doublets was observed, as were two more minor singlets. Based on the similar observations made using $\text{TerSn}(\text{Me})_2$ these species were assigned as **1***, **2*** and **3***.

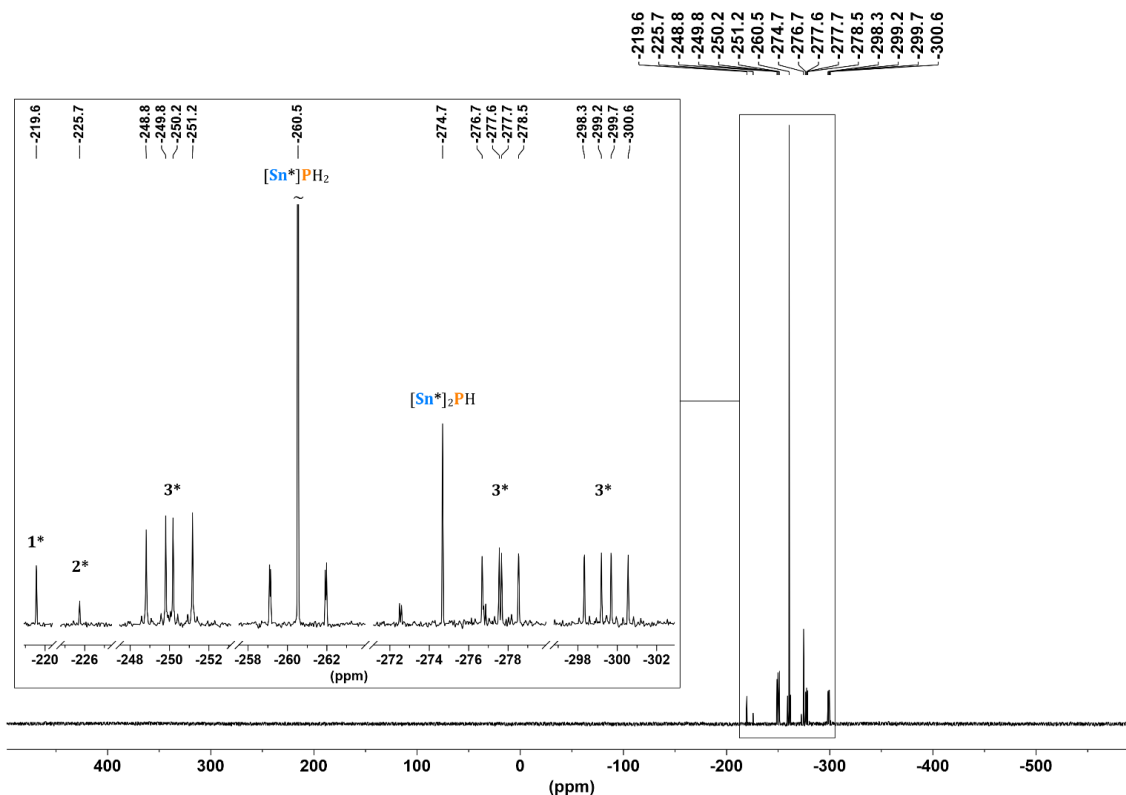


Figure 4.61: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the *ex situ* reaction of P_4 (0.005 mmol) with $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ (0.03 mmol) and AIBN (0.0005 mmol) in C_6D_6 , heated to 60 $^\circ\text{C}$ for 24 h in the dark. $[\text{Sn}^*] = \text{Ter}^*\text{Sn}(\text{Me})_2$. Peak marked with ~ has been truncated for the sake of clarity.

4 Unravelling White Phosphorus

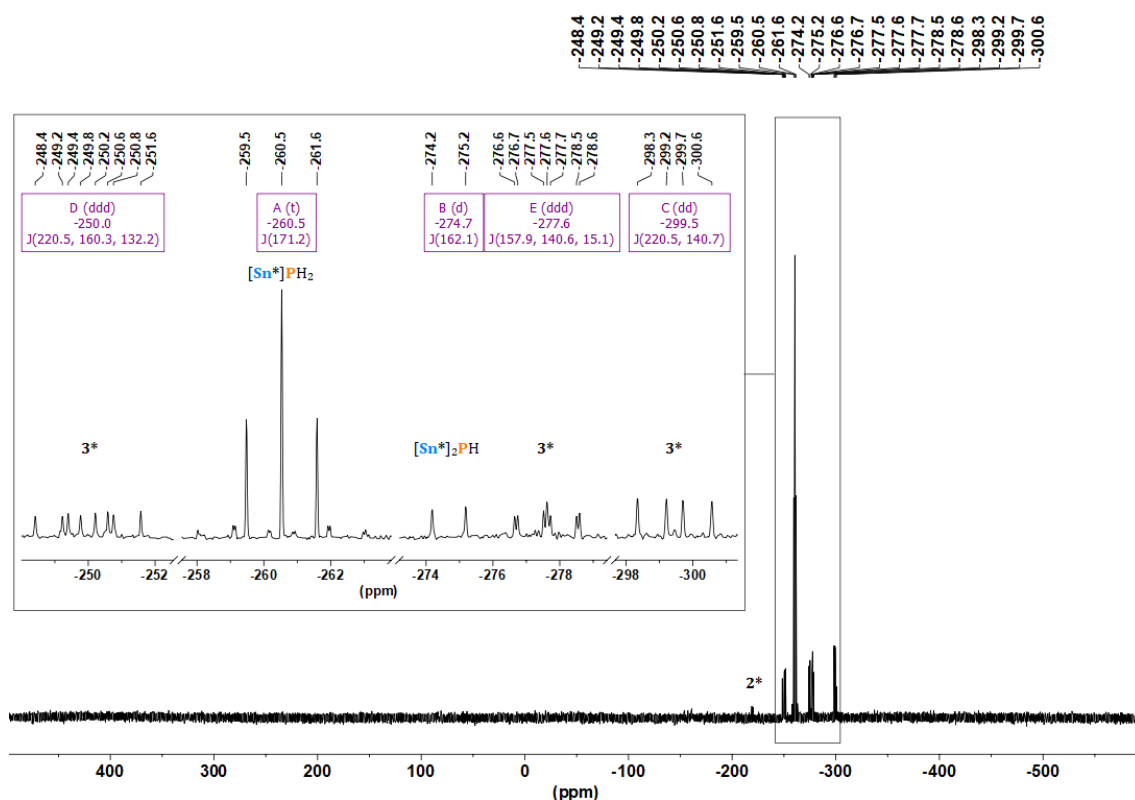


Figure 4.62: ^{31}P NMR spectrum for the *ex situ* reaction of P_4 (0.005 mmol) with $\text{Ter}^*\text{Sn}(\text{Me})_2\text{H}$ (0.03 mmol) and AIBN (0.0005 mmol) in C_6D_6 , heated to 60 °C for 24 h in the dark. $[\text{Sn}^*] = \text{Ter}^*\text{Sn}(\text{Me})_2$.

In situ, with AIBN

This reaction was prepared in the same manner as the *ex-situ* experiment described immediately above, but was transferred to a screw-cap NMR tube and monitored by *in situ* $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy (for general details, see Section 4.8.2.1) at room temperature (Figure 4.63).

Under these lower temperature conditions only formation of $[\text{Sn}^*]\text{PH}_2$ and 3^* was observed during the timeframe of the experiment, with neither $[\text{Sn}^*]_2\text{PH}$ nor $1^*/2^*$ being detected. This can be contrasted with the results using $\text{TerSn}(\text{Me})_2\text{H}$ where the equivalent species *were* observed at room temperature, highlighting the enhanced steric impact of the slightly larger Ter^* group, which further hinders reactivity.

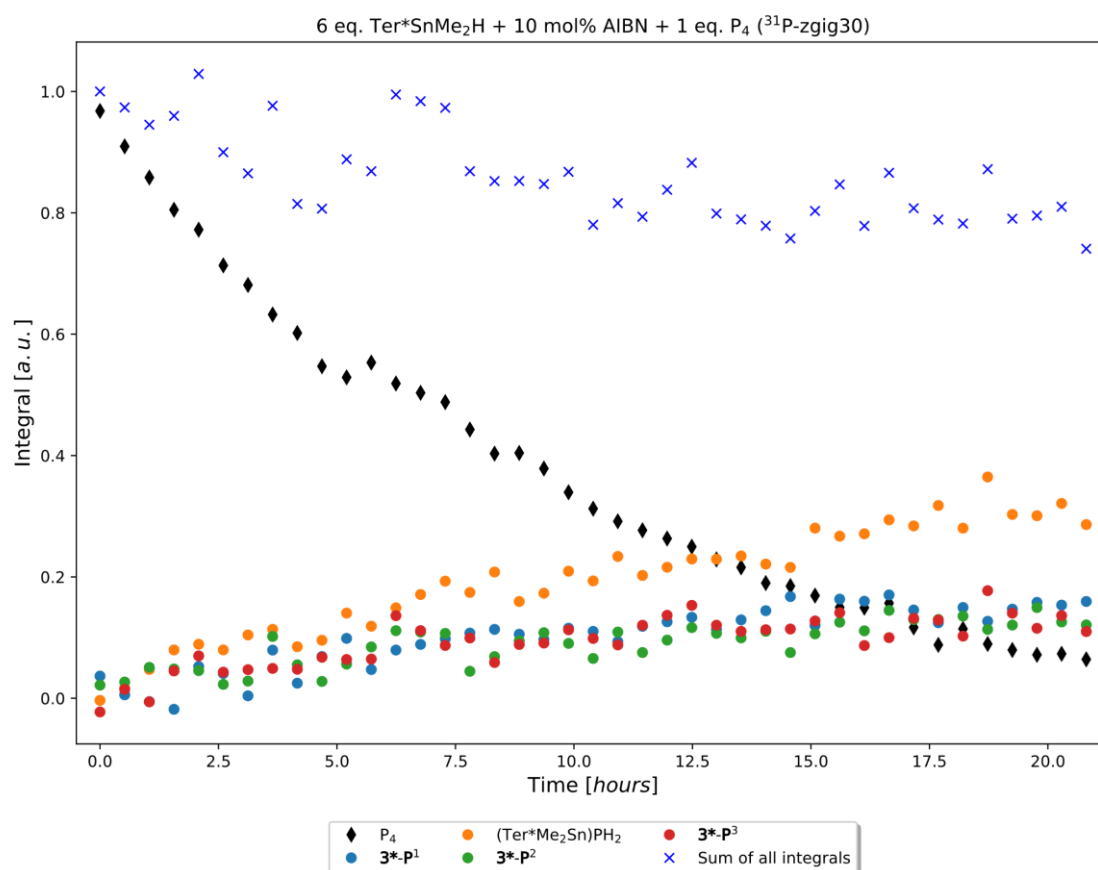


Figure 4.63: Evolution over time of P atom speciation in the reaction between P₄ and 6 eq. Ter*Sn(Me)₂H initiated by 10 mol% AIBN at 298 K in C₆D₆ as monitored by *in situ* ³¹P{¹H} NMR spectroscopy.

4.8.4.2.11 (Fluid)Sn(Me)₂H

To a 10 mL, flat-bottomed, stoppered tube were added C₆D₆ (600 μL), P₄ (0.005 mmol, as a stock solution in 62.3 μL C₆D₆), (Fluid)Sn(Me)₂H (19.9 mg, 0.03 mmol) and AIBN (0.0025 mmol, as a stock solution in 32.2 μL C₆D₆). The tube was sealed, wrapped in Al foil to exclude light, and heated to 60 °C for 4 days. The resulting mixture was analyzed by ³¹P{¹H}-NMR spectroscopy, as shown in Figure 4.64 below.

No appreciable consumption of P₄ was observed. Similar experiments using 455 nm irradiation also led to only minor P₄ consumption.

4 Unravelling White Phosphorus

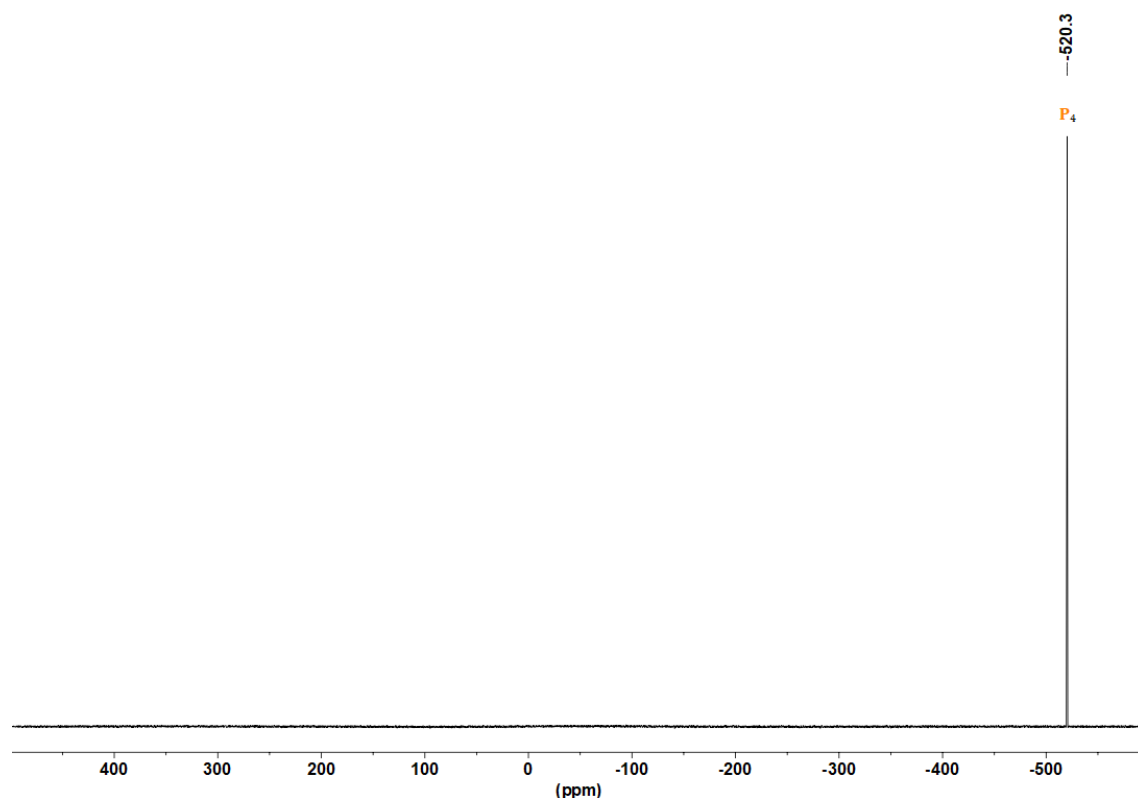


Figure 4.64: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the *ex situ* reaction of P_4 (0.005 mmol) with $(\text{Fluind})\text{Sn}(\text{Me})_2\text{H}$ (0.03 mmol) and AIBN (0.0025 mmol) in C_6D_6 , heated to 60 °C for 4 d in the dark.

4.8.4.2.12 Crystallographic characterization of $[\text{TerSn}(\text{Me})_2]_2\text{PH}$

Single crystal X-ray diffraction data for $[\text{TerSn}(\text{Me})_2]_2\text{PH}$ was recorded on a Rigaku XtaLAB Synergy DW R (DW system, HyPix-Arc 150) diffractometer with microfocus Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). The crystal was selected under mineral oil, mounted on a micromount loop and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data processing, reduction and multi-scan absorption correction^[47,48] was performed with the program CrysAlisPro (Rigaku Oxford Diffraction, 2021). Using Olex2,^[45] the structure was solved with the SHELXT^[44a] structure solution program using Intrinsic Phasing and refined using Olex2.refine.^[49] All non-hydrogen atoms were refined using anisotropic displacement parameters. All hydrogen atoms but the P bound hydrogen atom were located in idealized positions and refined isotropically with a riding model. The P bound hydrogen atom was located from the electron density map and had its position and isotropic displacement parameter refined freely. The disorder of the P bound hydrogen atom was treated with a geometrical restraint. To compute the non-spherical atomic form factors, the program NoSpherA2^[50] was used and the wavefunction calculations were performed with ORCA 5.0^[36,51-53] (on the R2SCAN/x2c-TZVP level of theory).^[54,55] Crystallographic data for this structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of this data can be obtained free of charge on quoting the depository number: 2315067; E-mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>.

Crystal and refinement data are collected in Table 4.3, and the structure itself is illustrated in Figure 4.65.

Table 4.3: Crystal data and structure refinement of [TerSn(Me)₂]₂PH.

	[TerSn(Me) ₂] ₂ PH
Formula	C ₅₂ H ₆₃ PSn ₂
Formula weight, g mol ⁻¹	956.474
Crystal system	123.00(10)
Crystal size, mm	monoclinic
Space group	P2 ₁ /n
<i>a</i> , Å	8.36845(3)
<i>b</i> , Å	21.44921(9)
<i>c</i> , Å	26.28771(12)
α , °	90
β , °	90.5395(4)
γ , °	90
<i>V</i> , Å ³	4718.35(3)
<i>Z</i>	4
ρ_{calcd} , Mg m ⁻³	1.346
μ (Mo <i>K</i> α), mm ⁻¹	8.971
<i>F</i> (000)	1968.4
2θ range, deg	0.462 $\times$ 0.13 $\times$ 0.091
Index ranges	Cu <i>K</i> α (λ = 1.54184) 5.32 to 150.36 -8 $\leq h \leq$ 10, -26 $\leq k \leq$ 26, -32 $\leq l \leq$ 32
No. of reflns collected	131932
No. indep. Reflns	9583 [<i>R</i> _{int} = 0.0258, <i>R</i> _{sigma} = 0.0091]
No. refined params	9583/2/692
GooF (<i>F</i> ²)	1.055
<i>R</i> ₁ (<i>F</i>) (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0167, <i>wR</i> ₂ = 0.0414
<i>wR</i> ₂ (<i>F</i> ²) (all data)	<i>R</i> ₁ = 0.0170, <i>wR</i> ₂ = 0.0416
Largest diff peak/hole, e Å ⁻³	0.49/-0.49
CCDC number	2315067

4 Unravelling White Phosphorus

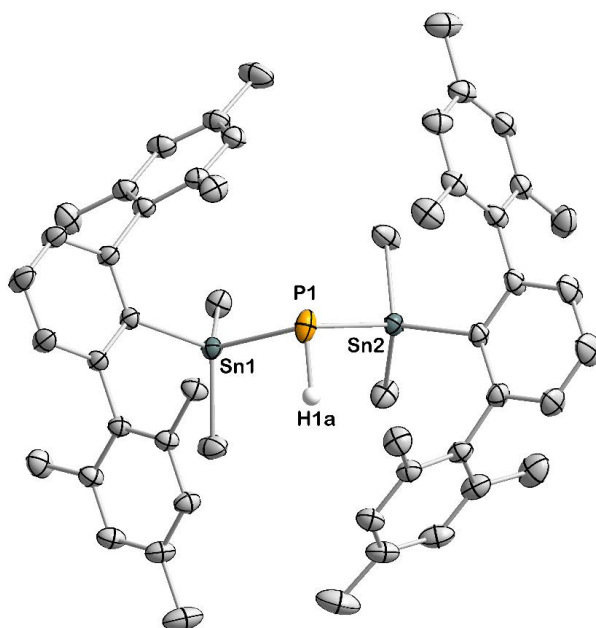


Figure 4.65: Single-crystal XRD structure of $[\text{TerSn}(\text{Me})_2]_2\text{PH}$. Thermal ellipsoids are shown at 50%. H atoms, except for the one bound directly to P, are omitted and only one position of the disordered P-bound H atom is shown for clarity. C atoms are shown in grey, H in white, P in orange, and Sn in dark grey.

4.8.4.3 Computational studies on NMR parameters of H/Sn substituted phosphines

The molecules were modeled in Avogadro 4.2.1, geometry optimization carried out with the ORCA 5.0.4 software package^[35] using the composite method B97-3c,^[56] which includes dispersion correction. NMR parameters of the optimized structures were calculated using the TPSSH functional^[57] and ZORA-DEF2-TZVPP basis set^[58] for all nuclei except Sn, where the SARC-ZORA-TZVPP basis set^[59] was used. Chemical shifts and J -coupling constants were calculated for the Sn, P and P- H nuclei of interest.

The conversion of ^{31}P absolute chemical shieldings σ_i to chemical shifts δ_i was done using linear regression referencing according to

$$\delta_i = A \cdot \sigma_i + B, \quad A = -0.7351, \quad B = 179.62 \text{ ppm}$$

with A and B being empirical values to account for systematic errors of the geometry optimization and NMR calculation method.

Using these methods, NMR parameters were calculated both for compounds **1-3** and for a selection of related H/Sn-substituted phosphines whose NMR parameters are known from experiment (all experimental data has been collected within this project), with the latter being used to validate the computational methodology. The results of these calculations are summarized in Table 4.4. After simple linear regression, a good correlation of calculated and experimental ^{31}P chemical shifts $\delta_{31\text{P}}$ for the set of compounds can be obtained. Deviations from the experimental values are intrinsically present, since no solvent effects were included into the calculations, thus chemical shifts are not scaling 1:1 linearly with the observed shift values. To the best of our knowledge, a calculation scheme like this has not been used previously to obtain $^1J(^{31}\text{P}-^{119}\text{Sn})$ coupling constants. Scaling according to the equation above eliminates this systematic error and allows for a quick evaluation of whether a measured ^{31}P chemical shift will fit to a proposed PSn-Cluster under similar conditions.

The calculated values for $^1J(^{31}\text{P}-^{119}\text{Sn})$ accord reasonably well with the experimentally observed scalar couplings. This again corroborates the structural assignments and may be useful to further evaluate Sn-P cluster structures with fast computational methods.

Table 4.4: Summary of observed and calculated ^{31}P -chemical-shifts and $^1J(^{31}\text{P}-^{119}\text{Sn})$ -coupling constants.

Compound	^{31}P NMR shifts (ppm)		$^1J(^{31}\text{P}-^{119}\text{Sn})$ coupling (Hz)	
	Observed $\delta_{31\text{P}}$	Calculated $\delta_{31\text{P}}$	Observed J	Calculated J
Bu_3SnPH_2	-289	-295	522	587
$(\text{Bu}_3\text{Sn})_2\text{PH}$	-325	-321	730	774
$(\text{Bu}_3\text{Sn})_3\text{P}$	-347	-343	911	943
$(\text{Ph}_3\text{Sn})\text{PH}_2$	-288	-282	545	581
$(\text{Ph}_3\text{Sn})_2\text{PH}$	-315	-331	741	705
$(\text{Ph}_3\text{Sn})_3\text{P}$	-326	-329	884	885
$i\text{Pr}_3\text{SnPH}_2$	-309	-290	589	614
$(i\text{Pr}_3\text{Sn})_2\text{PH}$	-348	-326	834	817
$\text{Ter}(\text{Me})_2\text{SnPH}_2$	-261	-262	470	548
$(\text{Ter}(\text{Me})_2\text{Sn})_2\text{PH}$	-274	-288	705	730
1 $(\text{Ter}(\text{Me})_2\text{Sn})_2\text{P}_2\text{H}_2$ -meso	-220	-218	higher order	/
2 $(\text{Ter}(\text{Me})_2\text{Sn})_2\text{P}_2\text{H}_2$ -C2	-226	-231	higher order	/
3-P¹ -H	-251	-241	No P-Sn bond	/
3-P² -[Sn] ¹	-270	-286	818	901
3-P³ -[Sn] ²	-293	-298	970	1049

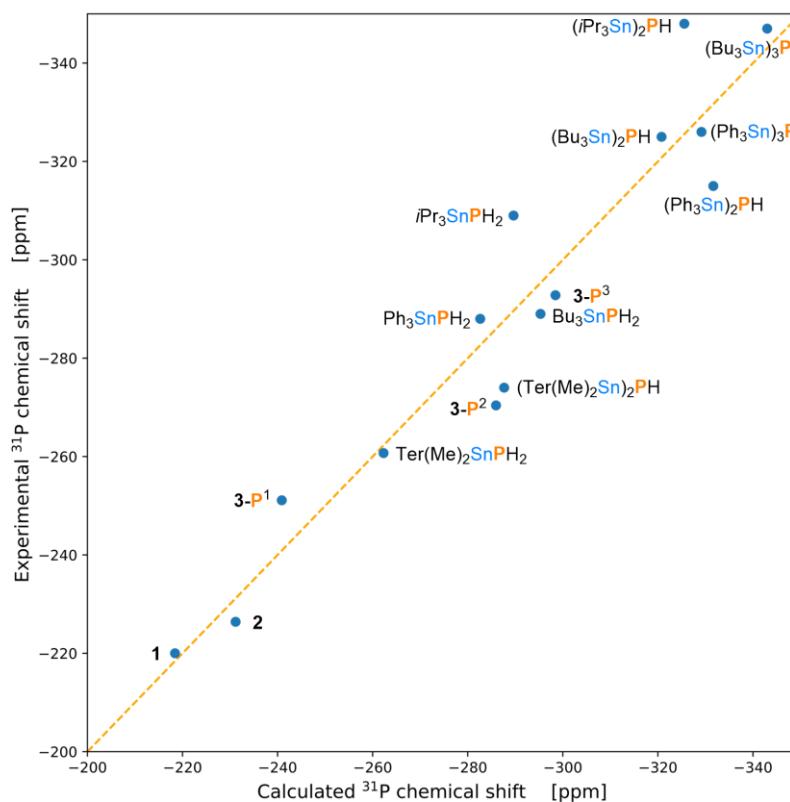


Figure 4.66: Plotted correlation between calculated and experimentally determined ^{31}P NMR chemical shifts.

4 Unravelling White Phosphorus

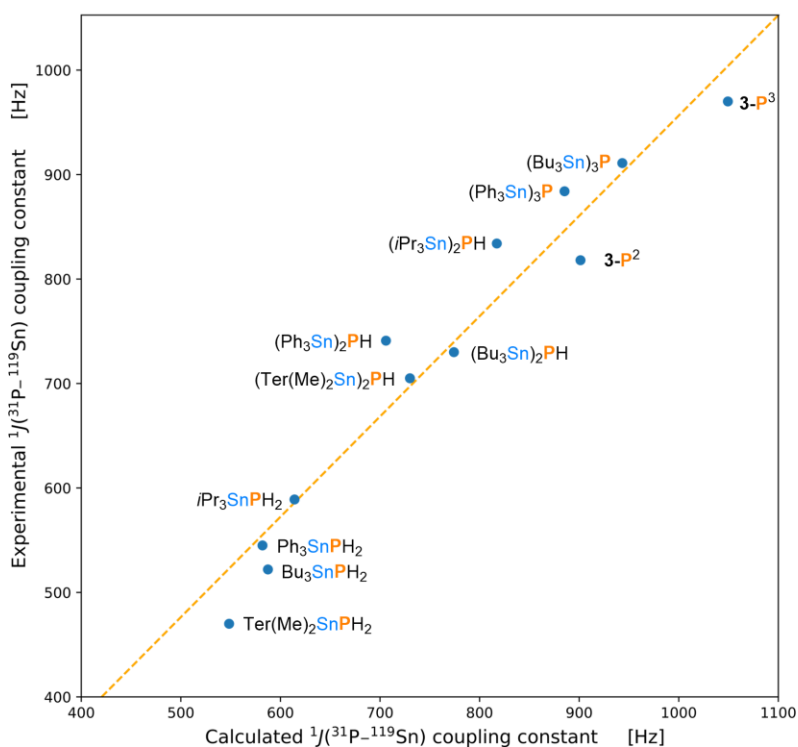


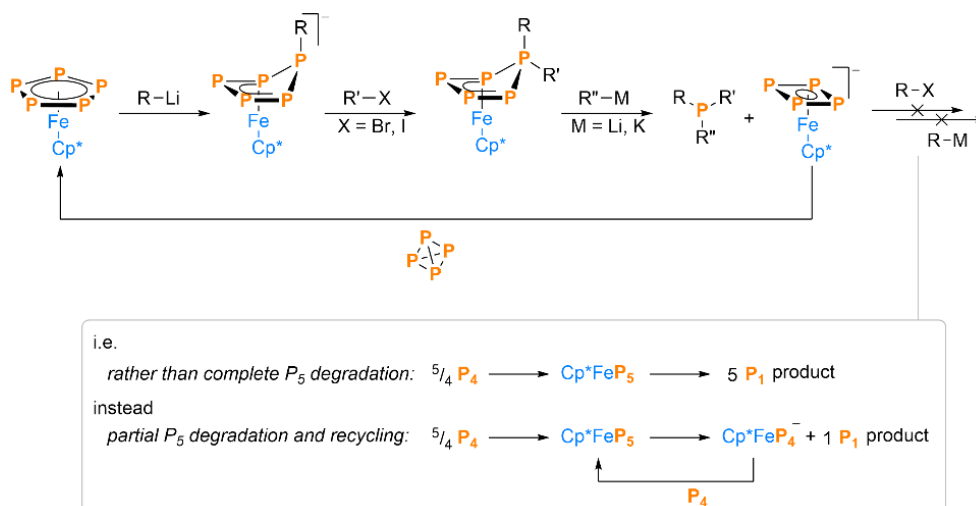
Figure 4.67: Plotted correlation between calculated and experimentally determined $^1J(^{31}\text{P}-^{119}\text{Sn})$ coupling constants.

4.8.5 Discussion of transition metal mediated P_4 functionalization

The divergent reactivity of different transition metal (TM)-bound P_n moieties means that during TM-mediated breakdown of P_4 each of the P atoms and P–P bonds originating from P_4 can end up manifesting very different reactivity, suggesting that it should be difficult to functionalize them with a common set of simple, mutually-compatible reagents. This presents a potentially significant problem for attempts at inner-sphere TM-mediated breakdown of P_4 into P_1 products since, for example, functionalization of a P_4 intermediate may lead to formation of a P_3 intermediate with very dissimilar reactivity.

As such, it is interesting to note that Scheer *et al.* have recently reported the direct transformation of P_4 into phosphines $\text{RR}'\text{R}''\text{P}$ *via* formation of the TM complex Cp^*FeP_5 (Scheme 4.6).^[6g] This shows that the above problem does not fully preclude the development of effective procedures for TM-mediated P_4 conversion, and it is therefore interesting to consider *how* this system manages to succeed, despite this apparent obstacle.

In this case, success can likely be attributed to $\text{RR}'\text{R}''\text{P}$ formation occurring entirely at a single P atom located on a single P_5 moiety. Once the product has been excised from the P_5 ring the remaining *cyclo*- P_4 moiety is not functionalized further, but rather converted back to the original P_5 ring by reaction with fresh P_4 . Thus the diversity of $\text{TM}\cdot\text{P}_n$ moieties involved is helpfully kept to a minimum. It may also help that functionalization of the P_5 moiety is achieved sequentially using otherwise likely-incompatible reagents, rather than having all P–P cleavage steps happen ‘in one go’.



Scheme 4.6: Functionalization of Cp^*FeP_5 recently reported by Scheer *et al.*^[6g]

4.8.6 References for Supplementary Information

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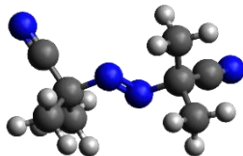
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4.8.7 Cartesian Coordinates of Optimized Structures

All values are given in Å (1 Å = 10⁻¹⁰ m)

4.8.7.1 Initiation

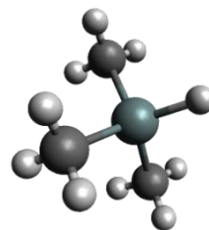
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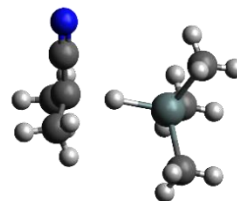
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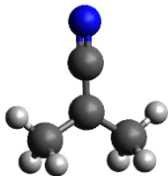
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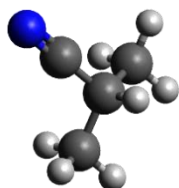


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0 2			
C	-7.16243138854857	1.06559324867526	0.07449569382908
C	-5.7555596606522	0.58286185830772	0.05074217055648
H	-7.35395047960832	1.72925610121400	-0.77642839525333
H	-7.34940794083417	1.65567232996323	0.97922931984843
H	-7.87841114969421	0.24589109230958	0.04322899501803
C	-4.63959117561663	1.56669575730585	0.06249393628400
H	-4.69905473991686	2.22365719275432	-0.81300038479448
H	-3.66493352667547	1.08141727752095	0.06409192279180
H	-4.70847890827036	2.21356613651884	0.94447382619041
C	-5.48597070315845	-0.77519817431721	0.01664384432620
N	-5.25759032161170	-1.91680282025255	-0.01799092879663

4 Unravelling White Phosphorus

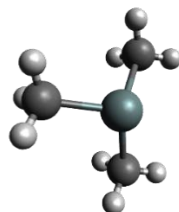
HC(CN)Me₂



E = -211.13175702 Eh H = -211.09613607 Eh

0 1			
C	-7.14359627165181	1.05970702855674	-0.04532441047755
C	-5.75205906106006	0.55802443843765	-0.42644296128321
H	-7.33852210619739	2.01127227039293	-0.54337220113809
H	-7.21347853315789	1.21413609844946	1.03294727001623
H	-7.91646858250299	0.34880388920177	-0.33927478054455
C	-4.65552081782110	1.55347002596461	-0.05229711729354
H	-4.83385449793600	2.50239486530725	-0.56134532662867
H	-3.67011519883375	1.18526376492804	-0.33943324022100
H	-4.6526707773814	1.73538684168632	1.02402323378706
C	-5.49345770807070	-0.73909943664365	0.19253968522003
N	-5.28562521479336	-1.75674242342320	0.68595310174594
H	-5.72191123023679	0.39212263714207	-1.50930325318265

Me₃Sn⁺



E = -333.83773926 Eh H = -333.79419951 Eh

0 2			
Sn	-0.04181811914409	-0.11771975225806	2.18561965993890
C	0.01624841845516	-0.03766963620385	0.02408622563928
C	1.95707088074064	-0.56728058815974	2.88224279632402
C	-0.55523065397075	1.85612096675477	2.90912231806715
H	0.34106820462594	-0.99425367785191	-0.38489706900594
H	0.72681657543460	0.73715997838795	-0.27485231550035
H	-0.96671998773747	0.20757913395128	-0.37752448186928
H	-1.54006851800091	2.15245397070418	2.54845420629491
H	0.18832079417249	2.56651605051999	2.53892030643005
H	-0.55323100757316	1.87485945633416	3.99882489447740
H	2.27918565815780	-1.54435600176422	2.52254509139057
H	1.99099649044407	-0.55860348753939	3.97155273552864
H	2.63847126439568	0.19588358712484	2.49769563228466

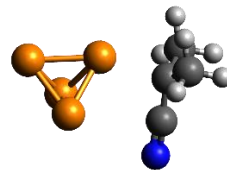
P₄



E = -1365.03900477 Eh

0 1			
P	-8.63724066817835	1.73405756013613	0.95356065420993
P	-7.30344057381550	1.81815961948766	-0.77432824026063
P	-6.96619533814420	0.33677370507047	0.79516442354124
P	-8.68358341986195	0.14155911530574	-0.53970683749054

TS(*C(CN)Me₂→*P₄C(CN)Me₂)

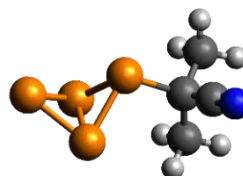


E = -1575.51660155 Eh

im. freq. = 282.91 *i*

0 2			
P	-9.18339464947762	3.26921534550439	0.39885091559647
P	-7.89665556026854	1.39907387994771	0.09926708701424
P	-7.47683203644588	2.85712317029539	1.68360163984355
P	-9.25993916443638	1.61111959666613	1.80511390061052
N	-9.79884369142118	4.43464597297972	3.92737967181232
C	-10.03885756473450	4.69168837132315	2.82489250889223
H	-8.57702758581726	6.24263320612897	1.21816469246345
C	-10.30312718651070	4.96800585615511	1.46037255112464
C	-9.61994783829653	6.18844881602649	0.90591818957018
H	-10.12784776108770	7.09499071380136	1.25423062019150
H	-12.11294445417590	3.79042306853096	1.39740028081834
C	-11.72079596462240	4.73262217256001	1.01454114102353
H	-9.66058257520279	6.18052088290283	-0.18547228768262
H	-12.3672563084730	5.54151296678704	1.37340525256139
H	-11.77487766365250	4.71938598033892	-0.07619616384001

*P₄C(CN)Me₂

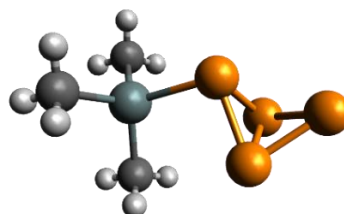


E = -1575.52083035 Eh

0 2			
C	-7.08735576209223	1.16879404201634	0.65087741087312
C	-5.67297603039902	0.64300391834781	0.86258124596311
H	-7.27002189685421	1.31641646435180	-0.41641475512892
H	-7.21150757785303	2.12905852619275	1.15462129406168
H	-7.84001914041938	0.47685784580870	1.03003678327340
C	-4.62659314218273	1.62413666980242	0.32359985246687
H	-4.77147961891649	1.77917079394561	-0.74789107219492
H	-3.61170854679090	1.25610511017752	0.48217471730177
H	-4.73219050809867	2.58459020287984	0.83175476107557
C	-5.52354245165176	-0.64849110212585	0.20955274959073
N	-5.40365712907633	-1.67750727643042	-0.29271855801529
P	-7.06778861321436	-0.17722569833279	3.68664400561671
P	-5.90869842830933	0.44472436510758	5.42709481506997
P	-6.23871874774672	1.86107173782412	3.80136660142719
P	-5.15694240639482	0.28716440043456	2.68413014861900

4.8.7.2 First P–P cleavage

I⁺



E = -1698.87329909 Eh H = -1698.81488688 Eh

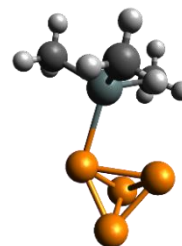
0 2			
P	-1.95523966599795	-1.67253689686902	2.74605314937196
P	-4.46913481145529	-1.75104588972784	3.78802426030406
P	-3.64964678899596	-0.29707612212079	2.37015468200861
P	-2.81542757308502	-0.43707801362512	4.36931651554389
Sn	-0.07502888407850	-0.06570514227185	2.04485724530151
C	0.00879311068946	-0.06560143856404	-0.09861950975743
C	1.74654435191822	-0.82572726558248	2.88612211424798

Unravelling White Phosphorus 4

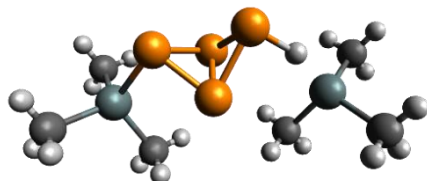
C	-0.48175123769149	1.90665066206422	2.77896956639695
H	0.83447392423197	0.56515094414195	-0.43235579842360
H	-0.92378221563992	0.32562000100411	-0.50521193561982
H	0.16242055058868	-1.07789405977524	-0.47240897596584
H	-1.46724553645603	2.23853193473814	2.45265525883124
H	0.27268975288791	2.59356365941020	2.39124909644244
H	-0.44879161676758	1.91659140180575	3.86818390953441
H	2.58342993755751	-0.19270279932788	2.58655002116582
H	1.92775103073342	-1.84183155510255	2.53547485654537
H	1.67954567136235	-0.83277942019756	3.97409554407247

H	5.11858302117921	2.03432132301868	4.44554633190407
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TS(P₄→^{endo}I[•])



TS(I[•]→II)



E = -2033.30911684 Eh

im. freq. = 771.71 *i*

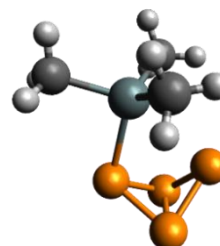
0 2			
H	0.06423181035575	-1.73612866467063	3.30241068825383
Sn	-0.20889869110693	-0.00204390311150	2.34204877368218
P	2.14953408882840	-2.62985782909297	6.79502752708436
P	0.57377560193294	-2.87782050273250	4.42838091071761
P	2.36010497775788	-1.65044831208672	4.81973330963943
P	0.56817678001534	-1.31073628529748	5.97583112593764
Sn	3.39345664481709	-0.82075258000473	8.10313762842307
C	2.67156601350831	1.12652783338235	7.55877446665433
C	5.47989741859054	-0.98037588984864	7.62234351453257
C	3.07403098652855	-1.16847994766599	10.19684985254100
H	2.73970662199042	1.27021447539667	6.48028876189557
H	3.27835294742562	1.88380077580779	8.05849278734947
H	1.63207068845080	1.24445352049963	7.86452605220644
H	3.62390732459128	-0.42954613041045	10.78181568131370
H	3.41987858782449	-2.16513919731435	10.47169273413650
H	2.01253664912419	-1.08633604478284	10.43152999218820
H	5.61866341980464	-0.85782730354501	6.54786373461452
H	5.86631657617706	-1.95540985461302	7.91942018339593
H	6.04039977564852	-0.20266808123123	8.14353225675101
C	0.77437304305083	1.62247735157282	3.36050967235314
H	1.84839295782703	1.44193547604309	3.39601127026933
H	0.39741716102985	1.70688404163896	4.37938120924122
H	0.58276377781308	2.55543478466263	2.82571809278882
C	0.59614159731586	-0.18734197178691	0.35166637906147
H	0.09581557022091	-0.99121866101514	-0.18838513477562
H	1.66415204387254	-0.40067182221209	0.39719213293675
H	0.44509818382991	0.74959369382293	-0.18854866801024
C	-2.32330748212930	0.39805420668573	2.22762646999092
H	-2.74646706000616	0.47819953260103	3.22890791137537
H	-2.83160982266577	-0.40301422413359	1.69076304260614
H	-2.48625819242375	1.33865151344217	1.69739764084497

E = -1698.85266583 Eh

im. freq. = -426.07 *i*

0 2			
P	-1.57480120697798	-1.77046254310728	3.32773860787774
P	-0.43583404017023	-3.38658668505784	1.86555816494630
P	-2.56382806563936	-2.92728581609856	1.76031466196820
P	-1.75996055451919	-3.99998056932073	3.50278421792178
Sn	0.11979233480492	-0.12307434317281	2.15348788415684
C	0.04019206741265	-0.31625045167003	0.01733273193828
C	2.09080134191980	-0.51574669675289	2.89977819731121
C	-0.52138035353784	1.84283819825781	2.76775683764214
H	0.56407874269684	0.52838244205018	-0.43428065483292
H	-0.99473964236641	-0.31546560261065	-0.32393880443456
H	0.51892423153487	-1.24399119474817	-0.29377853101321
H	-1.52082114141880	2.05029290786230	2.38554220771636
H	0.17214337778540	2.58911275753851	2.37514875719156
H	-0.53508473672533	1.90997480662649	3.85575450367283
H	2.79305029133586	0.21046373590877	2.48684170429270
H	2.39933908117814	-1.51957659563192	2.60876560103477
H	2.10108827268671	-0.44046435007314	3.98722391260984

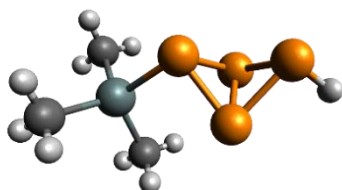
endo I[•]



E = -1698.87441458 Eh

0 2			
P	-1.95593742446611	-1.41141655072623	3.20357813874249
P	-0.25436499289183	-3.30228643246608	1.87971584717959
P	-2.42830487280259	-3.17331076716201	1.96766050559187
P	-1.27144144701074	-3.41674062009697	3.80445514207427
Sn	0.06288032839554	-0.22791118385495	2.08064891870088
C	0.02787875750900	-0.24151812029489	-0.06235322410595
C	1.97883476734465	-0.68453964044533	2.92560817791604
C	-0.49102228723822	1.75432301507173	2.72293391525905
H	0.46648894959237	0.68256471212208	-0.44234071816186
H	-1.00121217431683	-0.31450315066555	-0.41504199461839
H	0.59190043855142	-1.09506458462984	-0.43708563018021
H	-1.47828896020575	2.01418997547220	2.33918051479031
H	0.23570408133839	2.47558070151534	2.34414196324213
H	-0.51038256827896	1.81060303805192	3.81176690574504
H	2.57841432074204	0.22367291825386	3.00162643000221
H	2.49167923596744	-1.41164308949813	2.29639795290389
H	1.85013384777019	-1.10982022064716	3.92113715491859

II

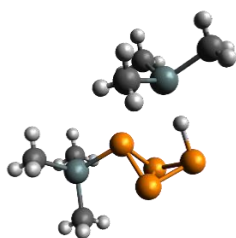


E = -1699.48597461 Eh H = -1699.42838521 Eh

0 1			
P	2.60825079651189	-0.27852527900993	2.25044672203470
P	4.83618138677669	0.90114854014262	3.61294963869152
P	2.72930937079770	0.66783647939390	4.25216617051788
P	3.17430640760397	1.85064563304859	2.50069754164659
Sn	0.11767835233257	0.08158718528474	1.89492329543462
C	-0.4788495851307	2.02029042606585	2.58867641859464
C	-0.90658708668548	-1.44399803208477	3.00011104950728
C	-0.26247665066296	-0.12429133016896	-0.20608062449968
H	-0.15551634111142	2.16966592351333	3.61877548901145
H	-1.56665037597744	2.09482322070214	2.54211007348659
H	-0.04123314402378	2.79952592334858	1.96503170424256
H	0.24993368701561	0.66368396790055	-0.75828784086817
H	-1.33420845352469	-0.05088767232442	-0.39675450940367
H	0.09295656157647	-1.09217111849208	-0.56034463311294
H	-0.70608613549304	-1.32503104317873	4.06516545889515
H	-0.57060112492773	-2.43215906141740	2.68557342335666
H	-1.98166070287450	-1.36523508574272	2.83138429056076

4 Unravelling White Phosphorus

TS(I[•]→*exo,endo*II)

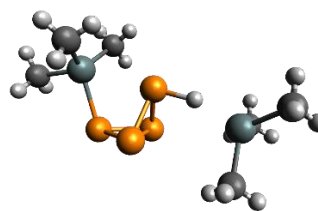


E = -2033.30746346 Eh

im. freq. = 489.11 *i*

0	2		
P	2.40841218277469	-0.51377098509146	2.46539602352361
P	4.46221203944362	0.25538174212727	4.66604627349224
P	2.27644801996696	0.08399548148143	4.60054100856517
P	3.29421045099721	1.39245769918736	3.19626804919228
Sn	0.14610569874089	0.36002218464731	1.71120353226947
C	-0.16960179577729	2.35735566714214	2.42283749071271
C	-1.32873935747759	-0.96929539205896	2.52443160331601
C	0.12429731327998	0.30442455920749	-0.43411844096584
H	-0.05179146054949	2.38972391487390	3.50598537196713
H	-1.17984642635458	2.67780938805844	2.16340712853869
H	0.54935979804334	0.3890690437426	1.96889109148410
H	0.87098127716742	0.99218815069318	-0.83149279518070
H	-0.85916151719989	0.59789179431750	-0.80430236531698
H	0.34799389275413	-0.70246557906304	-0.78751825080701
H	-1.27019845364115	-0.95787481506598	3.61308191821001
H	-1.15552766021558	-1.98639439567358	2.17225361238654
H	-2.32756913134244	-0.65380242456771	2.21953253916452
H	4.80178503433358	-1.06972537376691	3.62325505487172
H	4.16432491667123	-1.60519853708919	-0.08351084707276
C	5.17807889211717	-1.63286811544824	0.31539974424641
H	5.80360841153457	-2.25316754716414	-0.32917481569583
H	5.57990938034438	-0.61950066585933	0.32896091730172
H	2.78528493368369	-3.77315949576921	2.10881609483546
C	3.77452892084830	-4.09248583080111	2.43554331559321
Sn	5.14991370888322	-2.4455553888970	2.30591203280633
H	4.12024430254008	-4.90618698730733	1.79500255624777
H	3.71137213159531	-4.45403607640496	3.46200483588292
C	7.13482775642812	-3.15843322457825	2.7788623394869
H	7.41726622912131	-3.93465968739836	2.06449830052230
H	7.85522278789415	-2.34246127566453	2.71630125972729
H	7.16228772339453	-3.57783553844834	3.78480152623277

TS(*endo*I[•]→*endo,exo*II)

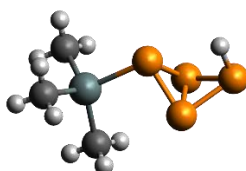


E = -2033.30715223 Eh

im. freq. = 796.30 *i*

0	2		
P	-1.50744335387707	-2.16046268013774	2.90373188945154
P	0.86703799471121	-3.47992656789805	1.62614712637516
P	-1.29457218743605	-3.86146625453138	1.51185192766667
P	-0.28930354238907	-3.92118666101954	3.43924812409003
Sn	0.09611745906437	-0.34725630737063	2.06072245210472
C	0.26196934112421	-0.31033670660618	-0.07768011655972
C	2.00049149003384	-0.31663658504431	3.04692775285168
C	-1.02147615009396	1.38591758538926	2.68459846318839
H	0.27012830235277	0.71994927225761	-0.43665647084309
H	-0.58446765774211	-0.83501804908328	-0.52106416486448
H	1.18234398984432	-0.81022559571654	-0.37883447336939
H	-1.99079685417147	1.40886736459913	2.18548623571293
H	-0.46946733413583	2.29155714757912	2.42670957937312
H	-1.18225616443522	1.36600134422948	3.76299508666836
H	2.34410405236867	0.71266623149685	3.16130673870521
H	2.72253496138603	-0.88141737375889	2.45786648197745
H	1.91439867513319	-0.77431262444945	4.03257963949208
H	1.24608368952988	-5.07219916013889	1.35571695840342
Sn	0.97173879846469	-7.07774202776328	1.10178220456022
H	0.39637355430883	-7.79367402821949	3.67493640695230
H	-1.16622036999153	-6.77081472809494	-0.55967627811655
H	3.33232368891299	-8.25324892521196	1.82406205828088
H	3.43903758314825	-7.75836639785690	0.12252908995591
H	0.31903885377029	-6.72484916615855	-1.53019651667127
H	-1.10696461029262	-7.35710843533156	2.83976231721594
C	-0.16119989728256	-7.89000653709358	2.7434827363216
C	-0.18872617231781	-7.22998871888471	-0.70834167157889
C	2.79487894122192	-8.21004980278669	0.76807169302023
H	-0.36070966207952	-8.94709891648911	2.55481635583791
H	-0.32468527374429	-8.28145182617562	-0.96967472971561
H	2.54424788161360	-9.22626485172969	0.56443762992072

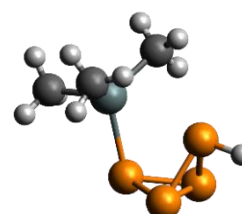
*exo,endo*II



E = -1699.48458835 Eh

0	1		
P	2.62125967782586	-0.36029845841697	2.25968102547963
P	4.88882259832934	0.95826392726916	3.78921359629020
P	2.76198786296987	0.57140952574505	4.25955846717542
P	3.26692482773391	1.74114036844592	2.50203013961839
Sn	0.13208463575774	0.04990729475995	1.88564911201067
C	-0.40815976567377	2.00217014699475	2.58881373585586
C	-0.93158816954655	-1.44570508195562	2.99639585709671
C	-0.27518159753755	-0.14165591839895	-0.21279057855617
H	-0.07838161051440	2.13408994621128	3.61940732580650
H	-1.49291457548149	2.11211273277034	2.54534740166258
H	0.05318957338114	2.77158755907560	1.97011860009444
H	0.23551123931026	0.64609381366751	-0.76681216558340
H	-1.34876440882590	-0.05966553028723	-0.38902079562392
H	0.06844876228225	-1.10997483224051	-0.57726537551261
H	-0.70233054061976	-1.34935762779056	4.05792483721808
H	-0.64485811127045	-2.44305532041003	2.66239231144376
H	-2.00598776394417	-1.32042121743424	2.85374183676092
H	5.12170736582369	-0.24405132800545	3.05879466876293

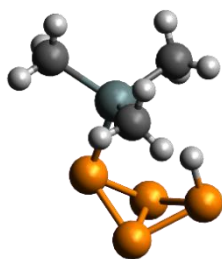
*endo,exo*II



E = -1699.48332552 Eh

0	1		
P	2.54867929375395	0.54245788634840	1.63084945500577
P	4.40048185616795	-0.01637584043454	3.94248763380066
P	2.52481809416700	1.12914048101186	3.75652361623590
P	4.23331232927102	1.65450197243258	2.51586651036697
Sn	3.20207735574868	-1.92763645566756	1.49438908361721
C	2.63485566986263	-3.08539396996764	3.20693749860416
C	5.26302260254735	-2.18055947607333	0.96123545201095
C	1.96800772529522	-2.51632981686055	-0.16529956188088
H	3.50703182074268	-3.24737572724783	3.83962686075701
H	2.22721486699614	-4.04593586480394	2.88826080725933
H	1.87913169305292	-2.54927439027477	3.78094242180284
H	0.91395690305382	-2.43088974703364	0.10078186756896
H	2.18197867404395	-3.55318850953608	-0.43072565975719
H	2.16339369952680	-1.88284805767744	-1.03091396000499
H	5.87792360737133	-2.16295731539994	1.86039453199856
H	5.57605521884978	-1.37163097812765	0.30079146961035
H	5.39815513940043	-3.13192544198257	0.44436608912237
H	4.98300345014828	0.69972125129469	5.04355588388196

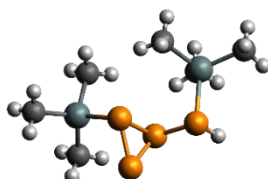
endo,endo II



E = -1699.47423495 Eh

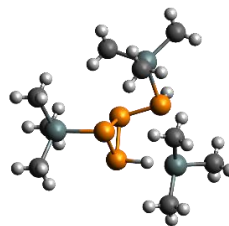
0 1			
P	2.64714428780813	0.47793127601730	1.85206147849550
P	4.56770781256127	0.01951271474481	4.44745678029267
P	2.60646385462928	0.95370109340001	4.00609076286542
P	4.34980887011499	1.49829355704657	2.81277810390365
Sn	3.16988229881781	-1.98370782231126	1.51826297874107
C	2.62943013712007	-3.20783157420907	3.19787950718374
C	5.21960693230470	-2.25801850142841	0.94843334991538
C	1.88275127969966	-2.45162564455583	-0.13463644697668
H	3.52218444429190	-3.51958701260286	3.74054607150119
H	2.09632857740802	-4.09239658108527	2.84690109672583
H	1.98415223372553	-2.64620007481772	3.87328858009875
H	0.83933215097190	-2.34870398368394	0.16431395492772
H	2.059478948002496	-3.47904519220023	-0.45676245671812
H	2.07662738997684	-1.77914566646728	-0.97023889622775
H	5.88164802062482	-1.86309645374691	1.71860906827210
H	5.41364268766229	-1.73311200565937	0.01280380271745
H	5.42505475210134	-3.32045857007553	0.80895109031441
H	4.40930532215643	-1.16242955836496	3.67839117396763

4.8.7.3 Second P-P cleavage

IIIa⁺

E = -2033.34115394 Eh

0 2			
P	-9.08028111769771	0.34638027548036	-0.66664245883960
P	-8.05620389213606	-1.07969065272234	-3.57892396587231
P	-7.78818857636186	-1.28989785521173	-1.41693107413077
P	-6.44622218108342	-0.01846163022721	-2.61938697431283
Sn	-4.60366756586053	-1.75673956781420	-2.71041422434098
C	-3.65303477605742	-1.60712334997732	-0.79284059949519
C	-3.26625219265219	-1.18864774177483	-4.28527806289004
C	-5.41071203317204	-3.71145975721413	-3.03551678143100
H	-2.88723180477389	-0.18223077819098	-4.10737861782102
H	-3.78935435949390	-1.20667376082153	-5.24161612980036
H	-2.42592954069039	-1.88311810751663	-4.32824157121649
H	-3.2023373391821	-0.62154718729493	-0.67410653541932
H	-2.87563143363659	-2.36690707870140	-0.69919590491024
H	-4.39420390629795	-1.75809692871135	-0.00764619196763
H	-6.18417881480807	-3.91917684109964	-2.29615484895822
H	-4.61662860515773	-4.45408425426509	-2.94407265940540
H	-5.84670051185671	-3.77220622676130	-4.03242566779182
H	-9.94986971639446	-0.52036955823915	0.05959881159957
Sn	-7.61799358504153	0.77569209839460	1.34782773171319
C	-5.82392294133414	1.74068355588324	0.68016794039856
C	-7.13423635155041	-1.07118063446978	2.32866287257763
C	-8.70611833160366	2.06170197627720	2.67831931428437
H	-8.84101541170071	3.04319081982156	2.22346112935393
H	-8.15463942198545	2.17538495701292	3.61292635766376
H	-9.68590513418560	1.63611558847479	2.89629799103272
H	-6.74166954929771	-1.78447455213722	1.60360447686574
H	-8.0274055875155	-1.49423861288451	2.78908914102171
H	-6.38349992341029	-0.89670425113922	3.10111310131308
H	-5.17894613323436	1.01932999126723	0.17901525460767
H	-5.29263035353260	2.15958360581710	1.53629873839823
H	-6.06561254232277	2.54075645874545	-0.01921059224515

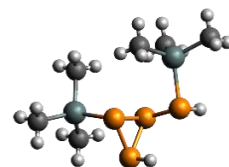
TS(IIIa⁺→IVa)

E = -2367.77708488 Eh

im. freq. = 342.20 *i*

0 2			
P	-9.69470719208407	-0.56606552779112	-1.38602323977716
P	-7.84131348578280	-1.91283311313409	-4.07095616734076
P	-7.98249030934994	-1.90043442715303	-1.89162064639787
P	-6.71670111276337	-0.42578162281354	-2.91527819954473
Sn	-4.55841892522453	-1.73456402340950	-2.79884873281430
C	-3.32359289704677	-0.80791430736344	-1.30459240736732
C	-3.65685674558960	-1.56175015322985	-4.73733401092703
C	-4.89389978049894	-3.79092853926497	-2.30508074407577
H	-3.46951190521329	-0.51486744849536	-4.97692003781919
H	-4.32601896277525	-1.98310463210115	-5.48795749901731
H	-2.71121266352529	-2.10552816664010	-4.75901696481380
H	-3.18789148656437	0.25011110038510	-1.52985254121163
H	-2.34620342068759	-1.29285785987726	-1.28300183592891
H	-3.78470481776790	-0.90492962582327	-0.32131619985456
H	-5.37847624974015	-3.87103880234461	-1.33246891772346
H	-3.93555956890989	-4.31223823650405	-2.27575290212094
H	-5.53274176207408	-4.25383069711787	-3.05688068830450
H	-10.34744049955750	-1.55466770412284	-0.59582761187736
Sn	-8.55582433576860	0.53074666748528	0.57928929246562
C	-7.76811910907368	2.41048060320262	-0.08060370785230
C	-6.94513579358345	-0.67588861365320	1.32399683316461
C	-10.03203207254960	0.83369521250672	2.10893831753166
H	-10.86491782242670	1.41721603256710	1.71597232559964
H	-9.58795296950132	1.37294301866433	2.94714245992898
H	-10.40878272634160	-0.12531561944658	2.46540246667136
H	-6.22358774567581	-0.85736263650845	0.52740813572867
H	-7.31720719942471	-1.63422770879757	1.68623185776006
H	-6.44856729479090	-0.15100221833955	2.14191492762394
H	-7.16352293940258	2.25828128434817	-0.97479316859270
H	-7.14382121325414	2.84020921695365	0.70442967978532
H	-8.57504346208864	3.10484780692275	-0.31366871260250
Sn	-10.06914243373180	0.86789436916331	-4.62141876613835
C	-12.17669399130880	0.52844688169903	-4.37171969503774
H	-12.40789284029770	0.44898735893299	-3.30986216007901
H	-12.47806669191170	-0.39115580903562	-4.87328609696396
H	-12.73233205147040	1.36442194638032	-4.80117362392103
C	-9.63560275363317	1.21656250584186	-6.70710705257631
H	-10.09716455881440	2.15158626425488	-7.03078280078322
H	-10.02526299313220	0.40071766115341	-7.31664992899226
H	-8.55781841624701	1.28545388305495	-6.85782694686027
C	-9.45622003930333	2.58746352290365	-3.49024986847333
H	-8.36883071856503	2.63767742100038	-3.44440542196151
H	-9.85115622588119	2.51375233920551	-2.47790571582356
H	-9.84063348899390	3.49188507308975	-3.96645287049225
H	-9.06865632767145	-0.73812267674867	-4.30310041219223

IVa



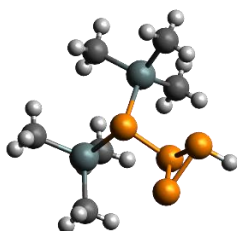
E = -2033.95073883 Eh

0 1			
P	-9.15829812152495	-0.04658349318398	-0.34134036485821
P	-8.32866963586198	-2.08853017086258	-3.02007565583009
P	-7.74607701340921	-1.64081344097112	-0.92687147454413
P	-6.84363763493486	-0.52266796845364	-2.59303264321663
Sn	-4.77616211837829	-1.97445444793403	-2.67067724328382
C	-3.60588170762208	-1.39785816413424	-0.96776624613497
C	-3.72472447549894	-1.53594403007675	-4.48857490435933
C	-5.27244905899667	-4.05533614654667	-2.55766634527766
H	-3.51126819219536	-0.46870208800499	-4.55106468310517
H	-4.32698058487812	-1.82720479048264	-5.34939600908141
H	-2.78363053697819	-2.08753948815355	-4.51286528087899
H	-3.36274351651586	-0.33586412312619	-1.01217348960024

4 Unravelling White Phosphorus

H	-2.67775219189294	-1.97088076952068	-0.94230100896409
H	-4.16816984972350	-1.59616420074955	-0.05486955830888
H	-5.85551899614469	-4.25135525848614	-1.65772379531423
H	-4.35207454148588	-4.64050005276180	-2.52115441561754
H	-5.85400083593732	-4.35462962516553	-3.42910101634310
H	-9.79226097801449	-0.80747650875842	0.68498207777639
Sn	-7.52415852607916	1.03751914153623	1.25213424365695
C	-6.11829630730531	2.13233683573842	0.06134421534289
C	-6.48814241322872	-0.43447863516629	2.42175600384970
C	-8.62600629298322	2.35098840888740	2.54487354744064
H	-9.21580209361147	3.05440958094837	1.95730302442448
H	-7.93318890540993	2.90978764423861	3.17601038338227
H	-9.29557947811184	1.77364372051967	3.18286159709009
H	-5.95504440473270	-1.12310860590851	1.76630824214829
H	-7.19566644500504	-1.00292637609844	3.02581007309320
H	-5.77091558787162	0.05640094834529	3.08152524234234
H	-5.45780683387492	1.43810496754161	-0.45801432308086
H	-5.51892957363263	2.78243143528380	0.70070036684386
H	-6.63980469376187	2.73843445007967	-0.67883466305358
H	-9.42144845439805	-1.17691874857328	-3.06295589653214

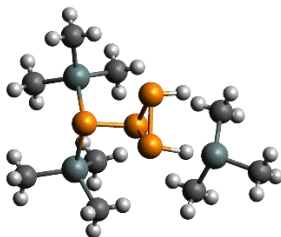
IIIb[•]



E = -2033.33859296 Eh

0 2			
P	-10.19235451895600	-1.65495731027914	-0.82528652910282
P	-9.27042702962039	-2.77437943090522	-2.46225223999009
P	-8.08210570525794	-2.28885031496718	-0.70672100848547
P	-7.24461901763920	-0.39886638487215	-1.51644650058000
Sn	-5.01391993264667	-1.39374465626325	-2.11558681600712
C	-3.93479166094911	-2.11297879859567	-0.40295718333588
C	-3.90154128773698	0.14625316602155	-3.11055079752724
C	-5.40619044254359	-3.03529720539443	-3.43789184127006
H	-3.71438010493812	0.97515465646303	-2.42745498385229
H	-4.46619415990949	0.51416022261806	-3.96740097661447
H	-2.94566885383263	-0.24877739060773	-3.45811558894178
H	-3.65292179583545	-1.28952165358245	0.25329590556894
H	-3.02908319104047	-2.62484391259227	-0.73255176453891
H	-4.55406628130063	-2.81706742199767	0.15351252398874
H	-5.94411242759870	-3.82022005148616	-2.90583292663820
H	-4.46642022857217	-3.44148905766624	-3.81543018297190
H	-6.01381978650911	-2.69911343083167	-4.27809404797209
H	-10.70753480270860	-2.80412100533844	-0.15401439918406
Sn	-6.70540139274784	0.63776594177584	0.71780843810537
C	-4.91966320831022	1.81738986516366	0.52159058470600
C	-6.46710245428939	-0.83509955149022	2.25903860259675
C	-8.37676984445785	1.89881827881057	1.17621160588201
H	-8.44612439627610	2.70213279431875	0.44238288938967
H	-8.26619398716646	2.33206321998962	2.17135684043129
H	-9.29519977271575	1.31221958893809	1.14022968786810
H	-5.62484554531778	-1.48916521638024	2.03714896283414
H	-7.37097583414787	-1.43854731402485	2.34221498835720
H	-6.28818196332444	-0.33089683089233	3.21026460921652
H	-4.04822421921692	1.17535201474646	0.39034200160855
H	-4.77902093159033	2.4200107552510	1.42021240548305
H	-5.00236507557372	2.48237643379656	-0.33861225902389

TS(IIIb[•]→IVb)



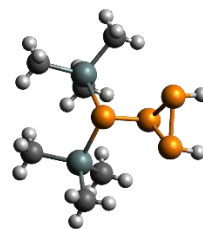
E = -2367.77684859 Eh

im. freq. = 593.78 i

0 2			
P	-10.62264920138730	0.24867790283560	-2.63779245471501
P	-9.74085883200065	0.35016012725744	-4.64199020174226

P	-8.80702560664887	-0.89577348877002	-3.09984086601178
P	-7.29696456650678	0.52349993311962	-2.34627308987078
Sn	-5.41846090225295	-0.73982630286085	-3.44605799042150
C	-5.37004361849156	-2.80091006526098	-2.86994244986054
C	-3.55719058160692	0.19709176509211	-2.93795636561546
C	-5.78917590117154	-0.61878664318513	-5.55610407789141
H	-3.33999660483502	0.05523896664717	-1.87921116514336
H	-3.60639636715098	1.26536574281007	-3.14937645078513
H	-2.75151620593069	-0.24398419680982	-3.52694784641206
H	-5.07951120745146	-2.91158588513800	-1.82407721345225
H	-4.64833646916752	-3.34364394719866	-3.48973346302087
H	-6.35483148757276	-3.25517892469490	-3.01099361470757
H	-6.73251445496957	-1.11293815572018	-5.79011597928063
H	-4.98465103815204	-1.10961708164488	-6.10602103010588
H	-5.85222284027709	0.42413418257828	-5.86661460307536
H	-11.49331410630160	-0.8903896430523	-2.88886820223079
Sn	-7.23103796996738	-0.44952309152801	-0.02437786412689
C	-5.20693103042690	-0.45250839425626	0.69384951707762
C	-8.02980115249236	-2.44072326401569	0.0176592438036
C	-8.44778085877725	0.83639140569989	1.18703829510159
H	-8.03491019122783	1.84528503921326	1.18888223969221
H	-8.48863899701371	0.46430711863439	2.21183586576273
H	-9.45763868394177	0.87120638163198	0.77752805069501
H	-7.45660495839936	-3.09561487876347	-0.63799234447396
H	-9.06845299384048	-2.43135219320362	-0.31304008192144
H	-7.98410912442472	-2.82649618813467	1.03757893506694
H	-4.61574833587232	-1.19998776909995	0.16368965547693
H	-5.19509058027394	-0.68708345077019	1.75933071083537
H	-4.75243550589708	0.52737280390621	0.54461746343865
H	-10.45045194093990	-1.13226418451257	-5.15296126896700
Sn	-10.65741784550630	-3.05193705773618	-5.25184274859766
H	-13.11625817492060	-3.13052726814041	-6.44016561625995
H	-8.38137396023387	-3.24804410556392	-6.74983368692104
H	-12.17336384565310	-3.56398879670095	-3.03524927848650
H	-10.45097694839770	-3.73815102610526	-2.63299921058023
H	-8.02141190110238	-3.68163640236859	-5.06674973837657
H	-11.86989607154870	-3.03724252233693	-7.69958431409522
C	-12.13940817380690	-3.50127429538573	-6.75075364742217
C	-8.73879874109529	-3.79837133978379	-5.87907200867945
C	-11.21547181725430	-3.95375204337994	-3.37907090450275
H	-12.19891009239110	-4.58269825130168	-6.88984760378001
H	-8.81638215428400	-4.85597934835301	-6.13832897687515
H	-11.29843795843000	-5.03502094239553	-3.50936365313509

IVb

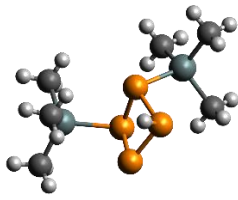


E = -2033.95274518 Eh

0 1			
P	-9.79882702093618	-2.81581014190555	0.00662682580978
P	-8.51629213895895	-4.01941427982513	-1.35140848738969
P	-7.60899998488411	-2.60375702913816	0.07057206990412
P	-7.55993803463892	-0.90922119151513	-1.35048099367537
Sn	-5.21455810791248	-1.28935897324994	-2.17659512995599
C	-4.02077564202547	-2.40844615836662	-0.78834626046002
C	-4.33112461097442	0.63385924609235	-2.54582158607952
C	-5.39163950909641	-2.39868370268303	-4.00280740490153
H	-4.17566563458618	1.16842221237009	-1.60828081297030
H	-4.98218471798262	1.22828921205924	-3.18752001953015
H	-3.36708498851081	0.51042392422040	-3.04164269994299
H	-4.00488581950623	-1.92257286216895	-0.18643501167384
H	-3.00075375313532	-2.47806930806643	-1.17010262483212
H	-4.42617454204037	-3.41384260890066	-0.67490516251689
H	-5.94936146465073	-3.31696292044370	-3.81686705848582
H	-4.40323057275869	-2.65205434620669	-4.38916334869270
H	-5.92713658549085	-1.80957032986933	-4.74749454613000
H	-9.84392883784690	-3.77197969959879	1.06173598032691
Sn	-7.15035900837946	0.82574933618451	0.42294671763511
C	-5.34891236407704	0.43931618337228	1.52797731326339
C	-8.82408219663010	0.73702023826343	1.76062869888654
C	-7.05699872152967	2.74243834688963	-0.53669502416483
H	-6.22297503431846	2.77674571658391	-1.23763066460765
H	-6.92320776465019	3.52526342757156	0.21145159395291
H	-7.98354719190900	2.92712056440517	-1.08064936837864
H	-8.83597849925660	-0.22266204510830	2.27744509962899
H	-9.75334722257507	0.84638376065219	1.20157658654801
H	-8.75296735903283	1.53866186621776	2.49749029903880
H	-5.37162058238281	-0.57709134701320	1.92181988190648
H	-5.27442232528636	1.13965261673811	2.36159585007433
H	-4.47081964838194	0.55505771091009	0.89225205610610
H	-8.37896011565469	-5.14115741847109	-0.48539200900108

Unravelling White Phosphorus 4

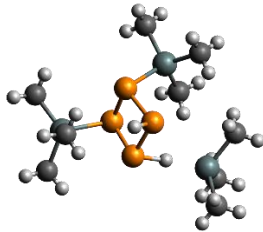
IIIc'



E = -2033.33604055 Eh

0 2			
P	-7.80589631990372	-2.84812355223838	-4.11178314652015
P	-9.27989939664299	-3.45828127336592	-2.62350351471447
P	-7.15643162099923	-1.16641757726711	-2.79928972033101
Sn	-4.76142562783724	-1.91625817621927	-2.52921839589823
C	-3.82793590877287	-0.73392053788750	-1.00097705983920
C	-3.84979656084080	-1.57294957889718	-4.43981093296469
C	-4.71440268330287	-3.99741940662227	-2.02941588435473
H	-3.88339788142473	-0.51254719682016	-4.69111294432452
H	-4.38282050346191	-2.13719614518015	-5.20595368449792
H	-2.80898502953666	-1.89935274098043	-4.42157349007131
H	-3.84509161507772	-0.32012528239715	-1.27868682689237
H	-2.79157480464852	-1.04937053855547	-0.87161811909438
H	-4.35502636645673	-0.86042669996905	-0.05509564211519
H	-5.16378186705033	-4.15491203753656	-1.04915348927439
H	-3.68255930719588	-4.35153484823797	-2.01342410656401
H	-5.27545553884774	-4.56363014750076	-2.77310474532756
Sn	-9.35664777038725	-1.50349717951093	-5.59689401751326
C	-10.58088889206570	-2.88311924881382	-6.69039379911981
C	-8.05156282831292	-0.38757335661091	-6.88624236357460
C	-10.53655432781980	-0.21033385100846	-4.36383448402709
H	-11.21841902854760	-0.80662171838425	-3.75828217051733
H	-11.11121564466220	-0.47854463310269	-4.98465906320537
H	-9.87877931944070	-0.35966509282572	-3.70751598664001
H	-7.45504189362341	-1.06837294034119	-7.49354178059076
H	-7.38536932131076	-0.22996111217090	-6.28308883002472
H	-8.63481318843375	-0.25886456304646	-7.54356542171900
H	-9.95768201302441	-3.53318477477011	-7.30443245519426
H	-11.26838373926730	-2.33532113559848	-7.33641352467466
H	-11.15826255337360	-3.49455769159434	-5.99689344589644
P	-8.07204430857239	-2.35490187244796	-1.16320334073143
H	-9.05189413915777	-1.43420645718428	-0.69144761378695

TS(IIIc'→IVc)



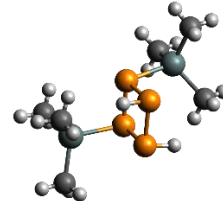
E = -2367.76935064 Eh

im. freq. = 819.09 i

0 2			
P	-8.01211792566107	-3.20231204258458	-4.58325611825265
P	-9.48746761367828	-3.91053168672615	-3.09926878149257
P	-7.14769389505215	-1.81431529416607	-3.06436438168849
Sn	-4.99430895862991	-3.05769928165645	-2.63668957809848
C	-4.54295130543541	-2.91896099374980	-0.54522292086967
C	-3.49618829905938	-2.06967861937957	-3.81446449362070
C	-5.16660088374777	-5.09710711001357	-3.27837474809902
H	-3.38424877876806	-1.03555094803315	-3.48812616808372
H	-3.78711638104754	-2.07772335617774	-4.86547603285414
H	-2.53778265630989	-2.58079174980465	-3.71195719768664
H	-4.42216204895168	-1.87448462342667	-0.25717395403923
H	-3.61798867293939	-3.45589049837577	-0.32981611983270
H	-5.35297291747678	-3.35768306221835	-0.0366535812205
H	-4.30897548122319	-5.67463477433820	-2.92947110648313
H	-5.20959809100883	-5.13227327789732	-4.36660472329686
H	-6.08151924329689	-5.53740871662331	-2.88314989637393
Sn	-9.603209957412788	-1.52528538236740	-5.59790331319280
C	-11.04245377248740	-2.64235495331257	-6.72925771086278
C	-8.43610268116332	-0.22929290854433	-6.85069943629627
C	-10.56309909749960	-0.39278942395332	-4.05088471923362
H	-11.19220871107790	-1.04840951819366	-3.44931726150993
H	-11.18031827633930	-0.38968123967992	-4.49521905461098
H	-9.80845907815489	-0.06812079259392	-3.41317206923858
H	-7.96450036614415	-0.80089917612918	-7.64991837710162
H	-7.66320564860364	-0.25584217356481	-6.25398476390035
H	-9.0762108950179	-0.53702047332000	-7.29050636306696
H	-10.54586147386200	-3.21551563339648	-7.51207278836571

H	-11.76401042987480	-1.96475309965352	-7.18788112804761
H	-11.57294651778570	-3.32750116931624	-6.06738516325620
P	-8.41377951146396	-2.79364230361358	-1.51744986805383
H	-9.36158581822105	-1.74207898498616	-1.37395897877822
H	-8.78484285502628	-5.35273286445199	-2.51980285604573
Sn	-8.27845049767571	-6.81354837364068	-1.311700242111088
H	-10.34298099536810	-6.41502296892142	-0.42344348378429
H	-8.44451868629239	-8.82871845498058	-3.14722191986067
H	-7.00255715368788	-5.33985648009525	-0.58243582348150
H	-5.77801983258157	-6.17359747038098	-0.39780735039485
H	-6.74798122706114	-8.33761244883675	-2.97683314879300
H	-10.89313660524650	-7.49165958156042	-0.87544204623309
C	-10.06740456913190	-7.26531592846662	-0.20082072857131
C	-7.66929035929712	-8.54944916642866	-2.43368114378077
C	-6.74117593516912	-6.28189666435405	-0.10046991828158
H	-9.88632595820866	-8.12988304090327	-0.44107484108905
H	-7.49685556221528	-9.38408187676596	-1.75105062577461
H	-6.66358476343857	-7.06365077073156	-0.85902965309600

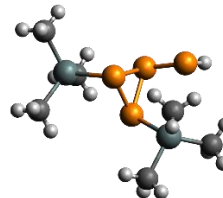
IVc



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P	-7.51626981783322	-2.69080043303453	-4.46241987445809
P	-8.70798618913605	-3.53282646215517	-2.78162725622411
P	-6.87584789170816	-0.99681072252808	-3.15265174346555
Sn	-4.63041713253193	-1.93885410488269	-2.50853421733894
C	-3.98282183894218	-0.89018777495348	-0.75243266272931
C	-3.37293899972281	-1.57474132598431	-4.20686997227473
C	-4.74495858634630	-4.04548540639277	-2.11931871413559
H	-3.31310273353691	-0.50525584423459	-4.40917384400826
H	-3.79208342865548	-2.07828047768600	-5.07875446425025
H	-2.36863738180388	-1.95993334465558	-4.02569258266375
H	-3.84068335788542	-0.16780675337652	-0.97268581503702
H	-3.04238559516591	-1.30875669371640	-0.39120763756766
H	-4.73799452039115	-0.99276785477451	-0.02752819255663
H	-5.33394194973273	-4.23201652690302	-1.22130851552678
H	-3.73985112404572	-4.44496801332546	-1.97489068705595
H	-5.20862903617093	-4.55020768268792	-2.96726631363839
Sn	-9.40847712936318	-1.49161868832642	-5.61536329609765
C	-10.71436200435470	-2.98193227202048	-6.43576045455822
C	-8.49211815150471	-0.32356815403958	-7.16226310097718
C	-10.46750956786220	-0.21059357598666	-4.25796044957810
H	-11.03238153352450	-0.80421439748049	-3.53937433349116
H	-11.15912220565310	-0.42098743093391	-4.81794768306352
H	-9.75999765294513	-0.42480187620088	-3.72474242758191
H	-7.98359611211805	-0.97558153684103	-7.87244560933213
H	-7.76532059370636	-0.36174158961921	-6.72501459008553
H	-9.24903063650373	-0.25676119570410	-7.69184290760169
H	-10.17106838675890	-3.60892374104071	-7.14286284532157
H	-11.54697464226390	-2.50233156070037	-6.95258881298835
H	-11.10793571927300	-3.60827639309945	-5.63487791575285
P	-8.03101535514206	-1.87538710162936	-1.46593683835879
H	-9.20452925069081	-1.09466242696778	-1.65782651654070
H	-7.71572147472638	-4.44699632978772	-2.33157611085281

IIIc'



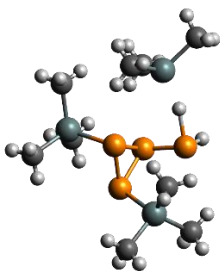
E = -2033.33324449 Eh

0 2			
P	-9.56406310542356	-0.07612454823220	-2.43058850417062
P	-7.88903477229072	-2.40027732711273	-3.98353412338323
P	-8.00998496279682	-1.37691184520528	-2.02071481331223
P	-6.57961431556113	-0.68623283924631	-3.54728217271117
Sn	-4.64788872074239	-2.12480345294262	-2.75706779910276
C	-3.21676239354215	-0.84400111643952	-1.80037845508218
C	-3.80622702595286	-2.99577236233947	-4.52560677198774
C	-5.32780851407737	-3.65609854640761	-1.42350290311723
H	-3.43389939420359	-2.21654935454200	-5.19103945624271

4 Unravelling White Phosphorus

H	-4.57075646459381	-3.57258625536020	-5.04669356310373
H	-2.98125699606353	-3.65825016434960	-4.25918996387175
H	-2.92596525730453	-0.03897448465900	-2.47561675756427
H	-2.32869052877168	-1.41885312016406	-1.53266711309875
H	-3.64329507973756	-0.41047064657782	-0.89566677799505
H	-5.63674479165146	-3.22324938877045	-0.47291237933945
H	-4.51422857324937	-4.36311260481854	-1.25191925032879
H	-6.17224294160913	-4.18555035920959	-1.86489186737286
H	-10.50673051069950	-0.57482412506913	-1.57781493295535
Sn	-9.51865900925200	-1.31218933394175	-5.61808301270105
C	-8.98626996031578	-2.38588015982371	-7.40578754931152
C	-9.21888635919494	0.78191162649890	-5.94428724252144
C	-11.53708098307860	-1.81003515717001	-5.08972226692087
H	-11.57406597958430	-2.81047554779464	-4.65804952274619
H	-12.16764160546460	-1.78613920223156	-5.97992611555757
H	-11.91682737371710	-1.09551611180805	-4.35972180216655
H	-8.24668984848062	1.07664890046360	-5.54876694703605
H	-9.99377883983737	1.34552413641653	-5.42575040517121
H	-9.25449208619921	0.99476236030126	-7.01379430133626
H	-7.96036706052703	-2.15230421332096	-7.69234300520140
H	-9.65386334341267	-2.09655548974296	-8.21930753734781
H	-9.07190320266425	-3.46067836286489	-7.24361268724211

TS(III^d→IV^d)

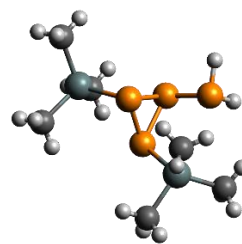


E = -2367.76982152 Eh

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P	-7.89333941502282	-2.13654309875620	-3.86323311846819
P	-8.16934752405251	-0.90615749058037	-2.05607766102871
P	-6.73563761614048	-0.28085313258187	-3.61295618791842
Sn	-4.68956005871626	-1.34903854638735	-2.58347665573186
C	-3.50116264382756	0.21047478567681	-1.70425847434918
C	-3.62640733849818	-2.30232882849689	-4.18454122528122
C	-5.24421360878484	-2.78959968721883	-1.09970522812330
H	-3.28138906083382	-1.56086148142328	-4.90533317191963
H	-4.28648852364060	-3.00880616155635	-4.68826476258773
H	-2.76388933826724	-2.84170784820307	-3.79006144201553
H	-3.20824224649011	0.93848046060277	-2.46101134368575
H	-2.60166346659361	-0.21881924520915	-1.25978897203485
H	-4.07047580694303	0.71821681969915	-0.92604659854523
H	-5.65852631525889	-2.29126511611201	-0.22375457193713
H	-4.36126108013469	-3.35987306699323	-0.80640184912266
H	-5.99139295053774	-3.47099122777329	-1.50669041648894
H	-10.38146821847470	0.44830953215201	-1.29986905697407
Sn	-9.60033660403810	-1.36911203094656	-5.57564180148065
C	-9.08508981279648	-2.60802761487037	-7.25774357603472
C	-9.41744942189816	0.69279211926757	-6.12937276037708
C	-11.56949401897470	-1.89224979363345	-4.90660157953954
H	-11.56266193471320	-2.89283854666603	-4.47374558799856
H	-12.26146920965130	-1.87619518556519	-5.75026461027358
H	-11.90014893098210	-1.17913319978854	-4.15225351141717
H	-8.47927682947017	1.09315715718901	-5.74436081742611
H	-10.24379102434700	1.25959035168749	-5.70184411407956
H	-9.42776430200422	0.77813496265031	-7.21702732300457
H	-8.08268922823313	-2.36337398454565	-7.61079904485373
H	-9.79464035551133	-2.44534068988902	-8.07087030873039
H	-9.11108373117725	-3.66017976950932	-6.97273708150825
H	-6.47851931484059	0.41884155590019	0.13564886391752
C	-6.58573344311077	1.42647074405234	0.53698300120275
H	-5.62016359055765	1.77298537406918	0.91021131407715
H	-7.29537467703384	1.39825978327221	1.36446105487767
H	-5.51853883135344	2.40395926194028	-3.00759223317052
C	-5.75469424664319	3.26530625141563	-2.38437610097331
H	-4.85931675992187	3.57397999791526	-1.84127274504523
Sn	-7.30634774551479	2.76257792029954	-0.98624861965652
H	-8.70893656387390	1.84614971615457	-1.87576289810476
H	-6.08490253235892	4.08416004290453	-3.0238558595067
C	-8.03256153994924	4.56400812110898	-0.06072767288516
H	-7.21063319889330	5.05631135609166	0.46296952566332
H	-8.82001174236367	4.33301764141304	0.65676218953632
H	-8.42728889865806	5.24462861053650	-0.81510200144957

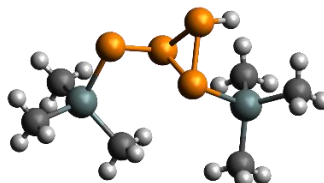
IV^d



E = -2033.95134584 Eh

0 1			
P	-9.61503881812363	0.01573960612941	-2.35681109360889
P	-7.89596914383565	-2.47613787811272	-4.01414158563310
P	-8.06669088169778	-1.53057964866608	-2.03280981869464
P	-6.63170916459926	-0.74669095793157	-3.50303659497291
Sn	-4.66039228599965	-2.14892033262863	-2.76079530922449
C	-3.24157012091860	-0.86710657434358	-1.78467969289830
C	-3.81762858333514	-2.95436445334013	-4.55973261797379
C	-5.28729278226082	-3.72907283869308	-1.45938547971622
H	-3.46751885222272	-2.15015972657788	-5.20730017707382
H	-4.57632409921934	-3.53183926891140	-5.08854793403241
H	-2.97703597657689	-3.60719764067884	-4.31951061447116
H	-2.98669258463365	-0.02863245952578	-2.43326486255487
H	-2.33302258051013	-1.42839649386191	-1.559734998008014
H	-3.65781865173251	-0.48131514570449	-0.85390300408396
H	-5.64465002926239	-3.32423883658155	-0.51331131299365
H	-4.44227903777692	-4.39398480475728	-1.27221156258333
H	-6.09040797772923	-4.29718313189489	-1.92910461030486
H	-10.64305320573330	-0.68072679747824	-1.66193099106209
Sn	-9.51908055371186	-1.36582792641017	-5.6222727232967
C	-9.05950956830980	-2.44825969244713	-7.42380869237309
C	-9.17255484311590	0.72192334431366	-5.94190186675904
C	-11.54388583098020	-1.79402225126386	-5.05006883355065
H	-11.61072499610540	-2.79608840286982	-4.62586733762994
H	-12.18922468397520	-1.73973147854368	-5.92830477100031
H	-11.88517734182260	-1.07001072263268	-4.31064760153796
H	-8.19107488707477	0.99098592487600	-5.55117033424013
H	-9.93023459233268	1.29862403414999	-5.41280447485373
H	-9.21152391733254	0.94184543599216	-7.00982939711706
H	-8.03370190702864	-2.24213707140995	-7.73133503905431
H	-9.73525668893292	-2.14040871008337	-8.22364773771176
H	-9.16936406885794	-3.52075650491884	-7.26100998393641
H	-9.26576134425159	0.78688140480638	-1.21395939794318

III^e



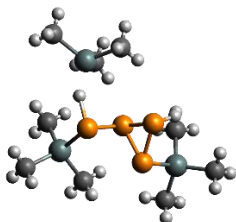
E = -2033.33203870 Eh

0 2			
H	6.26784110007609	1.36802730565232	4.99939727876020
Sn	5.51551279845439	3.92529732308090	3.37644894007894
P	2.55375767133331	-0.54455913688927	3.56461646344462
P	5.65487417565164	0.35011921989058	4.20659230671653
P	3.61450761925720	1.13082721810327	4.46414525546583
P	4.75207947256385	1.62982583836634	2.63755881972141
Sn	0.53439620983431	0.85583224892714	3.00975418668481
C	-0.65039299415836	1.08523555724908	4.78773618729085
C	-0.59065149705298	-0.19924516926425	1.51941696534571
C	1.11258894647736	2.79195906521542	2.27693686418163
H	-0.98281562884705	0.11009998474376	5.14382930237773
H	-1.52387895269597	1.70213149551318	4.57061999903209
H	-0.06061563069765	1.56575994057819	5.56858159415084
H	0.22984886793524	3.32712158729610	1.9234191586468
H	1.82150282855455	2.68498019833140	1.45586094034103
H	1.57996709231111	3.36493207508998	3.07819136703175
H	-1.54966936134083	0.29554618164656	1.35879860576934
H	-0.77128215845904	-1.22377820270180	1.84546290273051
H	-0.03982317626872	-0.22049314970773	0.57887531211697
C	4.99685853255597	4.28237656130441	5.42507476920446
H	5.36268626995062	3.47872460887047	6.06387652306371
C	3.91440132482379	4.34734819883954	5.52895283650054
H	5.44711001030422	5.22305981689768	5.74690463347165
C	7.64478017778960	3.98973350401137	3.1108585156947
H	7.89805882990587	3.80862389667792	2.06637972948157
H	8.11856343361356	3.22546334896202	3.72744187513651
H	8.02776234451510	4.96856519536896	3.40406450905138
C	4.54648330410929	5.34348908795902	2.09143690557306
H	4.86902465058572	5.19437287732059	1.06062997482918

Unravelling White Phosphorus 4

H	4.79828447336248	6.36009834443328	2.39703799448137
H	3.46494926551885	5.21541497823160	2.14325195452951

TS(IIIe⁺→IVe)

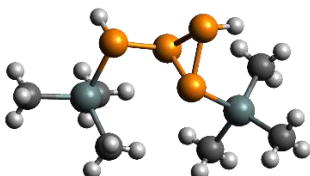


E = -2367.76952229 Eh

im. freq. = 602.91 i

0 2			
H	6.65319079021021	0.82387097583222	5.37231109089544
Sn	5.71963985236453	3.62286769362795	4.36645990584604
P	3.22906324180146	-1.04177269969991	3.25361797523802
P	6.19998517149835	-0.00942451821534	4.30401140769577
P	4.07723006151406	0.51392982990084	4.55928317538085
P	5.26482267153826	1.53267920982491	3.01886253638473
Sn	1.11852003896820	0.26231190427900	2.83943718227616
C	1.61416881175148	2.31647136542468	2.45040209660232
C	-0.19851255472197	0.18904304442698	4.53571825919951
C	0.14390120045444	-0.62030086158288	1.14404396915423
H	2.02238920871967	2.76972524461317	3.35443605512049
H	0.71813132904631	2.86266092260340	2.15081614941738
H	2.35812208665487	2.38161745578155	1.65661617040451
H	-0.79660287323620	-0.10441023076031	0.94468415902887
H	-0.06386310343614	-1.67250992477968	1.33992877688021
H	0.78409434782077	-0.54597470572803	0.26483476295528
H	-1.11507793354201	0.73756900219838	4.31209144736323
H	0.28380193829465	0.64518344068075	5.40011282859544
H	-0.45491504630921	-0.84365323196595	4.77513810140085
C	5.06603061664114	3.39075080237048	6.39668938322525
H	5.41344219098607	2.44350144022369	6.80930134049501
H	3.97765841758734	3.41203982377972	6.44068663339706
H	5.46925034054889	4.20813967564112	6.99700557312940
C	7.83343687203423	3.99435279163013	4.31101652087863
H	8.17581193938244	4.07443633808597	3.27918901492201
H	8.36568998742699	3.17593863666164	4.79654830482092
H	8.06194628117237	4.92431935484569	4.83399723733420
C	4.64804253864747	5.21435339983805	3.40262108208983
H	4.99795588296312	5.32906442153563	2.37640800620715
H	4.80543516628581	6.15204052973489	3.93765556558742
H	3.58134483454987	4.98966113543303	3.38648001435951
H	2.59656213945735	-1.78114855736070	4.72953449275656
Sn	2.51629249935176	-2.22350467081244	6.58237730307902
H	0.26251460146206	-3.75850592795781	6.72232841200632
H	1.64472466788643	-4.79729920455702	6.32044741610318
C	1.30872637939283	-3.96936153328527	6.94462144064918
H	0.69449462643286	-0.46796972206751	7.60295042585018
H	2.25456843300278	0.35766869626257	7.38448885199032
H	4.98386197142818	-3.37813665486314	6.46825119643182
H	5.14654534747689	-1.69595713083410	7.00188425088835
C	1.77363594269067	-0.55993841160007	7.72413111283391
C	4.56251475020184	-2.60935712798581	7.11606583538957
H	1.39614146104781	-4.25856962234803	7.99370953800346
H	2.00175685538936	-0.71182469271722	8.78079926580058
H	4.62181001715884	-2.94499770611599	8.15302573276344

IVe



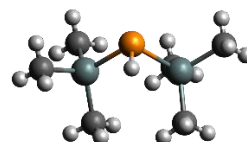
E = -2033.94962365 Eh

0 1			
H	6.51777116293063	0.78971513827211	5.88686040558748
Sn	5.64258536049816	3.44475824576299	4.25961922761656
P	2.9040240501562	-1.11653164365191	4.10143759278500
P	5.99986876776855	-0.20089070442742	5.00232096662905
P	3.93501082987697	0.55928381682354	5.11047788041153
P	5.21661249220065	1.10825407193696	3.40530570850448
Sn	1.11433362366020	0.36919799265656	3.12045722735769
C	1.98320130867312	1.48780398917243	1.51243734819698
C	0.32579389121562	1.70202009639628	4.60747882639165
C	-0.44129681048576	-0.90737524038013	2.37867448626689

H	2.59090865910359	2.29984276519253	1.91108962838554
H	1.19167201645826	1.90772981160468	0.88966996942257
H	2.61542676120040	0.84250749266100	0.90333225818367
H	-1.21446679006548	-0.30523362872183	1.89893537564673
H	-0.89091871371033	-1.47031355701874	3.19693996638446
H	-0.03419588810712	-1.60833290113873	1.64978803392830
H	-0.36799132533600	2.40526526236399	4.14400745358805
H	1.13621928923823	2.25912428831991	5.07796002564488
H	-0.20153955259995	1.13473575581744	5.37481267485514
C	5.90515685994455	3.49306725024773	6.38706435429589
H	6.91269816572516	3.18195719123194	6.66200211820422
H	5.17967759534478	2.83832552934506	6.87038536061694
H	5.74458374526039	4.51523048008345	6.73443321067880
C	7.37718963106151	4.21257741260546	3.25766040478765
H	7.23361970135506	4.17062671931604	2.17774505730022
H	8.25463505646533	3.62128348875702	3.52020641841511
H	7.54826522725914	5.24937348674381	3.55126187486038
C	3.89950493699563	4.56750054438192	3.70289064048514
H	3.781940080073296	4.56816314849598	2.61882958664426
H	3.99228026036518	5.59865513803211	4.047282425360254
H	3.01373892549521	4.12146432663103	4.15632197116625
H	2.11168067645970	-1.46504576751323	5.23514151118314

4.8.7.4 Third P-P cleavage

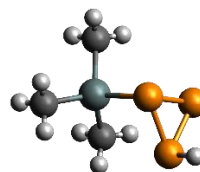
(Me₃Sn)₂PH



E = -1009.59731951 Eh

0 1			
P	-9.27028367417931	-0.27825866161086	-0.45852185088210
Sn	-7.99866152623144	0.90334426153167	1.35203122189747
C	-6.27451572951600	1.78776432054004	0.43258349098289
C	-7.39890501317862	-0.56801993971132	2.79518573876655
C	-9.11117221548755	2.43002493017660	2.38087617574503
H	-9.30568540302671	3.27853759024108	1.72431542471772
H	-8.53294910337380	2.77793500511970	3.23891984581536
H	-10.06167160343540	2.03115182951292	2.73635956618313
H	-6.82793750799174	-1.36032876867133	2.31094009983478
H	-8.27818120228378	-1.00643670858989	3.26826941919463
H	-6.78055636332638	-0.10190863651860	3.56419982043193
H	-5.68606381650810	1.02018882865271	-0.07076720076038
H	-5.65321063528421	2.27020095967191	1.18862009005852
H	-6.58122682803032	2.53400171737037	-0.30043642314775
Sn	-10.55418257436910	1.68595038198542	-1.35304247272027
C	-9.21149747914344	3.32281687924329	-1.71967570410864
C	-12.09793273560910	2.30310929421300	0.00457275894728
C	-11.43672184346900	1.07885323388346	-3.21300318578121
H	-10.32527633063910	-0.66875925916808	0.41452437025927
H	-11.65926797597800	2.72481481256466	0.90833208196105
H	-12.71549247832230	1.44706049962165	0.27834155187673
H	-12.73061942030700	3.05576387383009	-0.46908546211247
H	-8.84681570269723	3.73974113050884	-0.78032847464240
H	-9.73206539269401	4.10729445143867	-2.27117412081867
H	-8.35875543999293	2.98652189291908	-2.31030685482269
H	-10.65843526282230	0.74651067830294	-3.90030004254595
H	-11.97845106368640	1.91191546174235	-3.66385535454965
H	-12.13126567841600	0.25504994119959	-3.04515451041212

Va⁺



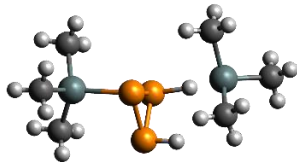
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0 2			
P	-7.90093545122749	-2.17351115561838	-2.31653765459743
P	-6.88065688965715	-0.80471721052803	-0.94179876742880
P	-6.50735631026189	-0.62980932388143	-3.05506082453023
Sn	-4.43136073745763	-2.09533454558035	-3.11177421849515
C	-2.84127355107693	-0.90726513293072	-2.30775130725035
C	-4.07653462569238	-2.56927115427814	-5.17365838056814
C	-4.72008111965624	-3.86809669082214	-1.94641495306201
H	-3.94147240150416	-1.65294099081828	-5.74838923798841
H	-4.92406595081831	-3.12156280785474	-5.57939873974097
H	-3.17766878284355	-3.18137290330935	-5.26347048704212
H	-2.73283203955828	0.01456465218174	-2.87936301950818

4 Unravelling White Phosphorus

H	-1.90405859188674	-1.46417611667101	-2.35207739016532
H	-3.05874459218751	-0.65796639028663	-1.26917277698399
H	-5.03932896664175	-3.60512136872767	-0.93810156089627
H	-3.77503380987963	-4.41117713750265	-1.89125727624862
H	-5.47460624160984	-4.50725347484549	-2.40335317180891
H	-9.07492993804054	-1.38306824926672	-2.48602023368512

TS(Va[•]→VIa)

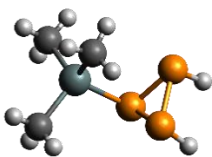


E = -1692.63957486 Eh

im. freq. = 552.56 *i*

0 2			
P	-7.30586985130880	-2.71414201566318	-0.42116604725080
P	-5.77037670164689	-1.37612298322640	0.38752196475429
P	-6.71765225327363	-0.90830937230881	-1.53120951099386
Sn	-4.86348089316136	-1.97427259741396	-2.88703591862330
C	-3.09968179530866	-0.83007942531472	-2.46883875505267
C	-5.40026048574864	-1.79836130003171	-4.95879222113214
C	-4.58702949535629	-4.03297778162698	-2.36010663080330
H	-5.46822094086893	-0.74735932849931	-5.24055067569553
H	-6.36361198677266	-2.27588525595525	-5.13908654748644
H	-4.64426664786203	-2.28312959437472	-5.57856006888141
H	-3.28067677647110	0.22586528369833	-2.67089895634814
H	-2.27194008709082	-1.17344371769101	-3.09110033753146
H	-2.83214916639422	-0.94905365504118	-1.41892059470307
H	-4.36276546922628	-4.12017708616952	-1.29715777531255
H	-3.75491850221153	-4.44073234873017	-2.93662847763870
H	-5.48920449799267	-4.60344965661389	-2.57868571459159
H	-8.41415126014469	-2.07859255138593	0.22430615840090
Sn	-8.35156165994351	0.92057420066602	1.30350917654463
H	-6.89628993194782	-0.38292290888024	1.13640009253030
C	-8.64724117826520	1.33443544372766	3.39789318513567
C	-10.21433800324990	0.27968178384530	0.43432586410566
C	-7.64266429621185	2.69819585981243	0.32283911463398
H	-10.63972599921020	-0.53971728413178	1.01384343727957
H	-10.04985691600230	-0.05240806877208	-0.59048456892782
H	-10.91592959247430	1.11688057717410	0.43169510855079
H	-6.78647660666518	3.10804825692868	0.85929969230847
H	-3.44687875993246	3.44689211050685	0.29651703567727
H	-7.34357465769485	2.45793538060937	-0.69719615748827
H	-8.99957513181961	0.44251554972657	3.91628923644624
H	-9.39186779447587	2.12537236712515	3.50964496276901
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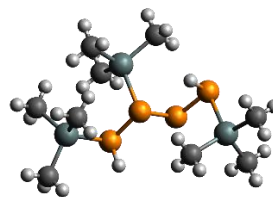
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E = -1358.81350048 Eh

0 1			
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P	-6.92746270086229	-0.95820515597042	-0.93151703960346
P	-6.50810865399932	-0.58686084180171	-3.06023182666939
Sn	-4.45141983510416	-2.06319339380828	-3.11309769604112
C	-2.83460619495955	-0.89494980586637	-2.32974917992692
C	-4.10123014934526	-2.57767638827932	-5.16479123497512
C	-4.73722863491022	-3.82186162231797	-1.91987314179033
H	-3.92510337704351	-1.67565346898829	-5.75127684349417
H	-4.96704068266917	-3.10069326244036	-5.57121812470835
H	-3.22760535431528	-3.22656981865285	-5.24247656531170
H	-2.69137485031020	0.00379962491828	-2.92988621942461
H	-1.91335970514479	-1.47946259953205	-2.34172561355698
H	-3.05665222761502	-0.60412284827113	-1.30274140466292
H	-5.14491693846533	-3.55703933206570	-0.94396388844507
H	-3.77214039353599	-4.31090826369086	-1.77754506363292
H	-5.41972355568881	-4.51148304454897	-2.41526343542571
H	-9.06850014431271	-1.38477418955026	-2.62849654687140
H	-7.94978135716375	0.02605118264900	-0.83189295441542

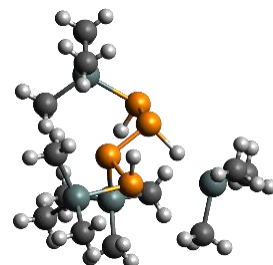
Vb[•]



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P	-6.42391456269313	-4.97264520348187	-0.16700244892630
P	-6.78102635986773	-3.33466560249838	-1.54507588917249
Sn	-4.42649891301782	-3.16198515307520	-2.47371539294716
C	-3.01732288177195	-3.15408771932245	-0.86317792154839
C	-4.26947650475719	-1.27981941705203	-3.50319705756916
C	-4.06182195163694	-4.82362214472022	-3.77596016231345
H	-4.52532562388950	-0.47163049705636	-2.81701856446022
H	-4.93328511503755	-1.23393479834264	-4.36520584632714
H	-3.24167920418605	-1.13973511082936	-3.84273608409784
H	-3.17944429446094	-2.29154350845304	-0.21719055652893
H	-2.00956912619665	-3.10106494629046	-1.27883345161794
H	-3.11262966907273	-4.06244894337978	-0.26914347686065
H	-4.20840077258681	-5.75000719516083	-3.22091191780205
H	-3.03590974306870	-4.78074485562274	-4.14499467294736
H	-4.74753114654072	-4.81027278571185	-4.62253264634329
H	-5.69611853621101	-2.53575086740559	0.99000347248316
Sn	-8.02397915700126	-3.55521873446478	2.55182439466415
C	-8.67967400362937	-5.49853108488758	3.17066121496385
C	-9.36962147232030	-2.72989926759857	1.10172351370682
C	-7.83899955093049	-2.23595721961532	4.23791834059465
H	-7.16129484719730	-2.66585074879534	4.97563144846961
H	-8.81751287529694	-2.08684792243061	4.69758282046739
H	-7.44870115635907	-1.26945516314528	3.91845842371945
H	-9.57154939374129	-3.46866801336762	0.32613826076951
H	-8.92701767883223	-1.84932406393440	0.63681919648867
H	-10.30656460210460	-2.45192797783859	1.58783839660241
H	-8.74447025873924	-6.15370462693434	2.30116120308026
H	-9.66271522916806	-5.42935270380774	3.63817264718840
H	-7.97624766171799	-5.92541685865808	3.88514691829826
H	-10.73674892299070	-2.97217594307648	-5.01865702676782
H	-10.11787420012980	-2.41598684114547	-6.58634966538913
H	-8.15483086498783	-0.00926873012334	-4.75938007447725
H	-8.89532652723246	-0.68969405343474	-3.29323544219594
C	-9.94765511757789	-3.10681687470093	-5.75902575689358
C	-8.05162410395802	-0.76566991024124	-3.97955958745158
H	-9.98991733388480	-4.12814475227884	-6.13808583168272
H	-7.13326916834989	-0.58342407512996	-3.42377763483441
Sn	-8.03490649035606	-2.71885795657928	-4.86771472889202
H	-6.66514465756639	-2.10506151393630	-7.13511408856683
C	-6.51985617723942	-2.88243604763684	-6.38315945555975
H	-5.51948356708013	-2.78008598206241	-5.96410595201143
H	-6.59843689836340	-3.85736448531691	-6.86548662745408
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TS(Vb[•]→VIb)



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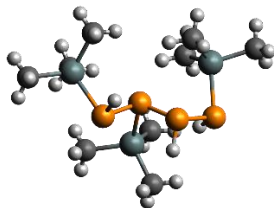
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P	-7.85467692201216	-5.49299817168387	0.26888061063396
P	-7.62727921850583	-4.09375800297926	-1.37165159360409
Sn	-5.24680313018424	-4.35765674717705	-2.21808425944878
C	-4.04575149254596	-5.76780416647068	-1.12768830118092
C	-4.34037845646950	-2.42284823009974	-2.00357900103274
C	-5.26835500106664	-4.86073140507021	-4.30914806076478
H	-4.32041258749037	-2.12920460665447	-0.95410246836908
H	-4.89960687017406	-1.67425787365576	-2.56571341142759
H	-3.31720225911354	-2.45509802262567	-2.38242000402909

Unravelling White Phosphorus 4

H	-3.23718368143724	-5.23258017266748	-0.62798023142431
H	-3.61854377919577	-6.49062502977802	-1.82340319108654
H	-4.63357523223798	-6.29575961416057	-0.37815072865334
H	-4.48981901418821	-5.59712639845441	-4.51044293272487
H	-5.07329541136178	-3.96452873177092	-4.89809012166139
H	-6.22920928854723	-5.28368918399065	-4.60131357646057
H	-5.40755080885521	-4.22368759865104	0.84713834486522
Sn	-7.46647999262726	-2.52994566369012	2.18032574534139
C	-9.56836576548836	-2.59073310127295	1.77437586560621
C	-6.50819801746243	-1.02733081132008	0.98639107522299
C	-7.13343479720841	-2.11325618260970	4.26184439545381
H	-7.61890542430519	-2.87162700852770	4.87656693763399
H	-7.54145960215841	-1.13404202144909	4.51803965641103
H	-6.06466147580738	-2.11787436219800	4.47808790956128
H	-6.68783542692519	-1.23561631115213	-0.06823518146088
H	-5.43408695539394	-1.02203137339795	1.17432319084966
H	-6.91307756221704	-0.04418213234806	1.23278534992142
H	-9.72743738441495	-2.65883037549892	0.69848810615737
H	-10.03476572948390	-1.67984893664471	2.15378340327467
H	-10.02531718419930	-3.45524696806710	2.25505452816070
H	-11.05491239357580	-4.52656375091572	-5.95831841555907
H	-10.52223521867200	-2.99513455012306	-6.67896192422115
H	-10.94972804217280	-1.19838336652610	-3.47801439642008
H	-11.72291294339730	-2.72985098055381	-3.01585192846147
C	-10.19671873395170	-3.87402165500840	-6.12020629549134
C	-10.77699450578070	-2.18932900187754	-3.0553828953978
H	-9.45111932420986	-4.41073420775614	-6.70728869058644
H	-10.38437809051690	-2.08180632164073	-2.04385545939242
Sn	-9.35389039209507	-3.26759087935731	-4.24092242468033
H	-7.97030680338453	-1.08931249376408	-5.04877624127670
C	-7.64220563573522	-2.02113570380083	-4.58517274414520
H	-7.15686581063822	-1.78569269668308	-3.63756354023601
H	-6.92888562134879	-2.51230641672861	-5.24570877176812
H	-9.90317854618216	-5.30870219715430	-2.23184557766401
H	-4.81879662514021	-7.98775068553314	-3.36684590780727
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C	-5.83244101215060	-8.38650357092304	-3.38521789267559
H	-6.45828442530339	-7.75692393618684	-4.01650371300106
H	-4.33986428879814	-9.20771209805662	-0.15400982137173
H	-5.28067368993320	-10.66539494673340	-0.53394890148079
C	-5.33892393134983	-9.64443332047043	-0.15135133420537
Sn	-6.65969158202707	-8.47973837168835	-1.39848361462194
H	-7.05146927337194	-6.81802620846770	-0.46948933265204
H	-5.71017748717568	-9.67058696959352	-0.87314658991273
C	-8.58546453932532	-9.43233593775727	-1.50064674671998
H	-8.48561616849087	-10.43111024230310	-1.92989504158698
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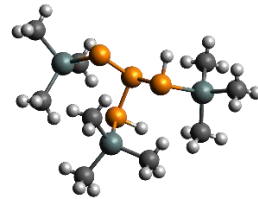


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P	-7.29872991270211	-5.48346844992108	0.52030887785442
P	-7.24089167629910	-4.12528631233740	-1.20550514302036
Sn	-4.84207311871073	-4.26717469997291	-1.98188530027342
C	-8.88420404797401	-6.02655027839918	-1.22058839438914
C	-3.77691919429200	-2.51453596953394	-1.34524656872189
C	-4.86012240996373	-4.33604587913448	-4.12765812433656
H	-3.60400394035789	-2.54442893095014	-0.26925669866999
H	-4.34858708952307	-1.61780147518588	-1.58481938914087
H	-2.81374452474086	-2.46868428283059	-1.85608956874701
H	-2.86685309575962	-6.07049304674158	-1.61317345738501
H	-4.42503945603228	-6.91809851471150	-1.53827162570449
H	-3.84197309201971	-6.00283344716806	-0.13162808710328
H	-3.85163720058310	-4.54386210820462	-4.48893674093097
H	-5.19059374536003	-3.38003796296851	-4.53225458033825
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H	-5.06756775527711	-3.88293130103895	1.14477153843393
Sn	-7.42538493879148	-2.27833864575711	2.06290040435959
C	-9.47830511957606	-2.68574215592831	1.60473379726243
C	-6.59952038134543	-0.81017973422337	0.73528603119598
C	-7.26762923790434	-1.57373078511745	4.08513772765091
H	-7.72628084236628	-2.29227893000470	4.76530705642236
H	-7.77726694865424	-0.61428908099864	4.18781982928220
H	-6.22050521803068	-1.44872058013748	4.36218208073643
H	-6.76728067833919	-1.12539541953688	-0.29411294319750
H	-5.52871117496534	-0.70239861644251	0.90906891865346
H	-7.08431769259681	0.15288036393560	0.903833008999204
H	-9.58791075547061	-2.84709899673507	0.53324095634225
H	-10.09249059765530	-1.83598038090802	1.90783778800303
H	-9.81755986536072	-3.57629978334902	2.13354336339469
H	-10.69851616785390	-5.18154360038252	-5.68913973872550

H	-10.46395509903560	-3.57406991249594	-6.40416732783002
H	-11.37494579086290	-2.11442424308529	-3.22886476594799
H	-11.56128378686750	-3.73959107447577	-2.53636300654332
C	-9.97817946473895	-4.37932539187539	-5.85081339927352
C	-10.85228662965750	-2.93600861488524	-2.73631666582929
H	-9.14792445884578	-4.76496502264980	-6.44319102760191
H	-10.44429746477630	-2.58052192697828	-4.59708606426663
Sn	-9.24825289019481	-3.64022511419744	-3.97157064064180
H	-8.44037506795487	-1.13386711372408	-4.59708606426663
C	-7.87828002405749	-2.02265405958610	-4.30595004908643
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H	-7.17344064026215	-2.26972736752797	-5.09937177244018
H	-9.25612380856439	-5.78524811404701	-1.99465138443253
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Vc'

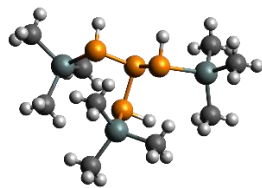


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P	-5.75978670985105	-0.99227163075292	-0.48235799974702
Sn	-4.40357060531706	-2.28739462965945	-2.16287126633852
C	-3.31159796536687	-3.69957823607334	-0.96514765235852
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C	-5.64178936758486	-3.32879075353360	-3.56986912033409
H	-2.45268459814321	-0.40351909280853	-2.42968952223513
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H	-2.24822213050296	-1.64552598507425	-3.67959951793544
H	-2.68032788229769	-3.17344178224329	-0.24844644714872
H	-2.67924391246024	-4.31865293882235	-1.60387798250529
H	-4.00128331982889	-4.34368370473470	-0.41937517650367
H	-6.38588023100535	-3.92193214131724	-3.03863990261520
H	-5.02402030857416	-3.99068595292199	-4.17916975287816
H	-6.14652775766359	-2.61083610752975	-4.21493359247182
Sn	-5.40679100855550	2.70416342066770	-2.86287320769521
C	-3.99497028585515	3.18078191120749	-4.41130496175031
C	-4.36015226098546	2.43359802181506	-1.02027221586887
C	-6.87140686345925	4.26802516711667	-2.74413084622821
H	-7.43898377172798	4.3215963100213	-3.67362443656814
H	-6.36827434049763	5.22336388753483	-2.58456810391181
H	-7.54807918977876	4.07353038406870	-1.91308066226891
H	-3.60686410768973	1.65400603828871	-1.13191033088445
H	-5.05627005681253	2.14584098091420	-0.23321319880730
H	-3.86945563476496	3.36914364177325	-0.74609153856592
H	-3.28684004884345	2.36040989864656	-4.53289079232692
H	-3.44531379811010	4.08468637751700	-4.14299018940336
H	-4.50661424466377	3.34949747173709	-5.35941976730987
H	-7.59541617639168	0.99753995219123	-4.13761633929466
Sn	-10.43643132575770	1.37622736670729	-1.81358268020068
C	-10.23575786166220	2.23405223935386	-3.77022592298135
C	-11.71076914593570	2.61135205848901	-0.60372614999553
C	-11.21197218647130	-0.61639295935594	-1.95509996944110
H	-8.66078178865854	5.6827314935695	0.40090955731065
H	-11.31288143656990	3.62510153851210	-0.55449863629718
H	-11.77584645540910	2.20785891596277	0.40702414150741
H	-12.71224692171550	2.64425492551300	-1.03538084348363
H	-9.56838349399506	3.09499012413924	-3.74026527983208
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H	-10.47981576866560	-1.25812674879168	-2.44546681255083
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4 Unravelling White Phosphorus

VIc

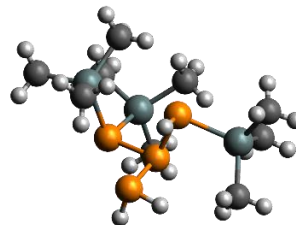


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P	-5.64592242205722	-0.91412914409895	-0.64408337433819
Sn	-4.33869391787121	-2.31391888531893	-2.29507187380191
C	-3.25227460999053	3.69570468894254	-1.05668973062598
C	-2.93236243102963	-1.04340948340318	-3.29801329470293
C	-5.59372419244663	-3.37276262897455	-3.67098421151396
H	-2.45573945457847	-0.37665757419747	-2.57830684855119
H	-3.44603551773813	-0.45017014610101	-4.05360608526787
H	-2.16247281463203	-1.64992917928048	-3.77770670698676
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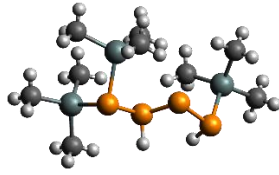


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H	-4.31900477155113	-0.97118234301117	-0.18211158458698
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Unravelling White Phosphorus 4

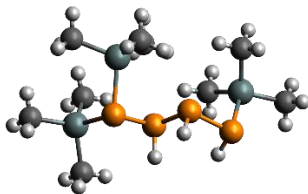
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P	-7.34480344977807	1.29354587943684	-4.34441522056762	
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H	-8.2016823523824	0.62459507318625	-0.38432747041477	
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C	-11.05901812387920	1.83232660081844	1.31986662156708	
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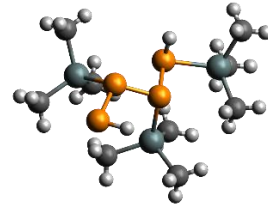


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H	-6.66270015273692	0.15411019808851	0.36428709588788	
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C	-10.78784469476790	1.79784997821574	1.17788951531751
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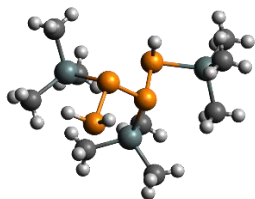


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C	-10.03395704454410	-0.79130597788799	-0.83532466495972	
H	-10.90470186612620	-4.49935959517024	1.43031824991314	
H	-11.01552892181910	-2.85219178734271	2.08784708811242	
H	-9.45579740268801	-3.47876074930737	1.51077070722568	
H	-13.48792089777310	-3.63805021805916	-0.88225517380551	
H	-13.27408831868870	-2.2275431300782	-1.93480768975566	
H	-13.51219393860790	-2.00324819316879	-0.18654136813377	
H	-9.39045423036760	-0.74430799697429	-1.71086199629044	
H	-9.42324954062992	-0.60063466164546	0.04715478949346	
H	-10.8107537112430	-0.02948302894795	-0.91387387320024	

4 Unravelling White Phosphorus

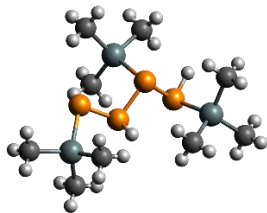
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E = -2368.40412701 Eh

0 1			
P	-8.24613127498912	-3.41617993444891	-3.52266751172572
P	-9.58374314890292	-4.48951522984253	-2.15204370242743
P	-7.00169050097489	-2.40910228570359	-1.98478183934464
Sn	-4.91207038199609	-2.54311811307356	-3.39696659742017
C	-3.35200488399598	-1.42977786427407	-2.42853036176941
C	-5.34350274143370	-1.70027776113714	-5.32217098445965
C	-4.37687505950817	-4.60634316295812	-3.61273856865094
H	-5.70086921900086	-0.67531813200738	-5.22498032110791
H	-6.10431000070742	-2.30203591036410	-5.81986372101149
H	-4.43982750240759	-1.70218242134384	-5.93355666449359
H	-3.64364498639236	-0.38329271684231	-2.33665822810354
H	-2.43238487848506	-1.49134679918354	-3.01247691436917
H	-3.16498050033782	-1.83206837428076	-1.43261274617310
H	-4.03123150336290	-5.00664117019816	-2.65945883286789
H	-3.58508781642474	-4.71908193131633	-4.35482781515548
H	-5.25520013364008	-5.16438285067825	-3.93829812198766
Sn	-9.39792912347243	-1.42099892250861	-4.58658443921802
C	-9.22750947572349	-1.77957748116259	-6.69629259991557
C	-8.36705714429881	0.39888902365466	-4.07189202505605
C	-11.48876497283670	-1.19706535557017	-4.15572982839771
H	-12.00256318539320	-2.14710764938538	-4.29607218815576
H	-11.89269588243530	-0.46765267749370	-4.86068202983284
H	-11.65287449842220	-0.83348244353393	-3.14289728169851
H	-7.75843417055314	0.72696546760624	-4.91495522309911
H	-7.72439323685526	0.24947651348374	-3.20360796548780
H	-9.09697048461559	1.17470783648820	-3.83699803678321
H	-8.18154290434029	-1.77775989144993	-7.0033801109029
H	-9.75880074521944	-1.00226506693939	-7.24818059499638
H	-9.66555917686610	-2.74822956094783	-6.93871162082047
H	-6.66368149512147	-3.63510754431872	-1.34047205842879
P	-11.13754482226870	-4.98903279321219	-3.65083201868712
Sn	-10.86515001179890	-2.84882191978305	-0.70308045821229
H	-12.08221486010140	-5.46433646296313	-2.70235965859097
H	-10.65427678984030	-6.29427354775547	-3.93867148622183
C	-12.97098833152240	-2.93436160765707	-1.13242092025044
C	-10.55792227360820	-3.58778009030832	1.28944431981534
C	-10.14031473758510	-0.83183468116757	-0.78774284195085
H	-10.84160488870230	-4.63886861257022	1.34871945291814
H	-11.15860329634210	-3.01650624839215	1.99916172058924
H	-9.50519992338515	-3.49291438934837	1.55777676039859
H	-13.37528663227470	-3.89536203212493	-0.81366402981877
H	-13.16488466882600	-2.80064105405047	-2.19583923794584
H	-13.47600075436530	-2.14046767313643	-0.57920553130568
H	-9.57135735471109	-0.64583343846582	-1.69594670062441
H	-9.48149124001825	-0.66265019840618	0.06379830673514
H	-10.98113838093320	-0.13801867003902	-0.74017874279959

Vg'

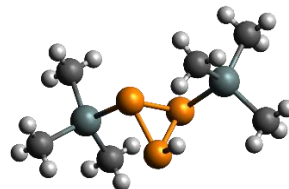


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P	-7.93725349790133	-1.60570089117841	-4.42632495058182
P	-8.78984275799899	-0.37199850837719	-2.81102280311937
P	-5.96411794677413	-0.84310823647695	-4.71553012107948
Sn	-7.17247523714521	-1.20056978726531	-1.03928592536721
C	-8.28774163916248	-1.18698829718509	0.79533761737496
C	-5.52872372216703	0.16606949507566	-0.89794880976098
C	-6.52963042752549	-3.19305964385551	-1.49314610638590
H	-5.88800198929300	1.15621491401034	-0.61709243866882
H	-5.02189122479387	0.22711979276429	-1.86046773513772
H	-4.82525004401122	-0.18575774598704	-0.14144351470266
H	-8.77842094709551	-0.22364521518790	0.93679664216375
H	-7.60855137028161	-1.36262986513683	1.63123371594063
H	-9.04257770609080	-1.97321918935255	0.78155968429396
H	-7.39009823026420	-3.78962544367036	-1.79681198816240

H	-6.07641342613376	-3.63796884230382	-0.60582614938835
H	-5.80106277581175	-3.17865850128343	-2.30306042804989
H	-10.78620077142440	-1.15756208411412	-1.12200067486336
Sn	-12.17033452509960	-0.62469708985099	-3.63564318954315
C	-14.00938913336340	-1.73083887956107	-3.55434580048134
C	-11.51679062346870	-0.45413440192957	-5.67314823939399
C	-12.41563391198230	1.33426269644004	-2.79953184407351
H	-12.85034222124420	1.26481977389256	-1.80196327565847
H	-13.06790806059780	1.94015555235089	-3.43015521961821
H	-11.43915705445550	1.81451347700160	-2.73031609202890
H	-11.22959374885490	-1.42838627159805	-6.06930521953946
H	-10.66430245744440	0.22338076955789	-5.73163354933372
H	-12.32857738586860	-0.05108039713956	-6.28104720669733
H	-13.85841119701980	-2.73633988183875	-3.94785872964099
H	-14.77047362783350	-1.22701055103634	-4.15233538222398
H	-14.36228843403090	-1.80455157159440	-2.52532166829830
Sn	-5.98323886070073	-1.30758869617922	-7.18618022276234
C	-3.98967921621590	-1.01983394889487	-7.92258534609272
C	-7.34145644991667	0.05276017308722	-8.14497834525916
C	-6.61811215812045	-3.33009941426185	-7.52638021678651
H	-8.34107202945251	-0.05193019997212	-7.72224930320757
H	-7.38700365043710	-0.16532132033337	-9.21327464773068
H	-7.00455830135198	1.07985261084340	-8.00545257733665
H	-6.59561502333549	-3.55171808275112	-8.59460857587660
H	-7.63318485013096	-3.46852360756522	-7.15356212006017
H	-5.9525553328582	-4.01924734546705	-7.00344925370478
H	-3.32052066109532	-1.76174141221288	-7.48644039344175
H	-3.63044981325501	-0.02398518496167	-7.66258783360990
H	-3.98022420787244	-1.12726964890648	-9.00836185385501
H	-8.66076353000644	-1.07209074102202	-5.52782508894217

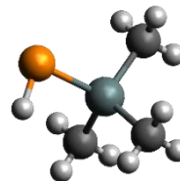
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E = -1692.10683267 Eh

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P	-7.71612665207127	-2.44840118716531	-4.69941932758126
P	-8.52260325153740	-2.27422295311125	-2.65071680699681
P	-7.05497569896513	-0.80289203112856	-3.40206495126797
Sn	-6.94842174321703	-3.91601733680203	-1.54787340127736
C	-6.02219498849969	-2.91710568093506	-0.11187813294250
C	-5.46596336122825	-4.60902869938543	-2.93187633677570
C	-8.13175846643720	-5.56694196377306	-0.85406297355236
H	-5.03287587260365	-3.77884269489670	-3.48959166630049
H	-5.91645888755963	-5.30598565694900	-3.63757567176524
H	-4.67486934831865	-5.11608689135992	-2.37678253644247
H	-5.41909550152932	-2.08318051920890	-0.24799620112231
H	-5.37918071325700	-3.61086175381110	-0.65568909206281
H	-6.78401033494735	-2.53426836410627	-0.79121248864311
H	-8.90157217382089	-5.21591101391594	-0.16638990066072
H	-7.49683802741291	-6.28746784369112	-0.33606559636875
H	-8.61143857488295	-6.06280272482455	-1.69819964982998
Sn	-9.54437131641580	-1.13019492357225	-5.84717379228794
C	-10.98441674316820	-2.55769452156875	-6.55175292590988
C	-8.65195581207507	-0.09933482022916	-7.50500732581518
C	-10.45924695031920	0.26314740942388	-4.50043633634797
H	-10.99223964557280	-0.27031928473214	-3.71424583553825
H	-11.16250097005020	0.88551069011284	-5.0562896582454
H	-9.70234870750874	0.90153972709970	-4.04489616285366
H	-8.18046230138932	-0.81220226192028	-8.18173273260952
H	-7.89755730158231	0.59967781568621	-7.14361695997025
H	-9.41635467804922	0.45471522524192	-8.05204803270257
H	-10.50984227897640	-3.26589520157003	-7.23147270938441
H	-11.78978321553040	-2.04514121189011	-7.08007079327382
H	-11.40744324578190	-3.10546686021507	-5.70938587828382
H	-5.84884323729148	-1.44347446679349	-2.98693554290511

(Me₃Sn)HP' = XIb'



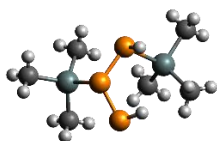
E = -675.68135662 Eh

0 2			
P	-2.04379445914334	1.02420699181242	-1.05586605321901

Sn	0.02017449621090	0.01765076694463	-0.03142632070508
C	-0.08876049093769	0.22964690246720	2.10049820108619
C	1.75847419366742	1.04342106938557	-0.76720497365601
C	0.14482498475284	-2.06337830198265	-0.55190878133248
H	1.69221949965412	2.10724944172850	-0.53887130700074
H	1.83934679582860	0.91810492725541	-1.84718939506377
H	2.65290946468595	0.63421241446371	-0.29458225208024
H	-0.13497387268385	1.28405898995917	2.37428145407432
H	0.79472345895238	-0.21488084591420	2.56133805643013
H	-0.97653803160648	-0.27259483290225	2.48577145474191
H	-0.70940304268924	-2.60532501799211	-0.14601920849694
H	1.06243568811034	-2.48942916993056	-0.14284539821437
H	0.15347177518984	-2.17770709554591	-1.63604382776817
H	-1.59464045999178	0.67751376025108	-2.36530164879572

4.8.7.5 Fourth P-P cleavage

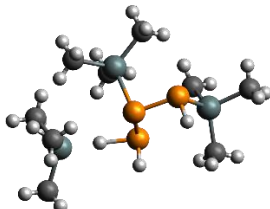
VIIa•



E = -1692.66305762 Eh

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P	-7.44517683831796	-2.10486246962328	-5.11252275106819
P	-7.47113111476989	-4.09723968192506	-4.35036926208966
P	-6.32977788345552	-0.64420108576472	-3.90301479189258
Sn	-4.77549116509255	-2.03943510533161	-2.48840666704193
C	-3.51288317279726	-0.63209655150895	-1.46730668705589
C	-3.59629185822836	-3.30341204350238	-3.75749676559434
C	-5.81901298731289	-3.21999687326140	-1.02962477020353
H	-2.90320167272722	-2.71422162757810	-4.35709936504908
H	-4.25021900170069	-3.87882783646793	-4.41253235928643
H	-3.02471343708541	-3.99576375160541	-3.13745307481234
H	-2.97323036064480	-0.01568653470548	-2.18639010467637
H	-2.79267018941833	-1.16417661723735	-0.84360573406293
H	-4.11531178875449	-0.01693425514928	-0.83066918267536
H	-6.79757885629030	-2.78872613126670	-0.81943625431063
H	-5.23844293117685	-3.24785345429349	-0.10592939245014
H	-5.95325280705261	-4.23580466651786	-1.40116558696642
Sn	-5.99569841597315	-2.29482555094054	-7.16312923755323
C	-5.50728505589244	-4.35597744789624	-7.48207977960910
C	-4.24660496877530	-1.07853995023064	-6.92911260882379
C	-7.18529286826720	-1.55023521564288	-8.78061396423139
H	-8.08559493297192	-2.15598049259582	-8.88607751677237
H	-6.62084392506128	-1.58525389832345	-9.71361845183336
H	-7.47698937795010	-0.51914124970252	-8.57961441797091
H	-3.52914595525441	-1.56859464101321	-6.27225885197887
H	-4.52142102087260	-0.11471955854574	-6.50091042833581
H	-3.78552872032838	-0.91862044499469	-7.90491649880007
H	-4.88119822217294	-4.72737267534083	-6.67121849343512
H	-4.96862077223122	-4.45910985068953	-8.42528911626300
H	-6.41791594253139	-4.95329438402998	-7.52471667736660
H	-7.31865502623081	-0.49659935300420	-2.89197940586041
H	-7.90540873066154	-3.69250511160918	-3.05586180192992

TS(VIIa•→VIIIa)



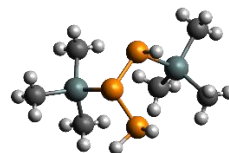
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P	-6.66203174162530	-1.05545806812200	-3.37121625367350
Sn	-4.70806326942698	-2.36231052718693	-2.44319028725576
C	-3.31846913362418	-0.83810035170524	-1.83015331303736
C	-3.76422321352489	-3.53068873779222	-3.97295138057819
C	-5.20793693365307	-3.54715597114237	-0.72304027563340
H	-3.76219715094080	-2.99356856576296	-4.92189954656250
H	-4.29422809783532	-4.47484893181935	-4.09288946836417
H	-2.73107383282042	-3.72982202271177	-3.68373504709125
H	-3.00299009367329	-0.24942233867478	-2.69207372486078

H	-2.44047658675695	-1.30442675685951	-1.37927956141870
H	-3.77646342968860	-0.1709889570608	-1.09910812536937
H	-6.10723573639667	-3.15187195803602	-0.25044901550916
H	-4.38710012454015	-3.52140404932157	-0.00406596249473
H	-5.39457111126258	-4.57593052034292	-1.03023725186580
Sn	-7.20929903403341	-2.65593449699869	-6.52622941264666
C	-6.24562256295098	-4.53989321380539	-6.88206343665411
C	-5.85469163321960	-1.03936414089032	-6.90562526622342
C	-8.89794239027317	-2.47983990104607	-7.8421733355369
H	-9.67148143263283	-3.19897755814061	-7.57391557073251
H	-8.58885429994625	-2.66241260144472	-8.87277196934085
H	-9.31869252828668	-1.47646280982968	-7.77080292897263
H	-4.97666543002152	-1.11635986963832	-6.26437882347323
H	-6.34556577332608	-0.08716406557589	-6.70687945616517
H	-5.53814015744058	-1.07169112367360	-7.94951494634178
H	-5.30283898626498	-4.59278752028482	-6.33930312157458
H	-6.04827651921634	-4.64071112996421	-7.95075986835153
H	-6.88285148553220	-5.36421001548604	-6.56170446434948
H	-7.28391059759830	-0.9219206563781	-2.09883047386441
H	-8.35817562332067	-4.48238220276616	-2.33867510729858
H	-8.71701599050021	-5.24679051362432	-4.42408353212650
Sn	-10.28452419145470	-5.77536540610326	-5.36235651493691
H	-10.58734799536520	-8.24834008871358	-4.24660070218792
H	-12.37975288393840	-4.16847293159113	-4.71926789837198
H	-9.06501620805097	-7.30624603179177	-7.26590251696881
H	-9.27225902581390	-5.66266346226494	-7.90053303476831
H	-11.04163562050280	-3.15924671963875	-5.29738199195764
H	-11.47016460876210	-7.05756679653473	-3.27022148591572
C	-11.23857316695040	-7.37516172736802	-4.28708984186894
C	-11.60044240805990	-4.07787348684298	-5.47671484886199
C	-9.75001640781800	-6.46077253483186	-7.33260416216459
H	-12.16710955630490	-7.64814471787040	-4.79194557164910
H	-12.06442901112100	-4.02900775880699	-6.46304889834308
H	-10.65246547390990	-6.77781830616387	-7.85897193308418

VIIIa

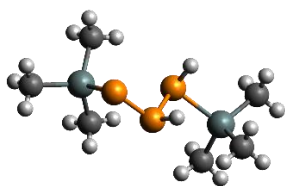


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P	-6.65840765788958	-1.05428652934832	-3.38349610497698
Sn	-4.69415651464597	-2.348990114489330	-2.46488301745109
C	-3.34249423952388	-0.82137302336307	-1.78735735161034
C	-3.73071375471220	-3.49163552155435	-4.00081487023251
C	-5.21402094737378	-3.58593351049681	-0.78806312114593
H	-3.72831729259594	-2.94997532224002	-4.94689674851977
H	-4.25373884142247	-4.43888719664883	-4.12781251910179
H	-2.69793834785937	-3.68692091699165	-3.70799019141166
H	-3.00737172629552	-0.21511733828473	-2.62928690133471
H	-2.47406585712937	-1.28477921773088	-1.31575295045168
H	-3.83261767662885	-0.17211153925840	-1.06121309888233
H	-6.06792470059352	-3.16018329693439	-0.26040880787082
H	-4.36862152448617	-3.64643357677593	-0.10053242642582
H	-5.47351546013161	-4.58554512305791	-1.13530275876190
Sn	-7.20824178450891	-2.6519598244046	-6.53114920760265
C	-6.28520869636342	-4.56155321936686	-6.85626275079059
C	-5.81714827397589	-1.06506896736914	-6.90092343695055
C	-8.89427261667552	-2.47496649696900	-7.84461984655267
H	-9.62972583908914	-3.24575967473603	-7.61241497096570
H	-5.7625820086342	-2.59165459849790	-8.88187519430166
H	-9.36128926771350	-1.49740808769954	-7.72363471399626
H	-4.94715652086280	-1.15723262841754	-6.25100709024171
H	-6.28986979720862	-0.10191150229459	-6.71173879818182
H	-5.49118277145049	-1.10927687132157	-7.94148194770572
H	-5.39572484636008	-4.67133689616738	-6.23755712313145
H	-5.99982217836132	-4.63892533213646	-7.90686173643297
H	-6.98050991206509	-5.36850395765331	-6.62387896246118
H	-7.26880859991412	-0.91286664983687	-2.10665990552812
H	-8.35955157817937	-4.44748631656579	-2.30770117213790
H	-8.45655706118207	-5.17982893424675	-4.23497608792134

4 Unravelling White Phosphorus

VIIb'

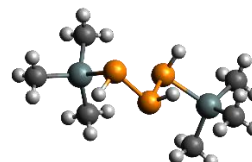


E = -1692.66005077 Eh

0 2		
P	-3.37082032476186	-0.00029262466348
P	-3.23909381607283	-1.03916851340757
P	-2.10132445615479	1.71900807651929
Sn	0.01271226836396	0.43528424971969
C	0.38220719170968	0.35922836977434
C	1.58456831988722	1.55174365984090
C	-0.06585072735740	-1.54317227990816
H	1.61907757740406	2.56503921906497
H	1.41260076406088	1.60499635838004
H	2.54507575231006	1.06701327684334
H	0.31862016773385	1.35819751286840
H	1.38012529445788	-0.04355901202718
H	-0.36020956866397	-0.28416641820324
H	-0.69477102536465	-2.18251181528064
H	0.94270970041352	-1.95873377993301
H	-0.47375359499651	-1.51099263496587
H	-4.63809261255488	0.62965383423604
Sn	-5.05496780607016	-2.72804300612559
C	-4.12619119977079	-4.26595114733744
C	-5.72362843644392	-3.50001642992378
C	-6.69606933389212	-1.86251740007265
H	-7.13197414959818	-1.04004588552002
H	-7.46141715079925	-2.62181020845494
H	-6.35397755330902	-1.48679357019089
H	-3.68616678474402	-3.83162091783872
H	-4.86463054553345	-5.01301079631356
H	-3.34062229517664	-4.75236329636299
H	-4.88376106777779	-3.92522856597963
H	-6.46850453026430	-4.27974287913388
H	-6.17238239011297	-2.70550493424754
H	-4.01923766692152	-0.14540171881418

H	-6.12029706487899	-2.81236225868246	3.61448688238936
H	-4.42686568866542	-0.21858728865610	1.47350431042905
Sn	-2.55434783934016	-1.16495794678515	-4.86066215053144
C	-3.36448414855817	-3.09787001662164	-4.37096526605705
H	-3.51482331457669	-3.66946150940575	-5.28924153917207
H	-4.31931929053975	-2.97255419370363	-3.86125750210366
H	-2.68532505013142	-3.64334925998534	-3.71638437682605
C	-0.58187562372758	-1.41231641511743	-5.69902611211778
H	0.08214284770364	-1.89741092702060	-4.98313052101280
H	-0.16034879703486	-0.44520919243018	-5.97400417118082
H	-0.64888456901636	-2.03454485194320	-6.59386085455626
C	-3.82824294317790	-0.23505221908783	-6.32523360440483
H	-3.47150358981867	0.76772635867183	-6.56026173085997
H	-4.84744734739188	-0.16751083918647	-5.94410624033742
H	-3.83080007519597	-0.83443171594888	-7.23779490024084
H	-2.50603567349435	0.00430335880938	-3.31490002473385

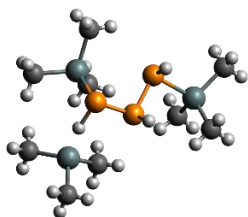
VIIIb



E = -1693.27546294 Eh

0 1		
P	-3.72357276694773	-0.51204995308379
P	-3.304057747038144	-1.43785026321918
P	-2.15958888114760	1.05271948114302
Sn	-0.18802769019653	-0.53237816432819
C	0.60234822607941	-0.66961970051922
C	1.26342738010122	0.38574581600189
C	-0.69881735605051	-2.47285632978066
H	1.46096015329871	1.40874086956027
H	0.89437562496942	0.40384484018720
H	2.19657428331636	-0.17901122952058
H	0.75452989032787	0.32904290753745
H	1.55766311427234	-1.19660811368004
H	-0.10010257967382	-1.21223246737953
H	-1.25397359200779	-3.03465966423202
H	0.21791805274286	-3.01189290994295
H	-1.30936072691040	-2.37886347253792
H	-4.80953785033532	0.31695497560322
Sn	-5.39426449749970	-2.83865972049013
C	-5.06017637653748	-4.44194226720782
C	-5.65561522215878	-3.58008433654642
C	-7.09809991442706	-1.68089622027585
H	-7.20796312578748	-0.81162568510119
H	-8.00027065939429	-2.29113019050553
H	-6.97778202777688	-1.34276935587309
H	-4.78965799597071	-4.03316647466003
H	-5.96464926719377	-5.04230426860881
H	-4.24990631211049	-5.08006906648144
H	-4.75814341246388	-4.10728515617268
H	-6.50069430981112	-4.26967070546743
H	-5.84949733537889	-2.75538523522894
H	-3.77970269327382	-0.41174471578332
H	-2.08241439167257	1.20477677659395

TS(VIIb'→VIIIb)

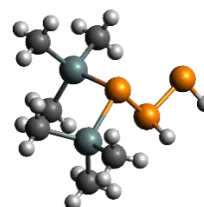


E = -2027.09620347 Eh

im. freq. = 750.49 *i*

0 2		
P	-4.20531842128533	-0.76573660837834
P	-3.76376457894695	-1.28380338393054
P	-2.71986161841542	0.76807149707787
Sn	-0.64712854911790	-0.48812462150463
C	-0.09902792006659	-0.08279124878290
C	0.86900418583347	0.31254859806662
C	-0.81980484079099	-2.60528001184047
H	1.04678552276933	1.36116691246766
H	0.55455122487424	0.23862336236765
H	1.80093175318892	-0.24115919076863
H	-0.15037697634133	0.98861087481959
H	0.92164598080691	-0.42734370413126
H	-0.78160270732888	-0.60265086278700
H	-1.80740848614315	-2.96215320732767
H	-0.06797532853297	-3.12400438708786
H	-0.65385906861914	-2.83422440412703
H	-5.30580906341696	0.10390370260538
Sn	-5.59389682399777	-3.00303042756205
C	-4.89425166639935	-4.59631722744661
C	-5.79900663153244	-3.64432354113197
C	-7.45331268076530	-2.21991478202082
H	-7.77759471689868	-1.38383878757743
H	-8.21833677174882	-2.99754476973076
H	-7.33354700405847	-1.87439036398142
H	-4.67038041154316	-4.20412489183619
H	-5.65298286955550	-3.57051637848878
H	-3.98773149120707	-5.03143742119878
H	-4.84442162746807	-4.01882411313400
H	-6.54109024514737	-4.44151643617574

VIIc'

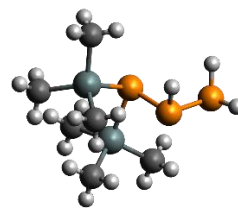


E = -1692.65980546 Eh

0 2		
P	-7.60734091067801	-1.93328882635743
P	-9.28707217484440	-0.65420778923897
P	-6.06878050231432	-0.47427751002966
Sn	-4.46408415644539	-2.17689147531703
C	-2.45048194635629	-1.57420990874089
C	-4.75103205722364	-2.14525617756730
C	-4.82239572229840	-4.15761162037926
H	-4.48549244340059	-1.16416156003191
H	-5.79460368926578	-2.34876879409811
H	-4.12326192428351	-2.90166853627601
H	-2.30914148009509	-2.96904114786184
H	-1.75712286133040	-2.16793332380315
H	-2.22373218737515	-1.72990433357928

Unravelling White Phosphorus 4

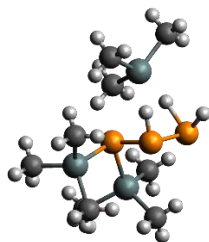
H	-4.81855631315185	-4.16047255804953	-1.33751840654609
H	-4.03555439162553	-4.82024228830763	-2.79127790311407
H	-5.78611290478108	-4.52726835734252	-2.77639428478462
H	-8.00396958023215	-2.41974971623979	-2.89038759039914
Sn	-5.04672489178877	-0.26432108571376	0.06296927818327
C	-4.38387197890949	-2.15022826686829	0.85248569760579
C	-3.41444640766466	1.12100824191363	-0.09027843110598
C	-6.55606106371995	0.53440450572175	1.348678308387903
H	-6.95282369082325	1.46523358774297	0.93480427706294
H	-6.14389479950530	0.72783321076163	2.33668104254575
H	-7.38811636244715	-0.17389579570428	1.44496886763739
H	-5.20993186155241	-2.86157524891860	0.83136169157572
H	-4.05820393928088	-2.01756193057888	1.88554727955525
H	-3.55289370782237	-2.54903081040433	0.27084675496452
H	-2.59582813707069	0.68756869153941	-0.66402689508157
H	-3.05288194376679	1.37098687629134	0.90850383127141
H	-3.74967543324059	2.03387930443205	-0.58275841023776
H	-10.20723053670600	-1.72636395200281	-1.35588308916703



E = -1693.28014147 Eh

0	1		
P	-7.62390568593204	-1.93794232240602	-1.60939004994098
P	-9.24316460080350	-0.43675466628822	-1.51637474784490
P	-6.04914324192591	-0.49847594045915	-2.21756361785286
Sn	-4.46367737536077	-2.20386593163401	-3.16673845693797
C	-2.44660653964377	-1.58543959018523	-2.76148858962685
C	-4.79900626797673	-2.19832909373451	-5.28661385300861
C	-4.80615044696290	-4.17642828416570	-2.39316415358328
H	-4.52471970338844	-1.22808826051837	-5.70133236917940
H	-5.85237533472598	-2.38427601511073	-5.49806274844430
H	-4.19900711644386	-2.97376291327689	-5.76535858859594
H	-2.31654846694471	-0.53494395962815	-3.02268102032396
H	-1.75605397934235	-2.18416621890723	-3.35749006985688
H	-2.20612378857285	-1.72064540516049	-1.70664780671977
H	-4.75688667658213	-4.17197400661235	-1.30520290087478
H	-4.04166784239342	-4.85000013273073	-2.78453755475656
H	-5.78685446691416	-4.54010573952457	-2.70000279258452
H	-7.87909542230658	-2.45770593814382	-2.90875683542420
Sn	-5.04481332489369	-0.27064036864749	0.07966353042184
C	-4.31405111878326	-2.13495013096854	0.86205931133701
C	-3.45624016506105	1.16720658113671	-0.05340257708172
C	-6.59274792058567	0.44762338137012	1.377273232852738
H	-7.05046766037218	1.34463756455444	0.96093448997727
H	-6.17228594723179	0.67844036510271	2.35759655465190
H	-7.36330715087705	-0.31512628090303	1.49351428324672
H	-5.11893120748482	-2.87059587604089	0.85735032988852
H	-3.97689474497050	-1.98893827981188	1.88979491441950
H	-3.48004144521086	-2.51251142418004	0.27059419860572
H	-2.65564475955913	0.79125158013086	-0.69046620898891
H	-3.05232554363372	1.36537159441424	0.94078545531900
H	-3.83457304412773	2.09951438140197	-0.47294073879436
H	-10.31008834842140	-1.37463237095783	-1.45272019634240
H	-9.39723066256690	-0.19539629811508	-2.90541041973162

TS(VIIc'→VIIIc)



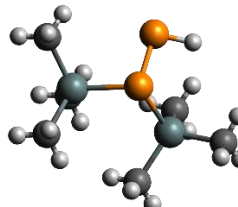
E = -2027.10293611 Eh

im. freq. = 364.90 i

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P	-8.12786234750712	-1.99129265467725	-2.06733773974088
P	-9.45642727866301	-1.18168377244938	-0.52513934978893
P	-6.78040515569119	-0.24031480199487	-2.24096066766846
Sn	-5.00213053464472	-1.45245435419785	-3.53288061727811
C	-3.50393313935219	-0.02208673655399	-4.09211233684222
C	-6.00016204448006	-2.21585868665037	-5.27170750213545
C	-4.14373045306533	-3.08153307830947	-2.429265533100694
H	-6.49271007330077	-1.40411084509058	-5.80775940875601
H	-6.74978054023257	-2.94891680519128	-4.97166300496363
H	-5.28188584895324	-2.69743012213157	-5.93686343821585
H	-3.96317068650472	0.79220446740452	-4.65309313410031
H	-2.74712501962628	-0.49974940682428	-4.71625863791839
H	-3.02249038708976	0.38763972299368	-3.20429537404105
H	-3.51735179586089	-2.71126363821166	-1.61751567381673
H	-3.53376685498627	-3.69622155352766	-3.09299819814839
H	-4.94399149587000	-3.69425474935917	-2.01370876497295
H	-8.90805649836262	-1.65703942139155	-3.21166673199286
Sn	-5.76706181603934	-0.28235888788213	0.06190329796430
C	-5.88486665296674	-2.21077746123071	0.97487024832876
C	-3.71830913146281	0.33557388640567	-0.14584163825504
C	-6.82314825012452	1.17288200391140	1.22969797038569
H	-6.76362521092779	2.14833070655301	0.74610357066182
H	-6.38575479189263	1.24194520172636	2.22698284925615
H	-7.86939809766031	0.87983532288375	1.31574644005040
H	-6.92126773301246	-2.55393702239123	0.99606705231770
H	-5.51081651432438	-2.1522283287214	1.99806746494033
H	-5.28533841408603	-2.93601870999704	0.41777990100416
H	-3.13395435782151	-0.42669773883001	-0.66170777614791
H	-3.28484398694855	0.49899589625242	0.84205498358301
H	-3.66294405720187	1.26696402637662	-0.71039712940722
H	-10.64018522000850	-1.72729907146500	-1.09371421789926
H	-9.67391165622313	0.34268421852703	-1.46475717694834
Sn	-9.67227765512590	1.80464569843439	-2.64447642659076
H	-8.27260019598518	0.84663616123380	-4.76657151226982
H	-12.39268054562780	1.89925199000920	-2.89715147887994
H	-7.26190699581059	2.91278660902968	-2.09346531463480
H	-8.45708347140618	3.54479650698431	-0.93869764200798
H	-11.91081012940260	2.90257824138892	-1.51626348705687
H	-9.98709848462256	0.42499743948591	-4.97692700533319
C	-9.29505535383564	1.21237736348833	-4.67715818656868
C	-11.66383986562000	2.62876655556053	-2.54229710235579
C	-8.27491674372379	3.29818304017973	-1.98506592958295
H	-9.4315256659239	2.07045286541695	-5.33838449244221
H	-11.72495244465290	3.52023276803106	-3.16977050086124
H	-8.38653640640238	4.20252165895190	-2.58622084986301

4.8.7.6 Fifth P–Pcleavage

IXa'



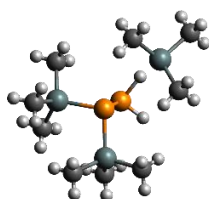
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0	2		
P	-7.70714827732524	-1.75424300896723	-1.68473458805887
P	-5.99161979426918	-0.55446673743605	-2.17994980524589
Sn	-4.43289315592785	-2.23930773267834	-3.20592585303524
C	-2.41593151358006	-1.59983089100164	-2.82692905321708
C	-4.83858296113213	-2.23847888997844	-5.31098661686967
C	-4.76474793166534	-4.19130363590783	-2.38633221508907
H	-4.52915637985537	-1.28924612571426	-5.74833120688864
H	-5.90689950388264	-2.37314834502629	-5.48165676023524
H	-4.29648147080194	-3.05086153811280	-5.79734277562319
H	-2.29201986618865	-0.55507584771022	-3.11244128190727
H	-1.72314120384088	-2.20982407262302	-3.40887652222033
H	-2.17458580978275	-1.70987124616142	-1.76917697934434
H	-4.63249111013522	-4.16716270850371	-1.30519066994535
H	-4.05797508755721	-4.90085434004678	-2.81984358271414
H	-5.78073535170435	-4.51725029812008	-2.60891250306582
H	-7.82560685541776	-2.34105922693156	-2.98043326654238
Sn	-5.04698163023931	-0.26960707778882	0.12968933770810
C	-4.28424397365974	-2.12019725566526	0.91015419495774
C	-3.47454763517893	1.18479411740105	-0.00124689332164
C	-6.63703404296018	0.42619441329620	1.38430931764940
H	-6.98711482568639	1.39995873318819	1.04194361560102
H	-6.28386723525623	0.51387141903312	2.41288290141495
H	-7.46759290425983	-0.27929436983640	1.35233618527055
H	-5.07678102454569	-2.86903470206763	0.90988454904981
H	-3.93799870455744	-1.97194173886002	1.93450452737970
H	-3.45042096515021	-2.48241858503673	0.30855918399382
H	-2.67806276347336	0.82143967141068	-0.65103037587274
H	-3.06101004814505	1.37528995180519	0.99044786887409
H	-3.86448797382101	2.11803006804016	-0.40765073270225

VIIIc

4 Unravelling White Phosphorus

TS(IXa⁺→Xa)

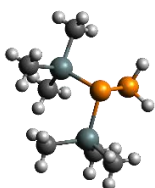


E = -1685.25813666 Eh

im. freq. = 759.05 i

0 2			
P	-8.03351353295921	-2.50816286537844	-0.94605572817798
P	-6.90798555025886	-0.81607962437746	-1.80108066836768
Sn	-5.30120100453810	-2.11060961435134	-3.22292366852706
C	-3.44775411896934	-1.02681471228819	-3.30300852091406
C	-6.20573072730226	-2.17496101399002	-5.16856956747306
C	-4.96900153087316	-4.10902213501581	-2.51828762331885
H	-6.28664147501584	-1.16464213544238	-5.57042986279449
H	-7.20577527462303	-2.60443139949779	-5.09800823301521
H	-5.60730061077702	-2.78280350356939	-5.84881636731394
H	-3.63199724951984	0.00662357118850	-3.59830072427719
H	-2.77897083405859	-1.48737656657526	-4.03174699597082
H	-2.96032760704249	-1.03478945807440	-2.32777261156127
H	-4.48894599182058	-4.09139569252202	-1.54048737401681
H	-4.32660746724410	-4.63925778075960	-3.22360189137829
H	-5.91832218063001	-4.63764360923725	-2.43521789468308
H	-8.29330330840278	-3.16003782491633	-2.18585939692748
Sn	-5.50249653445669	-0.37363791708275	0.22639242511971
C	-4.18947292298734	-2.00236658530617	0.70828852576752
C	-4.35281173210219	1.39839913415691	-0.15452805438364
C	-6.87659781249697	-0.05896580775830	1.84288068054107
H	-7.54092458160798	0.77345357733681	1.60869652694890
H	-6.33361044314382	0.16517423353372	2.76217576404667
H	-7.47572577198873	-0.95733055991243	1.99533958365585
H	-4.76206497575067	-2.92824170361829	0.76836853024772
H	-3.71294340816637	-1.81613146519378	1.67223094458182
H	-3.41394539606274	-2.10946135147415	-0.05075682704198
H	-3.68747918043917	1.23926688398613	-1.00351899873510
H	-3.75299482641204	1.64933102854232	0.72158306080855
H	-5.01793012443017	-2.23266591226927	-0.37891009934608
H	-9.51864394693289	-1.69421452467563	-1.18501548511418
Sn	-10.68182230897090	-0.43316667948449	-2.10076048836612
H	-3.34978044860690	1.58356207259618	-0.29109537188514
H	-9.11657796189226	-0.46539335762671	-4.31899635091459
H	-13.06478895380890	-0.73050928219891	-0.78667961629756
H	-13.03534600713700	-1.82809206089364	-2.18038415283116
H	-10.50984025783870	-1.53494632184402	-4.59451224479151
H	-9.18337042901477	1.77533427769350	-1.61709144193696
C	-10.21884179950030	1.53868071872275	-1.37257207436469
C	-10.19426847727460	-0.57156355240731	-4.19272383087801
C	-12.78876512636880	-0.82314189950014	-1.83721784602076
H	-10.87898201134360	2.27131926251572	-1.84131271739702
H	-10.69861933547180	0.22397750678922	-4.74466090692882
H	-13.36422675815380	-0.10019717435807	-2.41936240576613

Xa

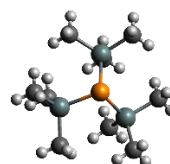


E = -1351.43838986 Eh

0 1			
P	-7.98896822879304	-2.55326868868729	-0.96812279206646
P	-6.95411171987155	-0.79045566816835	-1.84651252409435
Sn	-5.30342155387854	-2.09493374612712	-3.22484778592189
C	-3.43504171193725	-1.03664920252858	-3.25985122819502
C	-6.12863844971784	-2.15721962275329	-5.20554767168320
C	-5.02047213565489	-4.10334526539358	-2.52113904135849
H	-6.24260382464137	-1.14367537683524	-5.59071268982302
H	-7.10808604472171	-2.63619386423142	-5.18580992962043
H	-5.47348493002871	-2.72033884250954	-5.87219418273137
H	-3.60102670782636	0.00262728386373	-3.54550923952970
H	-2.76362147056728	-1.49731683120033	-3.98601733833956
H	-2.96014674283324	-1.06260970507808	-2.27898805347890
H	-4.58681248159118	-4.10242819755690	-1.52198879562888
H	-4.34787147232093	-4.62651874281175	-3.20307571088670
H	-5.97277291623221	-4.63275599498125	-2.49109136102065
H	-8.54298331885454	-3.03318510179252	-2.18768048745005
Sn	-5.52197345866410	-0.36549054521497	0.17500050203753

C	-4.22422391768812	-2.00449661220036	0.66482431958950
C	-4.37192582138125	1.40814075695549	-0.19284503429343
C	-6.88378546589606	-0.06174818369825	1.80643165301303
H	-7.57295905433693	0.75057833879187	1.57416123078152
H	-6.33358001159618	0.18634240836480	2.71523866137011
H	-7.45781324893716	-0.97254855139777	1.98210713029122
H	-4.80441224115768	-2.92584765217473	0.72270042227516
H	-3.75723482305723	-1.81963318088083	1.63364885205342
H	-3.44168350254017	-2.11971721279669	-0.08536529016524
H	-3.69078162478255	1.24863390411546	-1.02896953995823
H	-3.78980020823929	1.66474489345263	0.69341443026314
H	-5.03690917139092	2.23832759580570	-0.43208763846065
H	-9.18386374086162	-1.86249839233083	-0.62612086696837

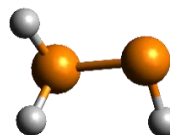
(Me₃Sn)₃P



E = -1692.65980546 Eh

0 1			
P	-7.16483580322155	-0.24953981262701	-1.37957884552407
Sn	-5.77334884650269	-1.61425403133997	-2.94598212935988
C	-4.18666325204371	-0.35714874331798	-3.65625830566778
C	-7.01625384219960	-2.19482543707897	-4.59971678133137
C	-4.90161772271171	-3.37740743275558	-2.07581259151523
H	-7.50539112984490	-1.31600099501526	-5.02093192946593
H	-7.78049678178102	-2.90336621727924	-4.27905039140233
H	-6.40697156970681	-2.66432256335182	-5.37382769874185
H	-4.60079058676460	0.53283141462774	-4.13044802245265
H	-3.57667954704546	-0.89754090127056	-4.38219038334499
H	-3.55363160382503	-0.04927165024436	-2.82349785275166
H	-4.19913056000557	-3.10889445095116	-1.28657595248275
H	-4.36319405982044	-3.92977435643197	-2.84831882586753
H	-5.67664429179881	-4.01984017480288	-1.65920996137968
Sn	-5.95137147146134	-0.72304651891160	0.75821092636294
C	-6.14907409319686	-2.73174953958016	1.50572641776556
C	-3.86456117842791	-0.30704952517973	0.44862078440982
C	-6.73733264440987	0.61997619547283	-2.23694589741940
H	-6.63642183531099	1.65000896013083	1.89482672111747
H	-6.19423960704724	0.50159104318885	3.17611173798708
H	-7.79287069576612	0.40765500163383	2.40919232538387
H	-7.19523840187796	-2.97334229521245	1.69434767303859
H	-5.59794828983913	-2.81612235918444	2.44429562309136
H	-5.74157910413573	-3.44758873515708	0.79246032088947
H	-3.41884380819025	-1.05060047420162	-0.21298669163023
H	-3.33739030117701	-0.32977234983040	1.40380369083200
H	-3.74273838999097	0.67976262288686	0.00124800879836
H	-9.99364527433053	-1.54132889204320	-3.66625784326965
C	-10.47039325426020	-1.36650088475670	-2.70134039507018
H	-10.77193829011650	-0.32036638952462	-2.64360490577261
H	-11.35654953350960	-1.99880507576585	-2.62524634732823
H	-8.19274875052720	-4.16597278258826	-2.18955170282665
Sn	-9.09572437458895	-1.81721591928120	-1.11671134860632
C	-8.61730203275292	-3.91235116214823	-1.21793496859253
H	-9.53248585325553	-4.49069411694073	-1.07697021653983
H	-7.90616399751557	-4.18217918609305	-0.43780118281824
C	-10.01318111142630	-1.41367829683423	0.78358416716150
H	-10.18521599133980	-0.34265853240995	0.89413571764040
H	-10.96940014750420	-1.93479608458379	0.85217323909976
H	-9.37134197076884	-1.75348935124682	1.59732022744611

IXb⁺

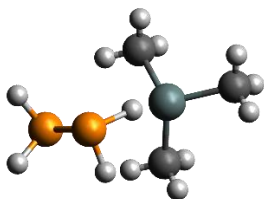


E = -684.23321649 Eh

0 2			
P	-8.08070897978483	-2.41594694703541	-1.75845799183545
P	-9.12972612284881	-0.51521405570690	-1.70815347710883
H	-7.25628883624939	-1.98444831225429	-2.83702497734667
H	-10.30687896162900	-0.98207557091480	-1.07206452861174
H	-9.67988709948788	-0.50474511408860	-3.01694902509730

Unravelling White Phosphorus 4

TS(IXb⁺→Xb)

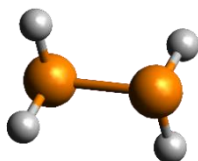


E = -1018.67319634 Eh

im. freq. = 658.17 i

0 2		
P	-7.55669373354324	-2.38024889392964
P	-8.60620170839089	-1.09351302955284
H	-6.72960506054019	-1.30592293788681
H	-9.73939504680262	-1.93825500293024
H	-9.23690225197792	-0.25822796833117
H	-6.31019930295628	-2.67648785902825
Sn	-5.14648919711443	-2.33419752870168
H	-7.12153223673983	-2.17575991872907
H	-3.58336860270264	-4.57420671265969
H	-5.55254186627696	-0.35242859748004
H	-4.14389838951919	-0.00578591299433
H	-2.82194308060136	-3.33585921270406
H	-6.47642358614332	-3.83199131054931
C	-6.2123525297221	-2.77530016423144
C	-3.34714457648246	-3.51313519174956
C	-4.64503466899665	-0.24570587022646
H	-5.58242440827803	-2.53399961667354
H	-2.69358684691823	-3.23189297732318
H	-3.97790291004280	0.00017151072151
		1.68035868973033

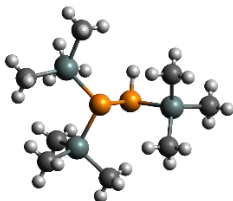
Xb = P₂H₄



E = -684.85224864 Eh

0 1		
P	-7.51911228213633	-2.02536444677048
P	-9.01885616154680	-0.39577233431868
H	-6.48239498997444	-1.13582960158210
H	-10.05539961538250	-1.28511677698287
H	-9.42738882415334	-0.44536792755009
H	-7.11149812680657	-1.97590891279578
		-0.54030976241647

IXc⁺

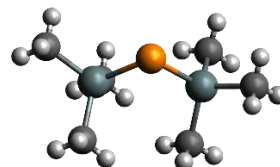


E = -1684.72851274 Eh

0 1		
H	-5.49324605080325	-3.70805633121696
H	-6.21199522531579	-2.08394267971464
C	-6.01248224408068	-2.96916558751830
H	-6.95981455218653	-3.38767575548696
H	-3.29764190091326	-0.49947516813012
H	-2.42518409311816	-2.04275543914942
C	-3.04523560148512	-1.39840351709441
Sn	-4.83309122921962	-2.43774789699471
H	-6.81706461899430	-0.30805100163990
H	-2.47623115472173	-1.11090644987246
P	-6.22434223392770	-0.94571265750080
C	-4.33019468831090	-4.18926504973517
P	-7.82044943673144	-2.48007907651720
		-4.22196667295358

H	-3.81969234736679	-4.90858463000447	-2.93394751259294
H	-5.24121424418706	-4.64585912657287	-3.96392027695698
H	-3.67694254973968	-3.92977681967944	-4.40885664413920
H	-4.7938847104450	-2.37136614512045	-6.51330808365623
Sn	-7.48738460827051	-2.64304422396929	-6.70473380798979
H	-5.18329190696375	-4.09975505194155	-6.63621260690681
C	-5.41585824527848	-3.10791764594563	-7.02337589726221
H	-7.43110475318802	0.01750882461526	-7.25433633058243
C	-7.94336025752644	-0.81555556513604	-7.73564098477644
H	-9.01726343692134	-0.62772989465310	-7.72966331457392
H	-8.54255003372578	-5.14420462886005	-6.90576694137974
C	-8.73909719649388	-4.22028828837078	-7.45009025493816
H	-5.19107822248080	-3.07968763346633	-8.09070157789109
H	-9.79010630423714	-3.95740371660148	-7.32599380138208
H	-7.60545423429197	-0.89104195315381	-8.77069396201397
H	-8.53972466676805	-4.38417324183523	-8.51020374081996
H	-12.29828586480530	-1.21273504948459	-5.14495747034964
H	-11.13787657320430	-1.79436350541193	-6.35212709148113
C	-11.38229194412380	-1.78751051387098	-5.28913745988658
H	-11.55092685763570	-2.81281045625063	-4.95933870231458
H	-9.50116186464163	1.10688590266492	-5.98883181115117
H	-9.95473285937101	1.78617281984170	-4.40980210155321
C	-9.32106747148602	1.05613504802613	-4.91577219179367
Sn	-9.77308799791250	-0.90651759894213	-4.17058349740457
H	-8.27587932059688	1.29881920477724	-4.72163572575306
C	-10.28463939253830	-0.74025652333670	-2.09230976358372
H	-11.12863637163260	-0.06087704077366	-1.96262660881277
H	-10.54640393983390	-1.71881818277628	-1.69010591219804
H	-9.43097878359632	-0.34969775319653	-1.53677954411371

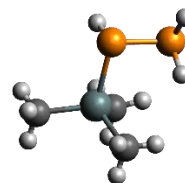
(Me₃Sn)₂P⁺



E = -1008.97300199 Eh

0 2		
P	-6.11927452751413	-0.54124390233318
Sn	-4.47094821877905	-2.17709989575890
C	-2.43478248195917	-1.64637574826993
C	-4.71565695656083	-2.18940229477586
C	-4.87340366875789	-4.14643861055150
H	-4.43220067860556	-1.22215526462501
H	-5.75690987727036	-2.38867432882914
H	-4.08690277960130	-2.96358115201707
H	-2.21357343833554	-0.62507341027685
H	-1.76226418810730	-2.32339397669125
H	-2.23874036528932	-1.72439193279946
H	-4.78692944623348	-4.15650082311490
H	-4.15476824054467	-4.85114613432616
H	-5.88031320260703	-4.45724787149411
Sn	-5.07627171559043	-0.26890727196880
C	-4.28405677364182	-2.09295953231670
C	-3.50028656720419	1.18727233043957
C	-6.58662272572133	0.44915992287272
H	-6.99454125918929	1.39457796731438
H	-6.15617689660798	0.59963790145096
H	-7.39657031044719	-0.27725831100339
H	-5.07815627828485	-2.83268378899073
H	-3.86587029585319	-1.88424358965520
H	-3.49810727529856	-2.50605881632510
H	-2.70494820946041	0.82007795822853
H	-3.09107867537690	1.37721885490467
H	-3.88958494715782	2.11999172091252
		-0.53132356455274

IXd⁺



E = -1018.14422327 Eh

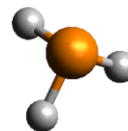
0 1		
P	-3.43463847967205	-0.15343780506294
P	-3.54214025806395	-1.02455827053313
H	-2.08926280742128	0.29787792374672
Sn	-5.32372961317677	-2.71619203376870
C	-4.40502693337542	-4.21392197447280
C	-5.98177570080498	-3.57432185896688
		2.30379458430424

4 Unravelling White Phosphorus

C	-6.95723376130158	-1.79233413609981	-0.58669729909492
H	-7.46758379871778	-1.09106202876602	0.07382289403840
H	-7.66723953676933	-2.55201925464683	-0.91696885818551
H	-6.58591751980534	-1.24896819565024	-1.45584003548500
H	-4.09789175653097	-3.78638330493576	-1.73163320502978
H	-5.11416018536446	-5.02071737619289	-0.96800994716184
H	-3.52816102749875	-4.62537529989146	-0.27612769206653
H	-5.13720700022887	-4.02740417091672	2.82335746436299
H	-6.73253566135577	-4.34200381074029	2.11046781103907
H	-6.41852198921617	-2.80594244550202	2.94195551052434
H	-4.51221088560296	-0.09166777464475	1.48277097549671
H	-3.04273308509343	-1.36531818295541	-1.65104985727752

H	-0.88017165191006	-2.30101315607590	2.96284013432262
H	-0.14782583221895	-1.17850382958438	-1.53282441586200
C	-0.50829122219063	-2.20613261540409	-1.48431456964819
C	-0.33020565810384	-2.14191089134436	2.03538835309745
C	-2.31866071819350	-4.55384717879095	0.41163773330716
H	0.34630980597831	-2.88315075338983	-1.53324616440715
H	0.52712370257351	-2.81729178891511	2.01337513286781
H	-1.48933635062768	-5.25523936232681	0.30573303059820

PH₃

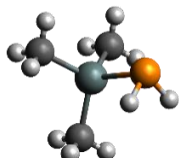


E = -343.01446629 Eh

0 1			
P	8.42936634074313	3.67709145784681	-3.03266937925800
H	9.82369998045064	3.43270048259611	-3.13961779057558
H	8.16866199131250	2.39548046574840	-2.48054200935607
H	8.17282168749374	3.24252759380868	-4.35959082081035

4.8.7.7 Sixth P-P cleavage

Me₃SnPH₂



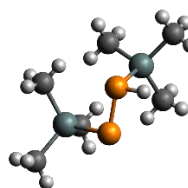
E = -676.30558319 Eh

0 1			
P	-2.81201260480117	1.67930210027558	3.17773689923815
Sn	-1.13876431612028	0.59297526653051	1.64326865756235
H	-3.24842334098322	0.42962817949309	3.69715220021181
H	-3.82799527544379	1.69824249112229	2.18285409017271
C	-0.44180547249197	2.06386715359104	0.24583658035546
C	0.00153694927950	2.90640585433468	0.77729386252111
H	-1.26722697034154	2.42896608431106	-0.36586583827567
H	0.31153427263498	1.62353091741855	-0.40927279113668
C	0.49344738417860	-0.07605411940201	2.86174601683436
H	1.26089336304546	-0.53837231342180	2.23923844082573
H	0.14576705804850	-0.80654928203007	3.59279508989829
H	0.93258361375999	0.76963637573117	3.39180088812534
C	-2.01145458278921	-1.06214197808275	0.59241822438377
H	-1.26357872253243	-1.54492376067852	-0.03864815194125
H	-2.83166471182548	-0.71260249300328	-0.03533729684345
H	-2.39867664361787	-1.79168047618959	1.30406312806792

4.8.7.8 Alternative P-P cleavage steps

4.8.7.8.13 Alternative fifth P-P cleavage starting from VIIa instead VIIc

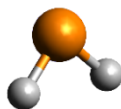
IXe'



E = -1350.82092032 Eh

0 2			
P	-8.06836795546902	-1.71335839683136	-4.03181838644448
P	-6.37220477763271	-0.48364577978070	-3.54862151875334
Sn	-4.64907919429222	-2.15625734340544	-2.76184790968182
C	-3.57465405713612	-1.18420767578314	-1.17857280552176
C	-3.32480729281363	-2.58758407538163	-4.39195919292210
C	-5.59721594399744	-3.93739607839543	-2.04372772477759
H	-2.81454976028232	-1.67559284728395	-4.70270161943848
H	-3.86743578642157	-2.99406126945040	-5.24434981857090
H	-2.57999631886804	-3.31675889673496	-4.06866283695424
H	-3.12934892562043	-0.25711438183195	-1.53974323516474
H	-2.78238178276585	-1.83994082726377	-0.81378910829460
H	-4.25208203778928	-0.95602102507637	-0.35545570708381
H	-6.14896980898753	-3.71301705457364	-1.13063781708718
H	-4.84838660952882	-4.70216179703084	-1.83151381478544
H	-6.29612241699282	-4.31401868249862	-2.78985061041048
Sn	-7.18924490265631	-2.62458383969085	-6.20305712120610
C	-6.41962659144988	-4.61574403437447	-5.91645850853104
C	-5.68143158087419	-1.36284980942816	-7.06954151673946
C	-8.85991611867868	-2.75094946891114	-7.54487361378432
H	-9.64153105279268	-3.37764673178039	-7.11441580510292
H	-8.54375168188690	-3.18242666562118	-8.49587090337809
H	-9.26759951933066	-1.75594219080027	-7.72535938761970
H	-5.04803996562775	-0.92500866446864	-6.29896112098441
H	-6.16370572914659	-0.55599574820651	-7.62203138285648
H	-5.06230404432441	-1.94451627455576	-7.75411519103703
H	-6.03610544100580	-4.99377396443956	-6.86585624064774
H	-7.22136062671713	-5.27095836236035	-5.57400871239864
H	-5.61590510164859	-4.63232684246090	-5.18108730168352
H	-6.77771497526231	-0.12027127157947	-2.23365108813939

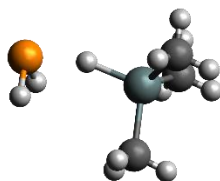
XI' = H₂P'



E = -342.38901676 Eh

0 2			
P	-5.48770299446212	-0.51334426298580	0.00997450380146
H	-5.80484252137937	-1.49807359591394	0.98803931784467
H	-5.80486448415851	-1.40898214110026	-1.05042382164613

TS(XI'→PH₃)



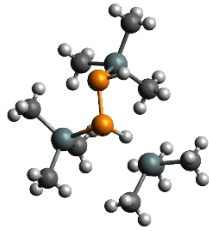
E = -676.82967765 Eh

im. freq. = 153.91 i

0 2			
P	-4.83286364436697	-0.81274091081630	0.07511698377862
H	-5.24002803740576	-2.03453134030190	0.67931374234404
H	-4.73529291242464	-1.42254297281811	-1.20664002768500
H	-3.05708771556827	-1.44252121648449	0.34882847594792
Sn	-1.58981160346889	-2.53635505717155	0.34098036445976
H	-1.15432631333166	-2.39309069787126	-2.34259998561871
H	0.03012588214966	-1.11355943099413	2.00859647972255
H	-3.02873010313179	-4.72303765876699	-0.39833121873384
H	-2.81887762775863	-4.74125113894351	1.36208595150875

Unravelling White Phosphorus 4

TS(IXe⁺→Xe)

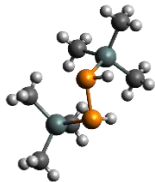


E = -1685.25400570 Eh

im. freq. = 868.44 *i*

0	2		
P	-8.35483986930780	-0.28870128794962	-4.60720487899636
P	-6.31118426899988	0.30932234625928	-4.15702404556715
Sn	-5.28931280885310	-1.27361067103072	-2.48770989523015
C	-3.86908561101088	-0.09265954171358	-1.39020792406524
C	-4.26556222140239	-2.82312988464196	-3.56438459138111
C	-6.67716744550559	-2.15001842091143	-1.10581179798623
H	-3.53478821863650	-2.38294877026150	-4.24338416844266
H	-4.9669356517242	-3.42435948549257	-4.14257149717943
H	-3.74494065473673	-3.47453983946133	-2.86062851404754
H	-3.18718600674178	0.41329698360083	-2.07370135492646
H	-3.28996624418442	-0.73563758688580	-0.72528867003221
H	-4.38886208583228	0.65584884458175	-0.79165299844455
H	-7.37706096776047	-1.39522971362020	-0.74709881159014
H	-6.12900815895227	-2.56193879249264	-0.25618214621055
H	-7.23605982770909	-2.95047868155154	-1.58881259417234
Sn	-7.87449909449810	-2.27846027168633	-6.05717723236663
C	-7.83073397724662	-4.09171178693528	-4.89336265879627
C	-6.00825678982250	-2.05169763227374	-7.08641832339717
C	-9.49037282743052	-2.43316038539021	-7.46248075109676
H	-10.43156254250800	-2.18483261411264	-6.97234345769214
H	-9.55256232767331	-3.44975819150697	-7.85209812140969
H	-9.33473875872677	-1.74269810066180	-8.29102342792432
H	-5.19763230928232	-1.89635857777125	-6.37480015125958
H	-6.05409543824634	-1.19267902308316	-7.75560565490457
H	-5.80333169492695	-2.95088558866389	-7.66969421076790
H	-7.25790890366284	-4.85376189127518	-5.42488440262878
H	-8.84620385608557	-4.46084387471964	-4.74477293759668
H	-7.37261718861639	-3.92294111427605	-3.91904047158068
H	-6.63049293439420	1.29743474866405	-3.18580154356150
H	-8.93092985514992	-1.33017695719401	-3.36473199601370
Sn	-10.28165081686190	-2.36008646407045	-2.40358481092484
H	-11.92883284297730	-1.67127309281074	-4.46922998451317
H	-9.32868817338457	-4.93024386075608	-2.27517449641650
H	-11.21887612395760	-0.08448454918942	-1.22423433808769
H	-10.37349697929330	-1.06324468893935	-0.00865796323484
H	-9.19917884357999	-4.17706615204185	-0.67155712432722
H	-11.44321493278360	-3.36640902636570	-4.66628232178413
C	-11.76790710028990	-2.6145211717927	-3.94582423457612
C	-9.83331639270341	-4.29182771135842	-1.55054940489420
C	-11.06860899607370	-1.09651986111576	-0.84815933734659
H	-12.71252361384640	-2.93710635102452	-3.50404038982493
H	-10.77075047098010	-4.76632490187370	-1.25234725998891
H	-12.02473616919020	-1.49176640681716	-0.49959910481169

Xe

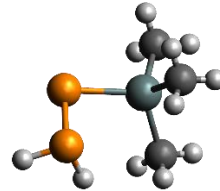


E = -1351.43353942 Eh

0	1		
P	-8.14815783708573	-1.70433505878414	-4.07317698708880
P	-6.39677313217733	-0.45870820518254	-3.56263621895481
Sn	-4.70845357423903	-2.09327675107952	-2.67695127902459
C	-3.55686079082221	-1.06983995476654	-1.18221494006168
C	-3.39256014608347	-2.69707275922652	-4.26164666820816
C	-5.63396926845419	-3.82909087974625	-1.81841095214624
H	-2.88487194081827	-1.82524311732209	-4.67558453015361
H	-3.93731334241099	-3.19868338374414	-5.06116605403833
H	-2.64290379525114	-3.38445510560953	-3.86606893372704
H	-3.12083700821839	-0.16224673483809	-1.60061352602485
H	-2.75201522186514	-1.71696317589040	-0.82969200228487
H	-4.18893312172949	-0.79999302246551	-0.33587172874069
H	-6.38152247557591	-3.53460320056227	-1.08154407655036
H	-4.86921132775196	-4.43290466745105	-1.32659486354302
H	-6.11488351958048	-4.43346103979672	-2.58753292010009
Sn	-7.30577811120848	-2.59127115110669	-6.27722806093547

C	-6.54274179521605	-4.58437183112948	-6.01997721948162
C	-5.80433069665120	-1.28565661810602	-7.0743377913439
C	-8.97065266995655	-2.64925463380013	-7.62756600415571
H	-9.75784573320343	-3.28984981337721	-7.22870067226386
H	-8.65662588771321	-3.03768495807434	-8.59752575295280
H	-9.37278154481672	-1.64461197709365	-7.76216452665688
H	-4.91855721134681	-1.27950582868611	-6.44029950053240
H	-6.19449738351496	-0.26984972642327	-7.13700533976121
H	-5.52667427687923	-1.62474089728965	-8.07369852231414
H	-6.06628040880091	-4.92337213804513	-6.94143122375971
H	-7.36293732020907	-5.26154725740493	-5.77875686040885
H	-5.81161162317313	-4.61946045698213	-5.21245503725935
H	-6.85314453628686	-0.08680527670538	-2.26789952236755
H	-7.87024429895943	-2.90879037931053	-3.36869833744877

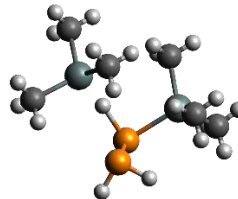
IXf



E = -1017.52670165 Eh

0	2		
P	-8.89890213816106	-2.97020493113288	-4.52336309456754
P	-7.22914106012661	-3.56501250028977	-3.29201818567944
Sn	-7.54850317775030	-2.86810052661564	-6.64509502547368
C	-6.52709691897928	-4.72744153601072	-6.97883678016806
C	-6.10591636202898	-1.28791532624751	-6.47727457262520
C	-8.91742841705922	-2.49581602435221	-8.25191967143247
H	-9.63771285466757	-3.31083597305570	-8.32589973337091
H	-8.37115439647980	-2.42036273805892	-9.19328033477611
H	-9.45600221066357	-1.56393836213567	-8.07952875021014
H	-5.42416076766392	-1.50305695909175	-5.65420552769729
H	-6.00624281641055	-0.33954521674213	-6.28289510726816
H	-5.53529742857507	-1.20820538056631	-7.40382214174385
H	-5.66134168216593	-4.80861009462968	-6.32135889102883
H	-6.18673232445105	-4.77210462428564	-8.01467231774279
H	-7.19603178229344	-5.56766689662376	-6.79110159534378
H	-7.92436722756595	-4.22823942677221	-2.24930894820775
H	-6.77384843495760	-4.75020348338945	-3.92760932266393

TS(IXf→Xf)



E = -1351.96439809 Eh

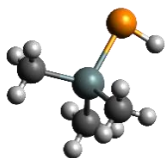
im. freq. = 651.19 *i*

0	2		
P	-8.88838269837942	-4.31238343691912	-3.91366998125796
P	-8.02019545593315	-2.93976799799059	-2.42589397933982
Sn	-8.31839156418412	-2.97440101887781	-5.96572696805225
C	-7.09891878226597	-4.22176712068977	-7.21699569760523
C	-7.26428220117906	-1.157771167469609	-5.51982002562126
C	-10.14498293888610	-2.50370203627208	-6.99733546158538
H	-10.77278170411650	-3.39154801309678	-7.07810010357414
H	-9.91782454554108	-2.13968017409945	-8.00063492201505
H	-10.69606955084530	-1.73061052999467	-6.46182931871578
H	-6.29414314035467	-1.37408906671572	-5.07259072042707
H	-7.84123759459517	-0.53852824393497	-4.83318250948442
H	-7.10633401494927	-0.60465724509413	-6.44736461450138
H	-6.11006832984666	-4.34109063328386	-6.77374180386994
H	-6.99360972054950	-3.76957162779458	-8.20446114092592
H	-7.55762012665183	-5.20496181934491	-7.32277118877619
H	-7.69418349472399	-3.92381058188936	-1.45522820607526
H	-6.69637494700075	-2.87784730642276	-2.93166650484700
H	-10.38149075240080	-3.40129100714656	-3.7869035779835
Sn	-11.62220859913460	-2.02962048697270	-3.30100374090033
H	-13.24913233469620	-2.08902235625767	-5.49145669936503
H	-12.42432212734970	-2.21314296380299	-0.9755571971535
H	-10.53689793187780	0.03143936888875	-4.74342466479726
H	-9.78198981190873	-0.04112836058249	-3.13569549071725
H	-11.10228134845330	-2.07752655730734	-0.63521233848025
H	-13.92517729263890	-3.15568663899070	-4.24463776603638
C	-13.45215254617890	-2.19026291366088	-4.42514606295450

4 Unravelling White Phosphorus

C	-12.02446720071050	-2.22378413907438	-1.19786263913131
C	-10.72430257701130	-0.11142310632967	-3.67905356406602
H	-14.13762532004250	-1.39812144873276	-4.11757272028406
H	-12.75245236293260	-1.47007173864087	-0.89170746986033
H	-11.39528898465850	0.67696097572752	-3.33198441921839

(Me₃Sn)HP*

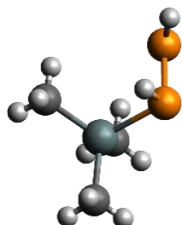


E = -675.68135662 Eh

0 2			
P	-2.04379445914334	1.02420699181242	-1.05586605321901
Sn	0.02017449621090	0.01765076694463	-0.03142632070508
C	-0.08876049093769	0.22964690246720	2.10049820108619
C	1.75847419366742	1.04342106938557	-0.76720497365601
C	0.14482498475284	-2.06337830198265	-0.55190878133248
H	1.69221949965412	2.10724944172850	-0.53887130700074
H	1.83934679582860	0.91810492725541	-1.84718939506377
H	2.65290946468595	0.63421241446371	-0.29458225208024
H	-0.13497387268385	1.28405898995917	2.37428145407432
H	0.79472345895238	-0.21488084591420	2.56133805643013
H	-0.97653803160648	-0.27259483290225	2.48577145474191
H	-0.70940304268924	-2.60532501799211	-0.14601920849694
H	1.06243568811034	-2.48942916993056	-0.14284539821437
H	0.15347177518984	-2.17770709554591	-1.63604382776817
H	-1.59464045999178	0.67751376025108	-2.36530164879572

4.8.7.8.14 Alternative fifth P–P cleavage starting from VIIIb instead of VIIIc

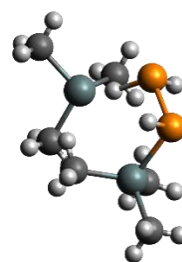
IXh*



E = -1017.52727334 Eh

0 2			
P	-3.30754552994930	-0.83943710609445	-1.47448329738396
P	-3.63644953355814	-1.20406969146510	0.63292490250261
H	-3.24212427630211	0.57489406608094	-1.33515497837332
Sn	-5.54435059753481	-2.83883838083351	0.39211121558630
C	-4.80799922820315	-4.42568781231388	-0.84068776519627
C	-6.03775842200333	-3.55498670843717	2.35229810202579
C	-7.21027455398281	-1.85291102037785	-0.52627905892980
H	-7.58696393325242	-1.06624781863406	0.12775747831395
H	-8.01175633920607	-2.56720449279909	-0.72123209801894
H	-6.88938080270985	-1.40865748328833	-1.46864969226952
H	-4.45292992316183	-4.02412802800950	-1.79002741168730
H	-5.60702058811394	-5.14255294295310	-1.03583754448454
H	-3.98577081727715	-4.93938456265959	-0.34231718829997
H	-5.15916226922056	-4.00842835251253	2.81148051335866
H	-6.83018695533195	-4.30222493173178	2.2872777268435
H	-6.37991480521916	-2.73188217052104	2.97995163008400
H	-4.40700142497338	-0.06352256344997	0.98197742008796

TS(IXh*→Xf)



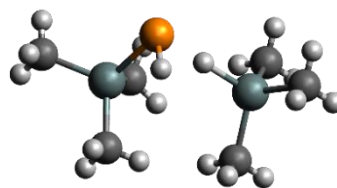
E = -1351.96166815 Eh

im. freq. = 838.16 *i*

0 2			
P	-2.00543488971176	-1.35809150684505	-0.82582987589325
P	-3.09633421217662	-1.78341677904766	1.01045269490239
H	-1.41139429176642	-2.64819417393330	-0.88401016169315
Sn	-5.12190594873870	-3.06628953543571	0.23177144002863
C	-4.39585035124843	-4.86523476593358	-0.68479714380671
C	-6.26846676425063	-3.59329068009216	1.97054359021229
C	-6.33178681271392	-1.86431496284392	-1.07436326725644
H	-6.89490977091133	-1.14602122995220	-0.47761205246474
H	-7.02979144284148	-2.49185472704859	-1.62982343196186
H	-5.69970749207009	-1.32307163229801	-1.77762607261137
H	-3.64304632810611	-4.63743855627438	-1.43931523624030
H	-5.21653889256718	-5.41054949131838	-1.15291922683764
H	-3.94475462316325	-5.49826743847367	0.08016208815280
H	-5.65672407494879	-4.18217108742841	2.65448755098988
H	-7.13947427485449	-4.18165854758011	1.67752868807771
H	-6.60811452157882	-2.69495900770995	2.48673133544699
H	-3.75890040869719	-0.52804216106287	1.06504742029856
H	-3.01603811687000	-1.86042553256153	-2.15499782210972
Sn	-3.45258321444014	-2.58132485244400	-3.90225316033202
C	-3.32947926251551	-0.97042605893155	-5.32510924628962
H	-2.36100585947835	-0.47563140322339	-5.25278652748753
H	-4.1153177167086	-0.23821240232011	-5.13863573275768
H	-3.45082323803340	-1.36757613452773	-6.33476551539116
C	-1.86243310643533	-3.98188022378061	-4.28417622229024
H	-1.94716736334305	-4.36440662933893	-5.30316302887020
H	-1.91796952123214	-4.82050415914544	-3.58923288529289
H	-0.89412749616728	-3.49405607104193	-4.16998709521551
C	-5.34095128023137	-3.58613401405076	-4.16074103540044
H	-5.34868139481946	-4.06830777594687	-5.14051624932249
H	-6.16145709619252	-2.87077952862055	-4.11107739588910
H	-5.48054023822527	-4.34562893078864	-3.39256642269522

4.8.7.8.15 Alternative sixth P–P cleavage starting from Xf instead of Xb

TS(XIb*→Me₃SnPH₂)



E = -1010.11947952 Eh

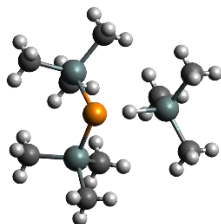
im. freq. = 205.28 *i*

0 2			
P	-3.12780017274960	1.95348724569212	3.06368492654077
Sn	-1.25517676643077	0.69453657803857	1.97255099358905
H	-3.57071155870625	0.35660536829919	3.94268909558746
H	-4.05896963104449	1.52918109006933	2.07304143296819
C	0.16473465262885	2.06013190003995	1.11848490107878
H	0.57314039286771	2.70859748457549	1.89399287097186
H	-0.31401995770848	2.67985115322261	0.36014626318266
H	0.98128456079223	1.50178833609673	0.65729681825380
C	-0.25594572547912	-0.47764261436098	3.47455656426756
H	0.75815183057127	-0.71392383239857	3.14859329103657
H	-0.79379007735453	-1.41158923485632	3.64279677210441
H	-0.20397228599979	0.07292036391279	4.41448237971729
C	-2.00555773146134	-0.61733144966690	0.44824015898632
H	-1.19045832267552	-1.19836076831635	0.01375763162139
H	-2.48540388002988	-0.03736496345067	-0.34066396251414
H	-2.73741897696405	-1.30179973888535	0.87825460683925
Sn	-4.13177583109283	-1.21107771464319	4.72789807815267
C	-6.20699962413711	-0.98106719802947	5.23145652428073

H	-6.33444657177307	-0.14607337281899	5.92066471902736
H	-6.57862362805064	-1.89116429730819	5.70514790714676
H	-6.79127460413465	-0.78687999091286	4.33170876794868
C	-2.95927238700621	-1.54471225986519	6.49684695601555
H	-3.08663740834443	-0.71577621930409	7.19331735081943
H	-1.90396398184790	-1.62929011422157	6.23675985354569
H	-3.28015892774777	-2.46748173172329	6.98321172684143
C	-3.89060944016718	-2.86207169794071	3.37033051747426
H	-2.84485144558266	-2.97637260722223	3.08390341859219
H	-4.48752291850541	-2.70347641752321	2.47172796119028
H	-4.22412958186624	-3.78147329649866	3.85478147473356

4.8.7.8.16 Alternative sixth P–P cleavage starting from Xa instead of Xb

TS(XIf → (Me₃Sn)₂PH)



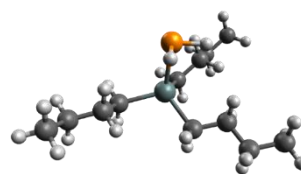
E = -1343.41596117 Eh

im. freq. = 362.61 *i*

0 2			
P	-6.39713088193473	-0.96440402487073	-2.25276920469705
Sn	-4.26117986502652	-1.90557989273870	-3.14875952177375
C	-2.46648962087018	-0.99305606523870	-2.38871323958775
C	-4.27122669256438	-1.58365392600953	-5.27577530815166
C	-4.19717470100858	-4.00641831053256	-2.71034276628984
H	-4.17966276292648	-0.51743461072662	-5.48870344532504
H	-5.20104914534772	-1.94883808689354	-5.71206269984344
H	-3.43143404925059	-2.10473655547546	-5.73843577231800
H	-2.46256938953469	-0.07356078204385	-2.61351441514755
H	-1.60120103383706	-1.45471496603936	-2.86827291234755
H	-2.38006938924939	-1.12829682842020	-1.31045484435391
H	-4.21178739399833	-4.15584498194023	-1.63027620334684
H	-3.28550497622894	-4.44703662628356	-3.11731185708431
H	-5.06136216491517	-4.50741184113205	-3.14650892075552
Sn	-5.59080527167440	-0.26824368214829	0.00928427124224
C	-4.61342998848821	-1.90590214211844	1.00498655256097
C	-4.23642745829942	1.40408003867386	-0.05145214649926
C	-7.32109614259082	0.32761471995890	1.13463210451828
H	-7.85614447827538	1.11179523492579	0.59754590184175
H	-7.02401841576116	0.70888699542035	2.11308428144029
H	-7.99148028776378	-0.52108429412133	1.27242763865457
H	-5.23309895791686	-2.80101492355263	0.94672109670109
H	-4.45121713361914	-1.65510825095699	2.05460646317929
H	-3.64895500713614	-2.11385635635081	0.54073247112507
H	-3.35741950425743	1.16545962491405	-0.64854854800685
H	-3.91878433294424	1.64726239632512	0.96422739349196
H	-4.73154581204629	2.27715062160513	-0.47781095745655
H	-5.89224901459772	0.66029097511499	-2.96135903960367
Sn	-5.49678731828305	2.28772287503072	-3.76366803794514
H	-2.99810934901749	2.69023638002664	-2.74096857005474
H	-5.63219971239308	1.46003330595564	-6.35561402352551
H	-6.17528683045350	3.90370669177765	-1.66759881462307
H	-7.61243347701058	3.59926614373383	-2.66134541666194
H	-7.25913623554248	1.89288313388971	-5.80002409518667
H	-2.85311736121005	1.93182024488634	-4.34065673008325
C	-3.38281642527874	2.68812043031806	-3.76069921507751
C	-6.21019434072336	2.18911841047564	-5.78727979396139
C	-6.54665944066663	3.82678055138513	-2.68968635677760
H	-3.19917156756074	3.66624279387712	-4.20917158718707
H	-6.11184289475820	3.16627170454518	-6.26348313434547
H	-6.40380107163773	4.78722231146599	-3.18809059673724

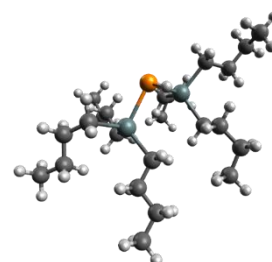
4.8.7.9 Structures calculated for NMR prediction

Bu₃SnPH₂



0 1			
Sn	-0.28936279533172	-0.74590173721437	0.42060385502517
P	-0.41989079856249	-0.45426649810538	2.93594834251022
C	-2.18189869417144	-0.06863344005175	-0.39545739587389
C	-2.80098237659643	1.08483494232518	0.37770615010488
C	-4.12069487030108	1.56806175804944	-0.21038105728990
C	-4.73775895151376	2.71923512167119	0.56584467403688
C	0.04323837876774	-2.85563619668520	0.05344507106154
C	1.28861898699752	-3.38756963763665	0.74418713105456
C	1.54073690954485	-4.86820191405256	0.48811130775924
C	2.78664755072586	-5.39299839579792	1.18141701358977
C	1.34952670172139	0.42357879334052	-0.39168313261699
C	1.20537074427757	1.91394716271391	-0.13565870922484
C	2.37256304816423	2.73999062115570	-0.66181986098974
C	2.21850044731523	4.22860036680591	-0.39953880373925
H	0.98984512062614	-0.56724511334948	3.09533117941555
H	-0.36444014850531	0.96497007929655	2.85826083359345
H	-2.85809864374353	-0.92418353194777	-0.41406012821581
H	-2.00552794691642	0.21452772428127	-1.43475497038088
H	-2.10392151905392	1.92624199737342	0.42049531352072
H	-2.96499780889401	0.78737440021088	1.41692449937049
H	-4.82101486783053	0.72952537440201	-0.24665874271897
H	-3.95847269501561	1.86833059718928	-1.24898681017334
H	-4.93820311216174	2.43584317062739	1.59956192951401
H	-5.68009557160209	3.04126573248991	0.12384502035660
H	-4.07178797360593	3.58259711838183	0.58746541977812
H	0.10974797978338	-2.99959875133604	-1.02646863131384
H	-0.84439151310476	-3.39352342502458	0.38839887576138
H	1.21242290477472	-3.22531926150621	1.82299869864028
H	2.16623256695245	-2.81962087999852	0.42160196469126
H	1.62034071893240	-5.03409065619856	-0.58948468105251
H	0.66760916821902	-5.43813038433400	0.81599092245050
H	3.67811889897331	-4.86109006901478	0.84699481785792
H	2.94121100279732	-6.45273694697892	0.98106260327987
H	2.71872103837993	-5.26855587433617	2.26265287541469
H	1.40056102700356	0.21748734595103	-1.46265289943864
H	2.27265466061413	0.04243931836168	0.04668906410108
H	1.09899968322774	2.09746051342779	0.93722330045357
H	0.28073404296634	2.280794648261987	-0.59046721988801
H	2.47966448244206	2.56308326154952	-1.73524724734280
H	2.9704239902108	2.37899746030597	-0.20442536097749
H	1.31834750887762	4.62185112067545	-0.87336327073380
H	3.06662497553281	4.79414666262320	-0.78417906696895
H	2.14181622847236	4.43520405178996	0.66848429489789

(Bu₃Sn)₂PH



0 1			
P	6.18264619950252	1.18217031078901	-0.10583371042508
Sn	3.88087546619954	2.16400731260384	0.24331692236538
Sn	5.65576694368287	-1.28038342770262	-0.19930867993347
C	2.96125312377423	1.55556644296313	2.11458674648960
C	4.17941757722979	4.32226267377374	0.15778277395513
C	2.67249591395247	1.49371753021214	-1.42821107631382
C	3.38269220722097	1.62276703112066	-2.76473221108864
C	2.56973212650336	1.08935637192471	-3.93666428944450
C	3.30105509735220	1.17741620448503	-5.26468775487289
C	3.17328587351453	5.08157887291839	-0.69288873450506
C	1.75564665564783	5.06500775667085	-0.14670594955108
C	0.76658088197500	5.82201400871753	-1.01511742704706
C	1.61936063781224	2.21931787265594	2.37234814181061
C	0.94346644572511	1.75191877633666	3.65594751705930
C	-0.39111128894949	2.43275107036737	3.90844284184801
C	4.71308170408044	-1.76127602993883	-2.09300376330791

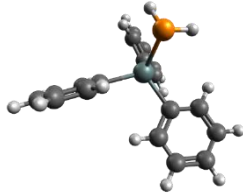
4 Unravelling White Phosphorus

C	4.79374708745384	-3.24179815631893	-2.43140884206591	C	-41.33010177830480	-5.69858101453220	2.77944620131053
C	4.14251059418582	-3.61819513113006	-3.76143238615865	C	-42.72212814051000	-5.81254883262014	2.1815298845606
C	2.63505882686788	-3.3009985754271	-3.79317278701812	C	-37.72506120496720	3.10761372682039	-0.23694009594932
C	7.57624472740528	-2.28806432046631	-0.094912419902459	C	-36.47765178077620	3.897051780653199	-0.59375119067495
C	7.46603280542192	-3.73369083689131	0.41155933714863	C	-36.74666951914100	5.36976978359239	-0.87670438102667
C	8.80095511044656	-4.47275914564558	0.49620753284149	C	-35.49417784611810	6.14627386148402	-1.245133007584256
C	9.75509075235785	-3.91644396763919	1.53943248584089	C	-35.70539829456700	0.95157847966706	1.59508612735077
C	4.45050520179030	-2.02390776488738	1.44877204897161	C	-34.31692713951390	0.93528740922681	0.97412116500780
C	5.04411956032883	-1.67367080946245	2.80325084808089	C	-33.17800696774730	1.13840035490108	1.97189693705886
C	4.36740953926306	-2.35810611126807	3.98968950995244	C	-33.05931931276960	0.04352289522008	3.01750762048473
C	2.92065613893629	-1.95116087098397	4.20762273887983	C	-36.60697795505970	-0.11565292971884	-1.59436038318652
H	6.49138814724558	1.14901305259356	1.28541009520128	C	-37.31383231117590	0.07448541752322	-2.92471181454291
H	2.85380511419015	0.47324721821011	2.07723768763957	C	-37.19008887236990	1.46233209499244	-3.53852786575262
H	3.66438959183212	1.77237895569737	2.91933849549087	C	-35.77163551419430	1.85037573003725	-3.91927748602614
H	5.19022677402125	4.46007606193967	-0.22360145840558	C	-41.43939998803620	3.08978222143618	0.70482283085759
H	4.17654015241853	4.69731357441475	1.18261636467252	C	-41.66296508910200	4.12253059264599	-0.38641490923046
H	2.40301210486079	0.45439991310665	-1.23373824919748	C	-41.80512372055970	5.55601699736357	0.12387499853303
H	1.74020392488991	2.05975848200817	-1.42969034994692	C	-40.54135974465450	6.11998817538484	0.75037924972183
H	3.63503072207970	2.66940894322770	-2.95406275126243	C	-40.89464149783510	1.05493366644877	-2.16097216770406
H	4.33925973874034	1.09659051476303	-2.73033925065141	C	-42.15669852142780	1.30870839278448	-2.96969506017397
H	2.30112316806360	0.04967602659424	-3.73469097858304	C	-41.90994405911080	1.44141629727212	-4.47197589127589
H	1.62540685510036	1.63708627493224	-3.99407325930887	C	-41.33897649741810	0.19374310849907	-5.12396656669535
H	2.69474464503426	0.79147170337898	-6.08358315842580	C	-42.98552104803620	-0.07742636143829	0.51080863136559
H	3.56248467941620	2.20856177069721	-5.50477087432186	C	-43.28712579918090	0.00574981504699	1.99832944817697
H	4.22795946255780	0.60323138770449	-5.24200948684200	C	-44.59606534129080	-0.66101500637225	2.416374842565803
H	3.49486496536240	6.12453638241550	-0.78963831191870	C	-44.60776768644960	-2.1697053682368	2.24643713492364
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Unravelling White Phosphorus 4

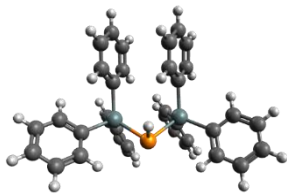
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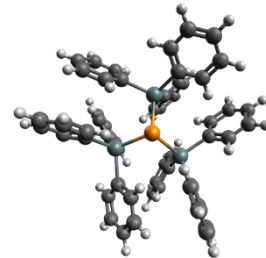
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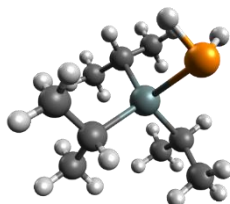


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4 Unravelling White Phosphorus

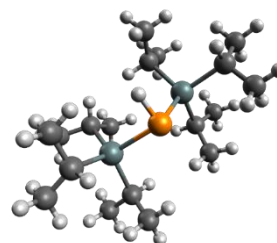
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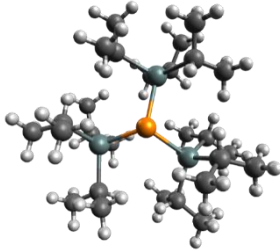


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Unravelling White Phosphorus 4

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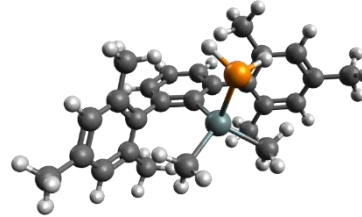
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(TerMe₂Sn)PH₂

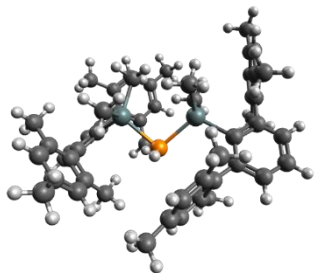


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C	5.49768182879980	0.55145639927903	-0.74901300201665
C	1.63662478116720	0.50795340339185	2.44661093149240
C	-3.36242106471632	-2.71656255323360	-1.46118290496362
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C	-3.40468443892697	0.29494910926071	2.57693436829245
C	-4.00866951998026	-1.64533721756597	-0.63749505290017
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C	3.55524585889872	-1.017400998918861	-1.05705502382588
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C	3.52274271260981	0.47629530951379	0.79968824533413
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4 Unravelling White Phosphorus

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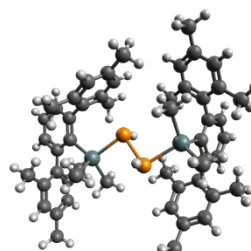
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C	-0.01389098465788	8.81969841310914	1.13064109487433
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C	2.39618361470972	8.5085685796950	1.07388264012705
C	2.35836294892043	8.17111589925861	2.42267821743380
C	1.16628465799409	8.11991647982555	3.13225462290742
C	-0.03457892519657	8.41850701366651	2.47211289038354
C	-7.62923155698566	3.30168441581967	3.74454797038073
C	-5.25697667795664	7.13519190886293	1.56719103465624
C	-3.42598942242395	5.10322635139325	5.80285693417228
C	-5.32652470660007	6.12619502172884	2.67248363907695
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C	-6.46212039630555	4.23875243721728	3.69817773951182
C	-5.49626495954842	4.23195469717318	4.69662395722067
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C	-3.72177975080788	8.30724191761146	4.59614401789613
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C	-3.50446669016182	2.15263180323435	-0.87069387110567
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C	2.17200238330101	1.99563000630248	2.89486076253296
C	1.02691309325881	1.20909274632888	2.93717686359200
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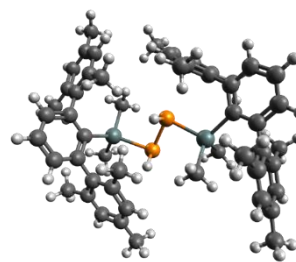
1 (TerMe₂Sn)₂P₂H₂-meso



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C	1.56328649677955	9.99541632569256	1.90661864246699
C	2.55016368309656	9.54276964536376	2.77382601151464
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C	-0.16523802815259	9.13251212190489	3.34033365453389
C	-7.12806964078758	3.66116172962550	1.00464448425809
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C	-3.85701720223862	-2.51240595733682	0.08438205139498
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C	-4.02565060916716	3.69074924716371	1.0507059780455
C	-4.62017559540120	-1.52378713044643	0.91248108613250

Unravelling White Phosphorus 4

2 (TerMe₂Sn)₂P₂H₂-C₂

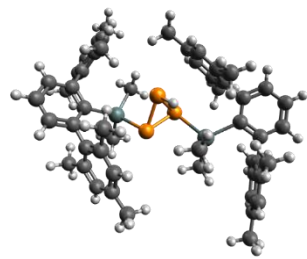


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C	-4.70137296928709	0.16130272133453	2.65537381375728
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C	1.59582858140544	-0.46892340997093	0.15616251842098
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C	0.09661327254192	-1.53908886959249	2.90342192620330
C	-0.92934025244756	-2.21337547221177	3.54381829066013
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C	-2.54173155168953	-1.00654527280024	2.20658610974245
C	-1.50765390642249	-0.32529917847487	1.55141882169914
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H	4.16993197529739	10.55636556137270	1.78542035077025
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4 Unravelling White Phosphorus

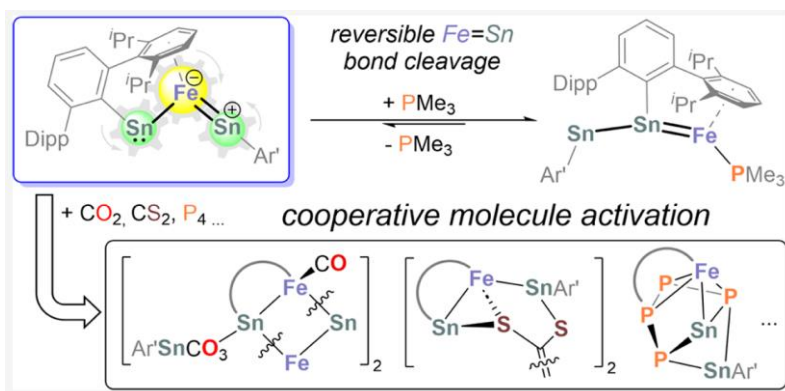
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3 (TerMe₂Sn)₂P₃H



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C	-4.18391700047130	6.85956282845085	3.37434587700097	H	1.59060495154514	-0.68660815581754	-1.74408513676409
C	-3.41335117310496	8.13041671823797	3.35358541245557	H	0.06248562982164	-1.15207351552516	-0.99816845017927
C	-4.05834071374627	9.27941368516683	3.81245830925571	H	1.52433174131901	-2.01001677283760	-0.58651148171367
C	-3.41022120813450	10.50181068406530	3.82749692146440	H	2.98109336244600	0.92923712121164	-0.73201794061344
C	-2.10147618504993	10.58447628695570	3.38281352146667	H	4.48409281301684	2.53305317547571	0.25605372854162
C	-1.43730687000818	9.45104800236016	2.92178777958845	H	3.38194713038317	3.73146482197531	0.91759548048406
C	-2.09055025755354	8.20941219496743	2.89882525501525	H	4.43910602572433	2.83545082107892	1.99211080962066
C	0.31834378074565	5.71101264277810	3.77322257063175	H	2.30894700494531	2.23008911304677	3.27207617549694
C	0.21111922725533	6.73130575321706	0.46619690394327	H	0.50953039982758	-0.32251541816138	4.41293735671534
C	-1.23521519943480	1.34780189647165	-1.69303796155866	H	-0.81296359964505	0.58423903004057	3.71966881720953
C	-4.15691923800440	1.82673170125042	0.05267648161850	H	0.50259238787459	1.43631164865196	4.52105270887325
C	1.12601650302646	-1.02113548356274	-0.81954032909315	H	-1.47877756264120	0.47637914103443	-2.29523718141998
C	3.82678828059712	2.75051174540581	1.09538714185521	H	-0.15694357699554	1.44352339182608	-1.62448150125331
C	0.26344457000537	0.59461004867510	3.87593407235211	H	-1.64016564962307	2.23198739749521	-2.17938666162506
C	-3.74503989404928	-2.25766088682250	-1.31815490648447	H	-4.16116700921589	2.79377664275338	-0.44135518809667
C	-8.28765694490905	-0.50538491376117	-0.10794226133202	H	-6.65260901983698	1.92203693508385	1.01099024311076
C	-4.59787042003015	-0.39022186362116	3.28293770003230	H	-4.69227404343085	1.10100155280806	-0.54997845497131
C	-4.66920498481047	-1.65309070309225	-0.30501581284322	H	-4.69227404343085	1.10100155280806	-0.54997845497131
C	-5.99409129794805	-1.38873152845577	-0.63338089224315				
C	-6.87664191558790	-0.82360097977235	0.28033344459435				

5 SYNTHESIS AND REACTIVITY OF AN IRON–TIN COMPLEX WITH ADJACENT STANNYLIDINE AND FERRIOSTANNYLENE UNITS



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Accepted, January 28, 2025 in

J. Am. Chem. Soc. **2025**

DOI: 10.1021/jacs.4c18423

This work is dedicated to Professor Philip P. Power, a pioneer in main group and transition metal coordination chemistry, on the occasion of his retirement.

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Yang Liu synthesized and characterized the complexes, performed, and analyzed the computational calculations, and prepared the original draft. **Franz F. Westermair** measured and analyzed the ^{119}Sn NMR data at room temperature and up to 353 K, and conducted DFT calculations on the ^{119}Sn NMR chemical shifts. Ruth M Gschwind supervised and analyzed the ^{119}Sn NMR work. Isabelle Becker recorded and analyzed the ^{57}Fe Mössbauer data. Franc Meyer supervised the ^{57}Fe Mössbauer measurements. Yang Liu, Michael Bodensteiner, Sebastian Hauer and Christoph Hennig collected X-ray diffraction data, and solved and refined the crystal structures. Gábor Balázs analyzed data and edited the manuscript. Robert Wolf conceived the original idea, supervised the project, analyzed data, and edited the manuscript. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

5 Synthesis and Reactivity of an Iron–Tin Complex

5.1 Abstract

Heavier transition metal carbyne analogs hold significant potential for cooperative activation of small molecules. However, complexes containing more than one tetrylidyne ligand RE (E = Si, Ge, Sn, and Pb) are rare due to the high oligomerization tendency of RE ligands. In this study, we describe the complex $[\text{Fe}(\text{SnAr}')_2]$ (**1**; Ar' = 2,6-Dipp₂-C₆H₃, Dipp = 2,6-*i*-Pr₂-C₆H₃), which features adjacent Fe–Sn single and double bonds. Complex **1** exhibits versatile reactivity with transition metal and main group compounds. Treatment of complex **1** with Ni(COD)₂ (COD = 1,5-cyclooctadiene) yields the tetranuclear complex $[\text{Fe}(\mu\text{-SnAr}')_2\text{Ni}]$ (**2**), characterized by an unusual “push–pull” interaction between nickel(0) and the two coordinating Sn atoms, as revealed by quantum chemical studies. The reaction of complex **1** with AlBr₃ results in Al–Br bond cleavage and Ar' migration to aluminum. CH₃I adds oxidatively to the Sn atom that is singly bonded to Fe, while PMe₃ coordinates to Fe, inducing reversible cleavage of the Fe=Sn double bond. In addition, complex **1** activates inorganic molecules. CO₂ undergoes disproportionation to produce a carbonate-bridged Ar'Sn(μ-OCO₂)SnAr' ligand, whereas CS₂ is reductively coupled to form an ethylene tetrathiolate ligand (C₂S₄⁴⁻). The reaction with white phosphorus (P₄) generates an unusual Ar'P₄Sn₂Ar' ligand. This multifaceted reactivity illustrates the behavior of the Fe and Sn sites in complex **1**, suggesting that complexes of this type are promising reagents for small molecule activation.

5.2 Introduction

Terminal carbyne complexes typically possessing a metal–carbon triple bond M≡CR (Figure 5.1a, **I**), have been widely investigated ever since the pioneering works by Fischer and Schrock in the 1970s,^[1,2] unfolding their broad applications in materials science and organic transformations, e.g., alkyne metathesis.^[3] In contrast, metal complexes with monosubstituted heavier tetrylidyne ligands RE (E = Si, Ge, Sn and Pb) are much less explored. These heavier carbyne homologues exhibit M–ER bonding interactions and reactivities that differ significantly from their carbon counterparts.^[4]

The heavier group 14 elements, Si–Pb, show a strong reluctance to engage in s/p valence orbital hybridization, resulting in a decreased tendency for heavier tetrylidyne RE to form multiple bonds.^[5] Nevertheless, a few examples of M≡ER triple bonds, similar to metal carbyne complexes (Figure 5.1a, **I**) and metallotetrylenes showing M–ER single bonds (Figure 5.1a, **III**) have been reported.^[4,6,7,8] The singly bonded RE ligands (M–ER) are usually amphiphilic due to a chemically active electron lone pair and vacant p orbital (s) on the p-block element (Figure 5.1a, **III**).^[9] Additionally, the Wesemann and Tilley groups reported several cationic metal complexes $[\text{M}=\text{ER}]^+$ (M = Ti, Ir, and Co; E = Ge, Sn) bearing M=E double bonds recently.^[10,11] In these complexes, the positive charge is largely localized on the p-block atom which also possesses an empty p-orbital to avoid the otherwise reactive RE radical (Figure 5.1a, **II**). Noteworthy, $[\text{Ir}=\text{ER}]^+$ (E = Ge, Sn) complexes have shown pronounced reactivity in cooperative X–H bond activation (X = N, O, H).^[10b]

Overall, the unique bonding characteristics, coupled with the cooperativity between the metal and p-block centers, endow $[\text{M}(\text{ER})]$ complexes with distinctive reactivity, positioning them at the forefront of synthetic chemistry in the quest for innovative molecular activation methodologies. The application of $[\text{M}(\text{ER})]$ (E = Si–Pb) complexes in cooperative small molecule activation, such as H₂,^[10b,12] NH₃,^[10b,13] CO₂^[10c] and aldehydes/ketones,^[14] as well as in catalysis^[9c] has been demonstrated, although the number of successful examples remains relatively limited.

Synthesis and Reactivity of an Iron–Tin Complex 5

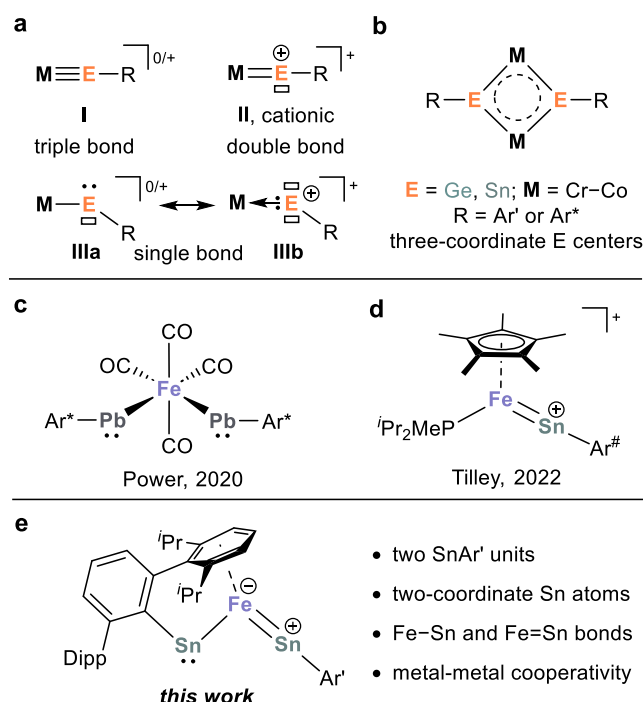


Figure 5.1: (a) Bonding modes between transition metal and monosubstituted tetryl element ligand. (b) M_2E_2 clusters. (c) Ferriobis(plumbylene) with two PbAr* units. (d) Iron–stannylidyne complex featuring Fe=Sn double bond. (e) The FeSn₂ cluster **1**.

Inspired by the rapidly growing family of multimetallic systems that exhibit enhanced reactivity due to cooperative effects,^[15] we sought to further develop this strategy by incorporating two heavier RE units into a transition metal complex. Specifically, we targeted a rare heterotrimetallic ME_2 core with two-coordinate p-block metal centers. Compared to the ubiquitous heterobimetallic ME core, such a system would be of fundamental interest not only in general synthetic chemistry but also in molecular activation, as it offers potentially greater flexibility for substrate binding in terms of available reactive sites from multiple M/E centers, and hence greater scope of reactivity.

However, the synthesis of type $[M(ER)_2]$ (E = Si–Pb) complexes with adjacent RE ligands is challenging due to the inherent propensity of RE moieties toward dimerization to form a ditetrylyne unit REER.^[16] Power and coworkers have described heterotetrametallic complexes $[M(ER)_2]$ (M = Cr, Mo, W, Fe, Co; E = Ge, Sn; Figure 5.1b) featuring rhomboid M_2E_2 cores.^[17] Each RE ligand bridges two metal atoms in those complexes, resulting in three-coordinate E centers with suppressed electrophilicity and nucleophilicity due to the additional $M \rightarrow E/E \rightarrow M$ interactions, reducing their reactivity. Nevertheless, the $Co_2Sn_2Ar'_2$ (Ar' = 2,6-Dipp₂-C₆H₃, Dipp = 2,6-*i*Pr₂-C₆H₃) cluster activated white phosphorus (P₄), affording an unusual ternary complex with a $Co_2Sn_2P_4$ core.^[17c] To our knowledge, the only well-defined complex containing more than one coordinating RE unit with two-coordinate group 14 atoms is $[(CO)_4Fe(PbAr^*)_2]$ (Ar* = 2,6-Trip₂-C₆H₃, Trip = 2,4,6-*i*Pr₃-C₆H₂; Figure 5.1c), synthesized by the reaction of a diplumbyne with $Fe_2(CO)_9$.^[18] The two Fe–Pb–C_{*ipso*} linkages are bent and feature Fe–Pb single bonds (type **IIIa**). However, its reactivity was not reported. Additionally, complexes featuring Fe–Sn multiple bonds are rare, with most known examples being iron-stannylene complexes $[Fe-(SnR_2)]$.^[11,19] Tilley's cationic complex $[Cp^*(^iPr_2MeP)Fe-(SnAr^\#)]^+$ (Figure 5.1d) and the related hydride $[Cp^*-(^iPr_2MeP)Fe(H)(SnAr^\#)]^+$ (Ar[#] = 2,6-Mes₂-C₆H₃, Mes = 2,4,6-Me₃-C₆H₂) appear to be the only iron-stannylidyne complexes reported so far. According to structural and quantum chemical studies, these complexes

5 Synthesis and Reactivity of an Iron–Tin Complex

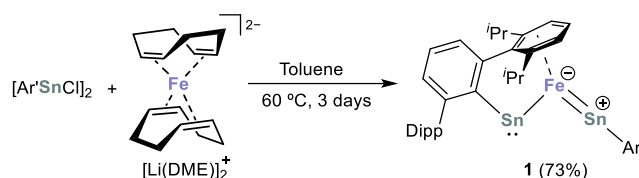
show a type II Fe=Sn double bond.^[11] Remarkably, the reduction of this complex by a single electron led to intramolecular C–H bond activation, which was proposed to proceed through a neutral iron-stannylyne intermediate featuring an Fe=Sn double bond. However, isolable neutral complexes featuring M=ER double bonds are still unknown to date.

Here, we report the synthesis and characterization of the neutral FeSn₂ cluster **1** bearing two adjacent Ar'Sn ligands (Figure 5.1e). The bonding situation and electronic structure of **1** have been established spectroscopically and computationally, revealing an Fe–Sn single bond and an Fe=Sn double bond within the same molecule. The reactivity of this hetero-trimetallic system toward Lewis acid (AlBr₃), Lewis base (PMe₃), and small inorganic molecules such as P₄, CS₂ and CO₂ was investigated. These studies illustrate a highly versatile and cooperative reactivity of the amphiphilic FeSn₂ core of **1**.

5.3 Results and Discussion

5.3.1 Synthesis and Characterization

Treatment of [Ar'SnCl]₂ with one equivalent of the Fe²⁺ synthon [Li-(DME)]₂[Fe(COD)₂] (COD = 1,5-cyclooctadiene, DME = 1,2-dimethoxyethane) in toluene at 60 °C (3 days) leads to the formation of the title complex [Fe(SnAr')₂] (**1**) in 73% yield as dark brown crystals after workup (Scheme 5.1).



Scheme 5.1: Synthesis of Complex **1**.

The reaction of [Ar'SnCl]₂ with two equivalents of the Fe[−] synthon [K(18-c-6)][Fe(η⁴-anthracene)₂] (18-c-6 = 18-crown-6) still yields **1**, showing the preference for a single Fe site of this system. Complex **1** is stable at room temperature (r.t.) in an inert atmosphere, both in the solid state and in common organic solvents (e.g., benzene, toluene and THF). Heating a solution of **1** in C₆D₆ to 80 °C for several days does not result in any noticeable decomposition as evidenced by NMR monitoring experiments. However, **1** decomposes rapidly in air to give intractable mixtures.

The molecular structure of **1** was determined by single-crystal X-ray crystallography (Figure 5.2) and further supported by multinuclear NMR spectroscopy, HR-LIFDI-mass spectrometry, inductively coupled plasma-optical emission spectroscopy (ICP-OES) and elemental analysis. The molecular structure of **1** features a unique FeSn₂ core where the iron atom bridges the two Ar'Sn moieties in an asymmetric fashion and is η⁶-coordinated by a flanking Dipp-aryl ring of one Ar' substituent (Figure 5.2a). The overall structure of compound **1** resembles an unknown metal η²-distannyne complex. Notably, in metal η²-disilyne^[20] and η²-digermynes^[16c,21] complexes, [M(η²-R'EER')] (M = Ni, Pd, Pt, Ag; E = Si, Ge; R' = alkyl, aryl or silylene substituent), the ME₂ rings are perpendicular to the C–E–E–C array so that the metal center can interact with the E≡E π_{out} orbitals in a classic way that is analogous to metal η²-alkyne complexes.

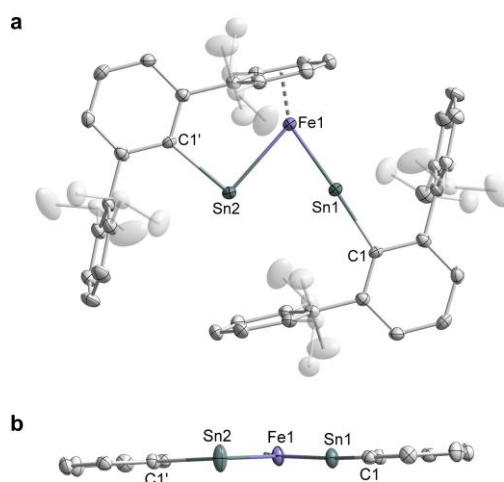


Figure 5.2: Molecular structure of complex **1** with 50% probability ellipsoids: front view (a) and side view without Dipp groups (b). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–Sn1 2.2954(7), Fe1–Sn2 2.6207(7), Sn1–C1 2.135(2), Sn2–C1' 2.243(2), Sn1···Sn2 3.0595(6); Sn1–Fe1–Sn2 76.66(2), Fe1–Sn1–C1 176.60(6), Fe1–Sn2–C1' 91.10(5).

However, the FeSn₂ plane in **1** is coplanar with the C1'–Sn1···Sn2–C1 array (Figure 5.2b). Given that the slipped Sn–Sn π_{in} orbital in the distannyne compound [Ar'SnSnAr'] is reluctant to engage in bonding, a distinct Sn–Fe–Sn bonding mode is expected for **1** (see below).^[22]

The Fe1–Sn2 bond length of 2.6207(7) Å and the bent geometry at Sn2 ($\angle$ Fe1–Sn2–C1': 91.10(5)°) in **1** signify a metallostannylene structural motif of the Fe₁Sn₂Ar' unit with a type **III** Fe1–Sn2 single bond (Figure 5.1a). Compared to the structures of known ferriostannylene complexes (Fe–Sn: 161 2.56–2.61 Å and $\angle$ Fe–Sn–C: 106.7–118.2°),^[11,17b,23] the Fe1–Sn2 bond length is slightly longer, and the Fe1–Sn2–C1' angle is more acute, probably due to the strain induced by the coordination of the arene moiety to iron. In distinct contrast, the Fe1–Sn1 bond length of 2.2954(7) Å is significantly shorter than the Fe1–Sn2 bond, and the geometry at Sn1 is nearly linear ($\angle$ Fe1–Sn1–C1: 176.60(6)°). These metrical parameters are comparable with those in [Cp*(ⁱPr₂MeP)Fe–(SnAr[#])]⁺ (2.2889(6) Å and 169.85(9)°; Figure 5.1d)^[11] and complex **4** (2.2960(4) Å and 175.45(8)°; see below), indicating the Fe1=Sn1 double bond character in **1**. The Sn1···Sn2 distance of 3.0595(6) Å is substantially longer than those of the relevant distannyne compound [Ar'SnSnAr'] (2.667(5) Å)^[16a] and complex [Co(SnAr')]₂ (2.8700(5) Å),^[17c] as well as a regular Sn–Sn single bond (ca. 2.80 Å),^[24] but shorter than the sum of the van der Waals radii of tin (Σr_{vdW} = 4.84 Å).^[25]

The ¹H NMR spectrum of **1** (C₆D₆, 298 K) shows three sets of signals attributed to the Dipp flanking groups with an integral ratio of 1:1:2, agreeing with the asymmetric coordination pattern (Figure S1). Neither broadening nor coalescences of these signals was observed at 341 K, indicating the absence of dynamic behavior, i.e., exchange of the coordinating aryl groups on the NMR time scale (Figure S4). The ¹¹⁹Sn{¹H} NMR spectrum of **1** shows two singlets with remarkably different chemical shifts at +466 ppm and +3229 ppm, which are assigned to Sn1 and Sn2, respectively. This assignment is supported by DFT calculations (Table S19). The downfield-shifted signal of Sn2 lies within the range of 2515–3762 ppm, characteristic of ferriostannylenes (type **IIIa**)^[11,23] and other metallostannylenes with two-coordinate Sn centers.^[10b,12a] The signal of Sn1 is markedly upfield shifted relative to Sn2, which indicates a strong Fe → Sn backdonation, namely the formation of a multiple bond, and is similar to that of the doubly bonded Sn1 in **4** (+768 ppm; see below). By contrast, the cationic complex

5 Synthesis and Reactivity of an Iron–Tin Complex

$[\text{Cp}^*(^i\text{Pr}_2\text{MeP})\text{Fe}(\text{SnAr}^\#)]^+$ shows a $^{119}\text{Sn}\{^1\text{H}\}$ NMR resonance at +1024 ppm.^[11] The zero-field ^{57}Fe Mössbauer spectrum of **1**, recorded at 80 K for a solid sample, displays a doublet with the isomer shift value of $\delta = 0.61 \text{ mm s}^{-1}$ and quadrupole splitting value of $|\Delta\text{EQ}| = 0.66 \text{ mm s}^{-1}$. Although the relationship between the $\delta/\Delta\text{EQ}$ values and oxidation states of iron complexes featuring low-coordinate and low-valent Fe centers remains ambiguous,^[26] the isomer shift of **1** is positively shifted compared with known low-valent, η^6 -arene-coordinate Fe^0 and Fe^{1-} systems, such as $[\text{bis}(\text{NHC})\text{Fe}^0(\eta^6\text{-arene})]$ (0.43 mm s^{-1} ; NHC = *N*-heterocyclic carbene),^[27] $[(\eta^6\text{-arene})\text{Fe}^0\text{Ge}(\text{N}''')(\text{NHC})]^+$ (0.47 mm s^{-1} ; $\text{N}''' = [\text{Ph}_2\text{PCH}_2\text{Si}(^i\text{Pr})_2](\text{Dipp})\text{N}$),^[12b] and $[(\eta^6\text{-arene})\text{Fe}^{1-}\text{Sn}(\text{N}''')(\text{NHC})]$ (0.52 mm s^{-1}).^[12b] The higher isomer shift of **1** may therefore indicate a comparatively high d-electron density at the Fe atom, which shields the s-electrons from the nucleus. The UV–vis spectrum of **1** (toluene, r.t.) shows a prominent band at 450 nm and two weak, broad bands at 590 and 730 nm. These absorption features are assigned to transitions primarily from the highest occupied molecular orbitals (HOMO and HOMO–1) to the lowest unoccupied molecular orbitals (LUMO, LUMO+1, and LUMO+2), based on time-dependent DFT calculations (Figure S61).

5.3.2 Electronic Structure and Bonding

To gain more insight into the electronic structure of **1**, quantum chemical calculations were performed at different levels of theory (see Supporting Information for details). The optimized structure agrees very well with the X-ray crystallographic data (Figure S60 and Table S7). The HOMO (–4.07 eV) represents the Fe1–Sn2 σ -bond with significant contribution from the electron lone pair on Sn2 (31% Fe, 46% Sn2; Figure 5.3a). HOMO–1 (–4.44 eV) corresponds to the Fe1–Sn1 out-of-plane π -bond with minor delocalization toward Sn2, forming a 3-center-2 electron (3c2e) π -interaction over the FeSn₂ core (37% Fe1, 30% Sn1, 13% Sn2; Figure 5.3b). The Fe1–Sn1 σ -bond is much lower in energy (HOMO–16, –7.27 eV; Figure S62). The LUMO and LUMO + 2 mainly consist of the Sn-centered p orbitals, specifically the orthogonally oriented Sn2 p_{out} and Sn1 p_{in} orbitals, while the LUMO + 2 is mainly contributed by the Fe 3d orbitals (Figure S62). The bonding modes between Fe and Sn atoms in **1** are further illustrated by electron localization function (ELF)^[28] analysis, which exhibits the electron distribution patterns consistent with a Fe1=Sn1 double bond, a Fe1–Sn2 single bond with weak π -interaction, and relatively low ELF value between the two Sn atoms (Figure S64). The Mayer bond order (MBO) of Fe1–Sn1 (1.50) and Fe1–Sn2 (0.94) bonds suggests their double and single bond character, respectively, which is in line with the canonical MO and ELF analyses. The MBO of the Sn1 $\cdots$ Sn2 (0.59) unit is relatively low, suggesting a rather weak Sn $\cdots$ Sn interaction in **1**. An independent gradient model based on Hirshfeld partition (IGMH)^[29] analysis also reveals that the Sn $\cdots$ Sn interaction is much weaker compared to the Fe–Sn interactions (Figure S65).

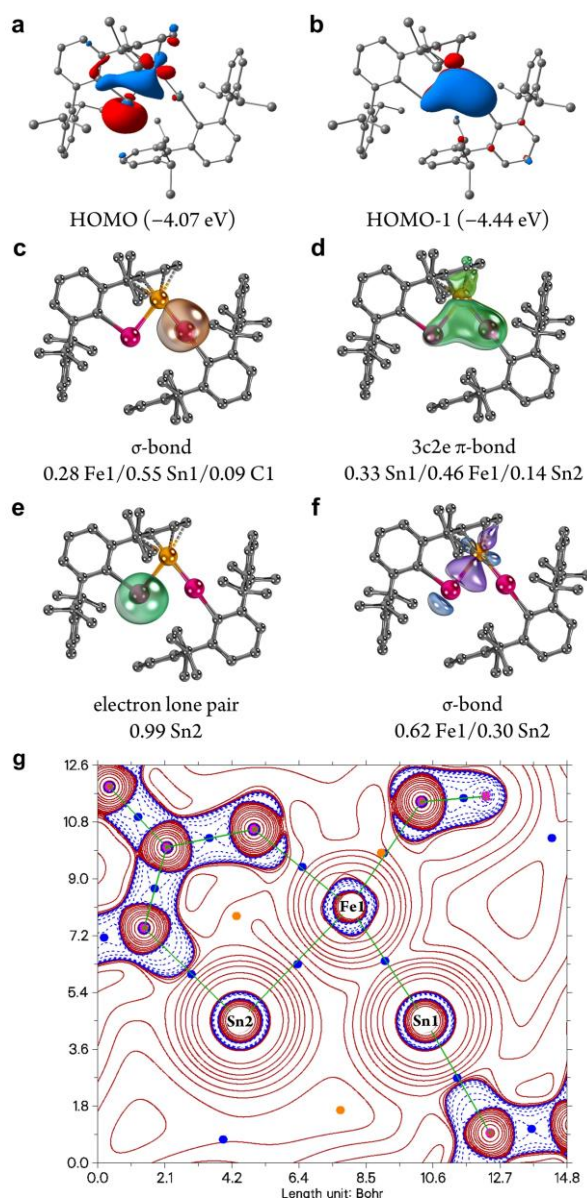


Figure 5.3: (a,b) Selected MOs of **1** (Isovalue = 0.04). (c–f) Selected IBOs of **1**. The bond type and percentage of the electron density on Fe and Sn are given. (g) Plot of the Laplacian of the electron density on the FeSn₂ plane of **1** (BCP: blue dots, RCP: brown dots, bond paths: green lines).

Intrinsic bond orbital (IBO)^[30] analysis provides further insights into the bonding situation of **1**. The Fe1–Sn1 σ -bonding interaction consists mainly of the Sn1-based lone pair, thus representing a dative bond (Figure 5.3c). The out-of-plane Fe1–Sn1 π -bond extends to the adjacent Sn2 atom, which aligns with the HOMO-1 of **1** (Figure 5.3d). A nonbonding electron lone pair resides exclusively at Sn2 and lies in the FeSn₂ plane (Figure 5.3e). The Fe1–Sn2 σ -bond shows strong polarization toward Fe1 (Figure 5.3f). The natural charge distribution (Fe1: -0.65, Sn1: +1.04, Sn2: +0.92; Table S8) reveals an electron-rich iron center, which is consistent with the high positive isomer shift value obtained from the ⁵⁷Fe Mössbauer measurement of **1** (see above), and the positive charge accumulation of Sn centers. Furthermore, substantial net electron transfer from the Ar'Sn1 moiety (+0.52 au) to the Ar'Sn₂Fe unit is calculated, implying a zwitterionic character of **1** (Table S8). Quantum theory of atoms in molecules (QTAIM)^[31] analysis reveals two Fe–Sn bond critical points (BCP; blue points). However, neither a

5 Synthesis and Reactivity of an Iron–Tin Complex

BCP between Sn1 and Sn2 atoms (Figure 5.3g) nor a ring critical point (RCP) within FeSn₂ unit could be located, indicating the absence of a Sn1–Sn2 bond. The energy density ($H(r)$) and ellipticity of electron density ($\epsilon(r)$) at the BCP of Fe1–Sn1 bond ($H(r)$: -3.1 e.a_0^{-3} ; $\epsilon(r) = 0.15$) are larger than those of the Fe1–Sn2 bond ($H(r)$: -1.5 e.a_0^{-3} ; $\epsilon(r) = 0.09$), providing additional evidence for the multiple bond character of the Fe1–Sn1 bond.^[32] The delocalization index (DI)^[33] values of the basins between Fe1 and Sn1 (1.41)/Sn2 (0.94), and Sn1 and Sn2 (0.46) agree well with the MBO.

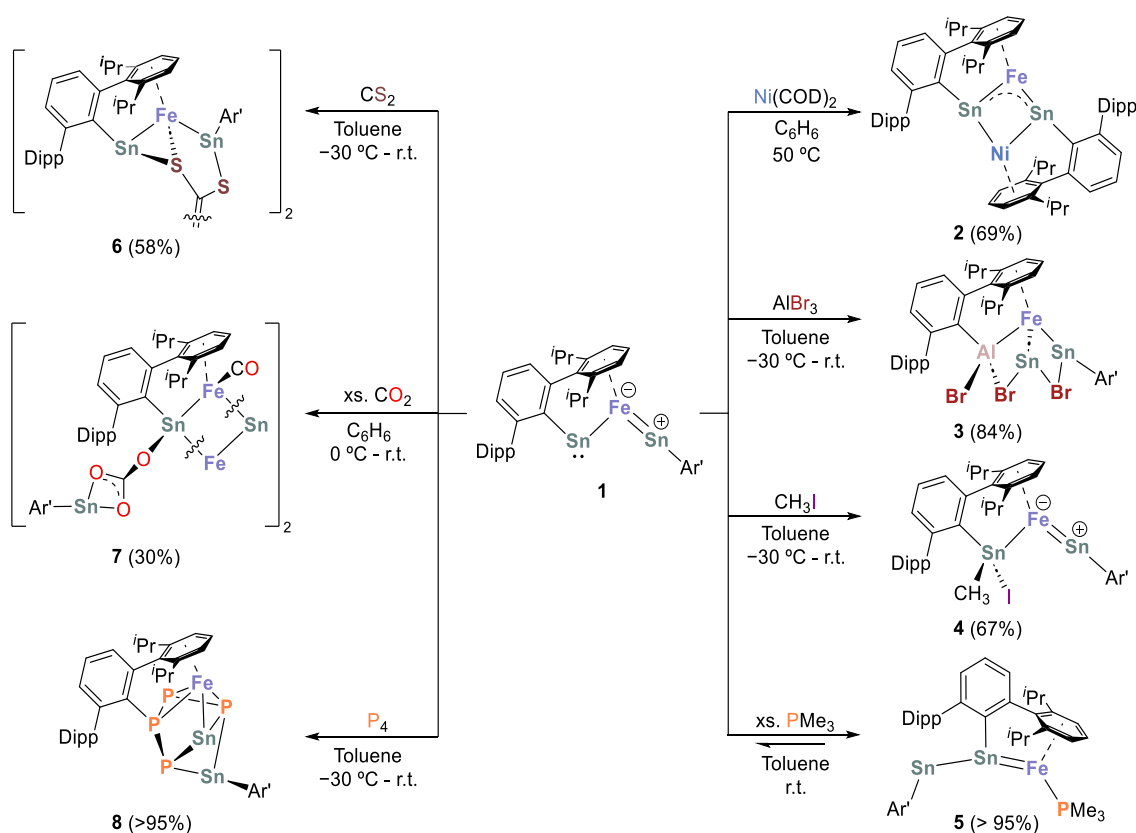
An energy decomposition analysis coupled with natural orbitals for chemical valence (EDA-NOCV)^[34] of the Fe1=Sn1 bond provides a consistent bonding scenario with the above analyses. The smallest orbital interaction energy $|\Delta E_{\text{orb}}|$ (139.62 kcal mol⁻¹) was found between the [Ar'Sn2Fe]⁻ anion and the [Ar'Sn1]⁺ cation fragments, both in the singlet state, which is significantly smaller than those of other states (e.g., $S = 1/2-4$; 198.59–331.16 kcal mol⁻¹; Table S17 and Figure S81 and see SI for details). These data further corroborate the zwitterionic character of **1** and indicate the presence of a σ -donor- π -acceptor type double bond between Fe1 and Sn1. Overall, the bonding of the FeSn₂ core in **1** can be best described as containing a Fe1=Sn1 double bond comprising of one σ - and one π -bond and a type **IIa** Fe1–Sn2 single bond, with little or negligible Sn1...Sn2 interaction. It is worth noting that the ligand constraint might play a crucial role in the formation of such a bonding situation. For example, the complex $[(\eta^2\text{-RSiSiR})\text{Fe}(\eta^6\text{-C}_6\text{H}_6)]$ ($R = \kappa^2\text{-amidinate}$),^[35] shows a three-membered FeSi₂ metallacyclic structure. Additionally, complex **1** has a zwitterionic character with the positive charge residing primarily at the doubly bonded Sn1 atom. Noteworthy, a few cationic transition metal complexes with M=ER double bonds have been reported (e.g., $[(\text{PMe}_3)_3(\text{H})\text{M}(\text{EAR}^\#)]^+$ ($M = \text{Ir, Co}$; $E = \text{Ge, Sn}$)^[10b,c] and $[\text{Cp}^*(\text{Pr}_2\text{MeP})\text{Fe}(\text{SnAr}^\#)]^+$,^[11] Figure 5.1d). To our knowledge, **1** represents the first isolable neutral iron-stannyldiyne complex featuring an Fe=Sn double bond.

5.3.3 Reactivity Study

To test if the lone pair on Sn2 and the p-vacant orbital on Sn1 could potentially form “push-pull” interactions, we performed the reaction of **1** with Ni(COD)₂. This led to the formation of complex **2** as dark green crystals in 69% yield (Scheme 5.2). The solid-state molecular structure of **2** (Figure 5.4a) reveals a planar, quasi-rhomboid FeNiSn₂ core structurally similar to the Co₂Sn₂ core in complex $[\text{Co}(\text{SnAr}')_2]_2$.^[17c] The Ni1–Sn1 (2.7018(24) Å) and Ni1–Sn1' (2.4328(22) Å) bond lengths are comparable to the *bis*-(stannylene) complexes reported by Wesemann and coworkers, where two stannylene (SnR₂) ligands serve as L- and Z- type ligands.^[36] The Fe1–Sn1 (2.3775(22) Å) and Fe1–Sn1' (2.4431(23) Å) bonds are elongated and shortened, respectively, compared to those in **1** (Table 5.1). Albeit isoelectronic, complex **2** shows a distinct electronic structure from $[\text{Co}(\text{SnAr}')_2]_2$.^[17c] The IBO analysis of **2** reveals that the electron lone pair from Sn1' coordinates to Ni forming a highly polarized Ni1–Sn1' σ -bond (0.29 Ni/0.53 Sn1'), while the Ni1–Sn1 bond is predominantly contributed by Ni 3d orbitals (0.90 Ni/0.13 Sn1; Figure S68). This suggests a Sn1' $\rightarrow$ Ni $\rightarrow$ Sn1 “push-pull” interaction, showcasing the electron donating and accepting properties of Sn2 and Sn1 in **1**, respectively. In addition, IBO and MBO analyses of the Fe–Sn bonds in **2** (IBO $\pi_{\text{Sn1-Fe1-Sn1'}}$: 0.29 Sn1/0.44 Fe1/0.20 Sn1'; MBO_{Fe1–Sn1}: 1.26, MBO_{Fe1–Sn1'}: 1.21; Figure S68 and Table S10), indicate a π -electron flow from Sn1 to Sn2 (via the central Fe) upon the addition of Ni. Despite the contraction of the Sn1...Sn1' distance to 2.8860(3) Å in **2** (vs 3.0595(6) Å in **1**), QTAIM analysis suggests no Sn1–Sn1' bond (Figure S69). The ¹H NMR spectra of **2** recorded at 298 and 341 K are nearly identical, displaying four sets of signals corresponding to the Dipp groups. This observation is consistent with the asymmetric structure observed in the solid state and indicates no dynamic behavior in solution on the NMR time scale (Figure S8). Due to the increase in the coordination number of Sn1', a considerable upfield shift of its

Synthesis and Reactivity of an Iron–Tin Complex 5

$^{119}\text{Sn}\{^1\text{H}\}$ NMR resonance signal (+1700 ppm vs +3226 ppm in **1**; Table 5.1) was observed,^[37] while the signal at +369 ppm was assigned to Sn1 (Table S19). The zero-field ^{57}Fe Mössbauer spectrum (80 K, solid state) shows a doublet with $\delta = 0.55 \text{ mm s}^{-1}$ and $|\Delta\text{EQ}| = 0.76 \text{ mm s}^{-1}$.



Scheme 5.2: Reactivity Study of Complex **1**.

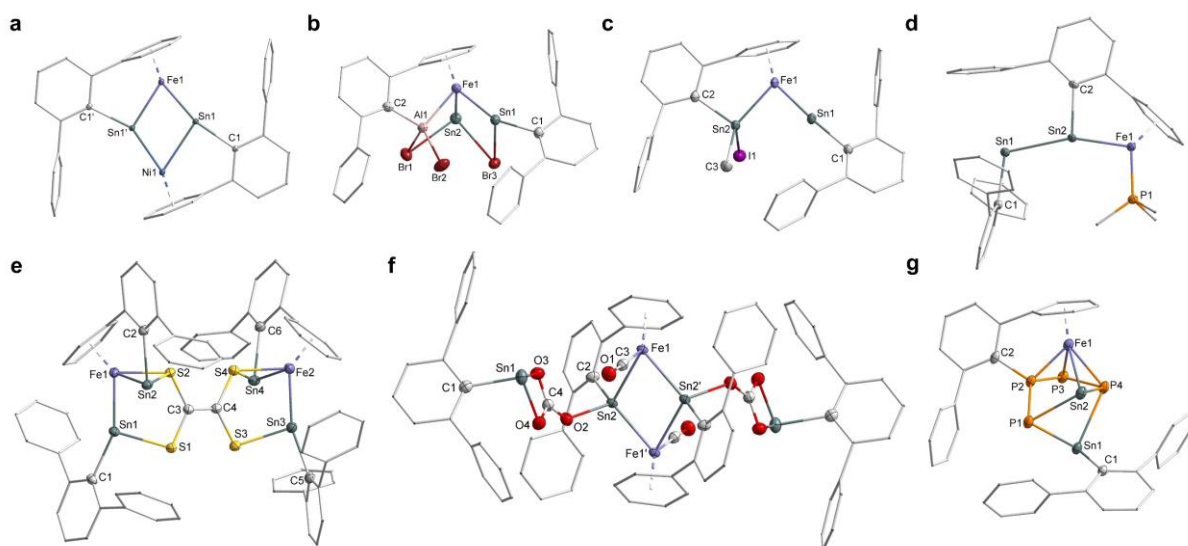


Figure 5.4: Molecular structures of **2** (a), **3** (b), **4** (c), **5** (d), **6** (e), **7** (f), and **8** (g), showing 50% probability thermal ellipsoids. Hydrogen atoms, solvent molecules, and the *i*Pr substituents are omitted for clarity.

The smaller δ value of **2** compared to **1** (0.66 mm s^{-1} ; Table 5.1) suggests a decrease of electron density on Fe1, which is consistent with the change of its natural charge (Fe1: -0.46 in **2** vs -0.65 in **1**; Table S8). To probe the potential amphiphilic reactivity of the Sn centers in **1**, as predicted by the canonical MO analysis, we investigated

5 Synthesis and Reactivity of an Iron–Tin Complex

the reactivity of **1** toward the Lewis acid AlBr_3 , the electrophile CH_3I , and the nucleophile Me_3P . At -30°C , **1** reacts readily with AlBr_3 , affording complex **3** as maroon crystals in 84% yield (Scheme 5.2). The solid-state molecular structure of **3** (Figure 5.4b) shows that, instead of a donor-acceptor adduct, $\text{Al}-\text{Br}$ bond cleavage along with Ar' migration occurred. The Ar' substituent migrates from $\text{Sn}2$ to Al , while one Br migrates from Al to bridge the two Sn centers with $2.6875(5) \text{ \AA}$ ($\text{Sn}1-\text{Br}3$) and $2.8765(8) \text{ \AA}$ ($\text{Sn}2-\text{Br}3$) bond lengths.

Table 5.1: Selected Bond Lengths and Angles ($^\circ$) and Experimental ^{119}Sn NMR and ^{57}Fe Mössbauer Data of Complexes **1–8**.

	Fe–Sn1 ($\text{\AA}$)	Fe–E ($\text{\AA}$)	Fe1–Sn1–C, Fe1–E–C ($^\circ$)	$\delta_{\text{Sn}1}$, δ_{E} (ppm) ^a	$\delta/ \Delta E_{\text{Q}} $ ($\text{mm}\cdot\text{s}^{-1}$)
1 , E = Sn2	2.2954(7)	2.6207(7)	176.60(6), 91.10(5)	466, 3229	0.61, 0.66
2 , E = Sn1'	2.3775(22)	2.4431(23)	165.29(7), 95.98(7)	369, 1701	0.55, 0.76
3 , E = Sn2	2.3768(9)	2.5249(6)	158.02(9)	15, 2393	
4 , E = Sn2	2.2960(4)	2.5188(5)	175.45(8), 97.45(8)	768, 107 ^b	
5 , E = Sn2		2.4864(7)	99.78(2)	2403, 1456	0.50, 1.17
6 , E = Sn2	2.4136(8)	2.7925(8)	154.92(5), 86.14(5)	–124, 655 ^c	
7 , E = Sn2/Sn2'		2.5421(5)/2.5874(6)	96.50(7), 132.50(7)	264, 343 ^c	
8 , E = Sn2		2.7892(7)		–455, –366 ^d	

^aSignals were assigned based on DFT calculations (Table S19). ^bSignals were assigned based on a comparison with literature data. ^cSignals were not assigned. ^dMultiplets due to the $\text{Sn}-\text{P}$ coupling.

The $\text{Sn}1$ center adopts a nearly T-shaped geometry with $\text{Fe}1-\text{Sn}1-\text{C}1$ angle of $158.02(9)^\circ$ and with the $\text{Fe}1-\text{Sn}1$ bond length of $2.3768(9) \text{ \AA}$, which lies within the range of the reported iron-stannylene complexes ($2.37\text{--}2.48 \text{ \AA}$).^[11,38] The $\text{Sn}2$ center has a pyramidal environment, which is typical for three-coordinate $\text{Sn}(\text{II})$ centers with a stereochemically active electron lone pair. The $\text{Fe}1-\text{Sn}2$ ($2.5249(6) \text{ \AA}$) bond is considerably shorter than those of ferriostannylene complexes ($2.56\text{--}2.60 \text{ \AA}$).^[11,17b,23] IBO analysis corroborates the presence of $\text{Fe}1-\text{Sn}1$ and $\text{Fe}1-\text{Sn}2$ single bonds and the nonbonding electron lone pair on $\text{Sn}2$ (Figure S71). The $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **3** displays two singlets at +15 ppm and +2393 ppm, which were assigned to $\text{Sn}1$ and $\text{Sn}2$, respectively, based on DFT calculations (Table S19). The high-frequency chemical shift for $\text{Sn}2$ indicates a low coordination number and is in agreement with the $^{119}\text{Sn}\{^1\text{H}\}$ NMR chemical shifts reported for ferriostannylene complexes.^[11,23] These structural features allow several possible Lewis-type descriptions of **3** (Scheme S1).

The reaction of **1** with CH_3I afforded complex **4**, resulting from an oxidative addition of CH_3I to $\text{Sn}2$ (Scheme 5.2). Complex **4** was isolated as dark red crystals in 67% yield. The solid-state molecular structure of **4** reveals a $\text{Sn}(\text{IV})$ center in tetrahedral geometry (Figure 5.4c). The $\text{Fe}1-\text{Sn}2$ bond length of $2.5188(5) \text{ \AA}$ lies in the expected range for a $\text{Fe}-\text{Sn}(\text{IV})$ single bond.^[39] The $\text{Sn}1\cdots\text{Sn}2$ distance of $3.3804(5) \text{ \AA}$ is much longer than that in **1** ($3.0596(6) \text{ \AA}$), indicating no interaction between the Sn atoms (Figure S75). Notably, the $\text{Fe}1-\text{Sn}1$ bond distance of $2.2960(4) \text{ \AA}$ and the $\text{Fe}1-\text{Sn}1-\text{C}1$ bond angle of $175.45(8)^\circ$ are almost identical to those in **1** ($2.2954(7) \text{ \AA}$ and $176.60(6)^\circ$; Table 5.1), indicating a similar bonding scenario. Indeed, the presence of an $\text{Fe}1=\text{Sn}1$ double bond and the zwitterionic character of **4**, which includes a $[\text{Ar}'\text{Sn}1]^+$ moiety, is supported by the canonical MO, IBO, NPA and EDA-NOCV analyses (Figures S73, S74, and S82, Tables S8 and S18), as well as the MBO ($\text{MBO}_{\text{Fe}1-\text{Sn}1}$: 1.68; Table S13). Hence, the $\text{Fe}1-\text{Sn}1$ bond is essentially unaffected by the oxidative addition of CH_3I to $\text{Sn}2$. The $^{119}\text{Sn}\{^1\text{H}\}$ NMR resonances of **4** were detected at +768 ppm ($\text{Sn}1$) and +107 ppm ($\text{Sn}2$), which is consistent with

Synthesis and Reactivity of an Iron–Tin Complex 5

an Fe=SnAr' moiety and a tetrahedral Sn(IV) center, respectively.^[11,39] This reaction highlights the amphiphilic character of Sn2 in **1** and demonstrates the potential of **1** to form other complexes with Fe–Sn multiple bonds via the derivatization of the ferriostannylene moiety.

Treatment of **1** with excess PMe₃ resulted in the clean conversion into complex **5**, which was isolated as dark red crystals in quantitative yield (Scheme 5.2). Intriguingly, PMe₃ was found to coordinate to the Fe center, inducing the cleavage of the Fe1=Sn1 double bond and the formation of a Sn1–Sn2 bond, giving rise to a distannyne (Ar'SnSnAr') ligand (see below). Monitoring the stoichiometric reaction of **1** with PMe₃ by ¹H NMR spectroscopy uncovered that the reaction is reversible. A van't Hoff analysis based on ¹H NMR data at various temperatures provides the thermodynamic parameters: $\Delta H^\circ = -14.77 \text{ kcal mol}^{-1}$, $\Delta S^\circ = -32.53 \text{ cal mol}^{-1}$ and ΔG° (298 K) = $-5.08 \text{ kcal mol}^{-1}$ ($G_{calc}^\circ = 5.34 \text{ kcal mol}^{-1}$; Figure S77 for details). The K_{eq} (298 K) was calculated to be $5.3 \times 10^3 \text{ M}^{-1}$, indicating that the formation of **5** is favored. The solid-state molecular structure of **5** shows the Ar'SnSnAr' ligand coordinating to the iron center via one η^1 -Sn atom (Sn2) and one η^6 -Dipp group (**Figure 5.4d**). The three-coordinate Sn2 center adopts a planar geometry with a large Fe1–Sn2–Sn1 angle of 160.12(1)° and a Fe1–Sn2 bond length of 2.4864(7) Å. This Fe1–Sn2 bond is considerably shorter than the Fe1–Sn2 single bond in **1** (2.6207(7) Å; Table 5.1) and lies slightly above the range expected for iron-stannylene complexes (2.37–2.48 Å).^[11,38] In line with this relatively short Fe1–Sn2 bond, IBO and MBO (MBO_{Fe–Sn1}: 1.34) analyses suggest double bond character, comprising both σ and π components (Figure S78 and Table S15). The zero-field ⁵⁷Fe Mössbauer spectrum (80 K, solid state) of **5** reveals a doublet with $\delta = 0.50 \text{ mm s}^{-1}$ and $|\Delta EQ| = 1.17 \text{ mm s}^{-1}$, which is slightly lower than those of **2** (0.55 mm s^{−1}) and **1** (0.66 mm s^{−1}; Table 5.1). The ¹¹⁹Sn{¹H} NMR spectrum of **5** exhibits two singlets at +2403 ppm and +1456 ppm, for Sn1 and Sn2, respectively, which is consistent with the presence of two-coordinate stannylene (Sn1) and metal-stannylene (Sn2) units. The coordination of Lewis basic ligands, such as isocyanides,^[40] amines,^[41] imines^[42] and NHCs^[43] to distannynes, forming L → Sn σ -bonds, has been well established. By contrast, the coordination of distannynes to transition metals is underexplored. So far, only two distannyne-iron carbonyl complexes were reported, where the distannynes are intramolecularly stabilized by amine ligands and act as electron donors, forming Sn → Fe σ -bonds.^[44] Notably, the bonding of the distannyne in **5** is distinct, featuring an Fe1=Sn2 double bond. Moreover, the reversible cleavage and formation of an M–E multiple bond, as observed for **5** in solution, represents a new reaction pattern for heavier tetrylidyne complexes.

The reactivity of **1** toward small molecules, such as carbon disulfide (CS₂), carbon dioxide (CO₂), and white phosphorus (P₄), was also investigated. The addition of one equivalent of CS₂ to **1** in toluene at −30 °C immediately gave a red solution, from which complex **6** was isolated as red crystals in 58% yield (Scheme 5.2). The solid-state molecular structure of **6** shows the reductive coupling of two CS₂ molecules, resulting in a C₂S₄ unit which bridges two FeSn2 clusters in a μ - κ^2 (S¹,S^{1'}): κ^2 (S²,S^{2'}) fashion (Figure 5.4e). One pair of the S atoms (S1 and S3) is each bonded to a Sn atom, while the other pair (S2 and S4) bridges between Sn and Fe atoms. The C₂S₄ unit is planar, with a C3–C4 bond length of 1.355(3) Å, which is close to a typical C=C double bond.^[24b] The C–S bond lengths (1.762(2) Å to 1.786(2) Å) are characteristic of C–S single bonds.^[24] These structural features suggest the presence of an ethylene tetrathiolate (C₂S₄)^{4−} ligand in **6**. The ¹H NMR spectrum (C₆D₆, r.t.) displays only one set of signals that can be assigned to two Ar' groups. Additionally, its ¹¹⁹Sn{¹H} NMR spectrum (C₆D₆, r.t.) exhibits only two singlets at +655 ppm and −124 ppm, supporting a C₂ symmetry of **6** in solution on the NMR time scale. A few p-block element-mediated CS₂ reductive coupling reactions have been reported,^[45] including three examples with stannylenes.^[45b–d] In these cases, the (C₂S₄)^{4−} ligands were proposed to be formed via carbene intermediates and

5 Synthesis and Reactivity of an Iron–Tin Complex

favor a $\mu\text{-}\kappa^2(\text{S}^1, \text{S}^2):\kappa^2(\text{S}^1, \text{S}^2)$ coordination mode (Figure S59). The formation of **6** is proposed to proceed through an initial [3 + 2] cycloaddition of CS_2 to the $\text{Fe}=\text{Sn}$ double bond of **1**, assisted by Sn_2 , generating a carbene species, which then dimerizes to afford **6** (Scheme S2). This mechanism is underpinned by the reactivity of a disilene with CS_2 , where a [3 + 2]-cycloadduct with a bridging $[\text{C}_2\text{S}_4]^{4-}$ unit was obtained.^[46]

The ability of **1** to reduce CS_2 motivated us to explore its reactivity toward CO_2 , a much less reactive inorganic molecule. Exposure of a benzene solution of **1** (dark brown) to a CO_2 atmosphere (4 bar) led to an orange solution, from which complex **7** was isolated as orange crystals in 30% yield (Scheme 5.2). According to the solid-state molecular structure of this complex, **1** reacts with two equivalents of CO_2 , forming a CO and a CO_3^{2-} ligand. The CO ligand coordinates to Fe, while the carbonate ligand bridges the two Sn atoms in a $\mu\text{-}\kappa^1(\text{O}):\kappa^2(\text{O}', \text{O}'')$ fashion. Two of these units are held together via a planar, centrosymmetric Fe_2Sn_2 ring (Figure 5.4f). Recently, Wesemann and coworkers reported the CO_2 reduction with a cobalt-stannyldiyne complex $[(\text{Me}_3\text{P})_3\text{CoSnTbb}]$ ($\text{Tbb} = 4\text{'Bu-}2,6\text{-(CH(SiMe}_3)_2)_2\text{-C}_6\text{H}_2$),^[10e] which is proposed to proceed via an initial [2 + 2]-cycloaddition of CO_2 to the $\text{Co}\equiv\text{Sn}$ triple bond. The Aldridge group has reported distannyne-mediated reductions of CO_2 , giving $[\text{Ar}^R\text{Sn}(\mu\text{-OCO}_2)\text{SnAr}^R]$ ($\text{Ar}^R = \text{NCN}$ pincer ligand) as products, where a *bis*(stannylen)oxide $[(\text{ArEtSn})_2\text{O}]$ intermediate was identified.^[47] Given the simultaneous existence of a metal–tin multiple bond, the electron-rich nature of the Fe center, the electrophilic Sn centers, and the closely positioned $\text{Ar}'\text{Sn}$ moieties in **1**, we propose that the first step in the reduction of CO_2 by **1** occurs through a [2 + 2]-cycloaddition of CO_2 to the $\text{Fe}=\text{Sn}$ double bond, assisted by the second Sn atom (Scheme S3). This is followed by the splitting of the $\text{C}=\text{O}$ bond, resulting in the formation of a carbonyl iron intermediate with a $(\text{Ar}'\text{Sn})_2\text{O}$ ligand which then inserts a second equivalent of CO_2 to yield the carbonate-bridged ligand $\text{Ar}'\text{Sn}(\mu\text{-OCO}_2)\text{SnAr}'$. Dimerization yields the final product **7**.

The distinct reactivity of **1** toward CO_2 and CS_2 is likely caused by the different polarity of $\text{C}=\text{O}$ and $\text{C}=\text{S}$ bonds; the more polarized $\text{C}=\text{O}$ bond favors a [2 + 2]-cycloaddition with the $\text{Fe}=\text{Sn}$ double bond of **1**, while CS_2 favors [3 + 2]-cycloaddition. By contrast, the digermine compound $[(\text{Ar}^\#(\text{Me}_3\text{Si})\text{N})\text{Ge}]_2$ has been shown to reduce both CO_2 and CS_2 in the same manner.^[48]

Complex **1** also activates the unpolar bonds of white phosphorus. The reaction of **1** with P_4 proceeds smoothly in toluene at room temperature and furnishes complex **8**, which was isolated as orange crystals in quantitative yield (Scheme 5.2). The solid-state molecular structure of **8** reveals a P_4Sn five-membered ring in an envelope conformation, coordinating η^4 to iron via three P and one Sn atoms (Figure 5.4g). The $(\eta^6\text{-arene})\text{Ar}'$ substituent migrates from Sn_2 to P2, and the $\text{Ar}'\text{Sn}_1$ unit bridges two P atoms (P1 and P4) with bond lengths of 2.6657(5) Å (P1–Sn1) and 2.8070(6) Å (P4–Sn1). The P–P bond lengths in **8** are very similar and range from 2.1313(7) to 2.1666(7) Å, being typical for P–P single bonds.^[24] Both Sn centers adopt a trigonal pyramidal geometry with a $\text{Sn}_1\cdots\text{Sn}_2$ distance of 3.1262(2) Å. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** shows four multiplets of an AEMX spin system, with J_{PP} coupling constants ranging from 490 to 3.0 Hz. $^{117/119}\text{Sn}$ satellites were detected for these multiplets with coupling constants ranging from 753 to 107 Hz (Figures S31 and S33, Table S1). In the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum, two multiplets due to the Sn–P coupling were detected at –454 ppm (Sn1) and –366 ppm (Sn2; Figures S32 and S34, Table S19). P_4 activation by heavier tetryl elements remains limited.^[49] To our knowledge, only two examples of low-valent tin compounds, the distannyne $[(\text{DippNC}(\text{CH}_3))_2\text{C}_6\text{H}_3\text{Sn}]_2$ ^[42] and the stannylen $[\text{Ar}^\#\text{Sn}(\text{SitBu}_3)]$,^[50] have been reported to react with P_4 to give butterfly like P_4 units via cleavage of one P–P bond. By contrast, the reaction of the Co_2Sn_2 cluster $[\text{Co}(\text{SnAr}')_2]$ with P_4 results in a P_4 chain,^[17e] while a heterobimetallic CoSn cluster reacting with P_4 gave the triple-decker cobalt complex $[(\text{tBu}_2\text{C}_2\text{P}_2)_2\text{Co}_2(\mu, \eta^5:\eta^5\text{-SnP}_4)]$ with a planar P_4Sn unit.^[51]

5.4 Conclusions

In summary, we synthesized and characterized $[\text{Fe}(\text{SnAr}')_2]$ (**1**), the first complex to feature both ferriostannylene and stannylidyne functionalities. The combination of iron and two monosubstituted tin centers, along with the constrained ligand structure, forms an Fe–Sn single bond and an Fe=Sn double bond ($\sigma+\pi$). This arrangement results in a positively charged Sn center and an electron-rich Fe center. The unusual coordination environment effectively reduces the tendency of the two aryl-tin moieties to dimerize, thereby maintaining the high reactivity of the two-coordinate Sn centers. Additionally, the proximity of the metal centers enhances cooperative reactivity. Comprehensive spectroscopic characterization and theoretical calculations support the existence of an amphiphilic FeSn_2 core with multiple reactive sites. This was demonstrated in the reactions of **1** with $\text{Ni}(\text{COD})_2$, AlBr_3 , CH_3I , and PMe_3 . The lone-pair electrons and vacant p-orbital of the two Sn atoms in **1** create “push-pull” interactions with nickel due to their optimal distance and orientation. In the reaction with AlBr_3 , the cleavage of the Al–Br bonds was observed, accompanied by the migration of Ar'. The formation of a **1**· AlBr_3 adduct may initiate this reaction. The oxidative addition of CH_3I leads to the formation of a Sn(IV) center, illustrating the amphiphilic nature of the ferriostannylene site. Interestingly, PMe_3 binds to the iron center, resulting in the cleavage of the Fe=Sn double bond and the formation of a Sn–Sn single bond. Notably, this process is reversible. Furthermore, compound **1** activates CS_2 and CO_2 through different reaction pathways, and P_4 , which leads to the cleavage of multiple P–P bonds.

Our results emphasize the significant synthetic potential of complexes that feature multiple coordinatively unsaturated sites from group 14 elements. Complexes similar to **1** should be easily obtainable using comparable strategies with other low-valent transition metalates^[52] and appropriate main group precursors. This bodes for future investigation pursuing further challenging synergistic bond activation reactions. Studies in this direction are in hand.

5.5 Acknowledgements

We thank Dr. Christian M. Hoidn for preliminary studies on the synthesis of complex **1**, Vanessa Tomanek and Martina Amann (University of Regensburg) for assistance with ICP-OES and IR measurements, and Serhiy Demeshko (University of Göttingen) for the discussion of the ^{57}Fe Mössbauer results. We gratefully acknowledge the European Synchrotron Radiation Facility (ESRF) for the provision of synchrotron radiation facilities under the proposal number CH-6760 by using the ROBL beamline (BM20). Franz F. Westermair and Ruth M. Gschwind would like to thank the Deutsche Forschungsgemeinschaft for funding (DFG, RTG 2620 IonPairs in Reaction Project 426795949). This work is dedicated to Professor Philip P. Power, a pioneer in main group and transition metal coordination chemistry, on the occasion of his retirement.

5.6 Conflict of Interest

The authors declare no competing financial interest.

5.7 Supporting Information

All figures, schemes, tables, etc. referenced in this chapter with a “S” are available in the full Supporting Information available under pubs.acs.org/doi/10.1021/jacs.4c18423, which further contains: Synthesis and

5 Synthesis and Reactivity of an Iron–Tin Complex

characterization of all compounds by single-crystal XRD, NMR-, IR- and UV-Vis spectroscopy, LIFDI-MS, and ^{57}Fe Mössbauer spectroscopy and details on computational studies and additional references.

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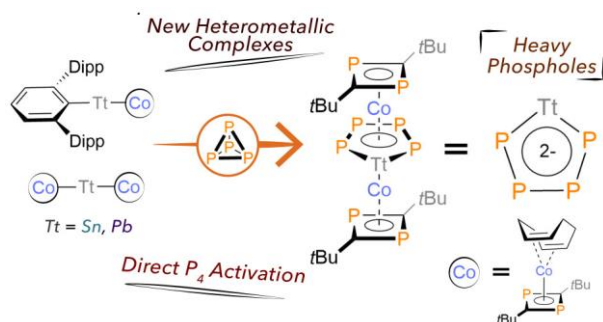
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6 TRANSITION-METAL-STABILIZED HEAVY TETRAPHOSPHOLIDE ANIONS



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J. Am. Chem. Soc. **2022**, *144*, 20434-20441

DOI: 10.1021/jacs.2c08754

This work is dedicated to Prof. Oliver Reiser on the occasion of his 60th birthday.

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John A. Kelly carried out all experiments, syntheses and characterizations of compounds. Verena Streitferdt conducted initial heteronuclear NMR measurements. **Franz F. Westermair** acquired heteronuclear NMR of compounds **2** and **3** at room temperature and -40 °C. Maria Dimitrova and Raphael J. F. Berger performed quantum chemical calculations. Ruth M. Gschwind supervised heteronuclear NMR studies. Robert Wolf conceived, coordinated and supervised the project. The manuscript was prepared with contributions of all authors.

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions

6.1 Abstract

Phosphorus analogues of the ubiquitous cyclopentadienyl (Cp) are a rich and diverse family of compounds, which have found widespread use as ligands in organometallic complexes. By contrast, phospholes incorporating heavier group 14 elements (Si, Ge, Sn, and Pb) are hardly known. Here, we demonstrate the isolation of the first metal complexes featuring heavy cyclopentadienyl anions SnP_4^{2-} and PbP_4^{2-} . The complexes $[(\eta^4\text{-}i\text{Bu}_2\text{C}_2\text{P}_2)_2\text{Co}_2(\mu, \eta^5:\eta^5\text{-P}_4\text{Tt})]$ [Tt = Sn (**6**), Pb (**7**)] are formed by reaction of white phosphorus (P_4) with cyclooctadiene cobalt complexes $[\text{Ar}'\text{TtCo}(\eta^4\text{-P}_2\text{C}_2i\text{Bu}_2)(\eta^4\text{-COD})]$ [Tt = Sn (**2**), Pb (**3**), $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-}\{\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2\}_2$, COD = cycloocta-1,5-diene] and $\text{Tt}\{\text{Co}(\eta^4\text{-P}_2\text{C}_2i\text{Bu}_2)\text{-(COD)}\}_2$ [Tt = Sn (**4**), Pb (**5**)]. While the SnP_4^{2-} complex **6** was isolated as a pure and stable compound, compound **7** eliminated Pb(0) below room temperature to afford $[(\eta^4\text{-}i\text{Bu}_2\text{C}_2\text{P}_2)_2\text{Co}_2(\mu, \eta^4:\eta^4\text{-P}_4)]$ (**8**), which is a rare example of a tripledecker complex with a P_4^{2-} middle deck. The electronic structures of **6–8** are analyzed using theoretical methods including an analysis of intrinsic bond orbitals and magnetic response theory. Thereby, the aromatic nature of P_5^- and SnP_4^{2-} was confirmed, while for P_4^{2-} , a specific type of symmetry-induced weak paramagnetism was found that is distinct from conventional antiaromatic species.

6.2 Introduction

The diagonal relationship between phosphorus and carbon in the periodic table has inspired the development of a wealth of phosphorus analogues of classical hydrocarbons.^[1] Among this family of low-coordinate phosphorus compounds, phospholes take a prominent position due to their relationship to cyclopentadienes.^[2] The sophisticated chemistry of phospholes and the corresponding phospholide anions developed over the last decades has inspired numerous applications in supramolecular chemistry, homogeneous catalysis, and molecular electronics, e.g., in organic light-emitting diodes (OLEDs).^[3–5]

The synthesis of the pentaphospholide anion, P_5^- (**A**, Figure 6.1), by Baudler and co-workers was a seminal achievement in phosphole chemistry.^[6] Phospholide **A** is the pure phosphorus analogue of the ubiquitous cyclopentadienyl anion, Cp^- ($\text{Cp} = \text{C}_5\text{H}_5$). The synthesis of **A** is achieved by reacting white phosphorus (P_4) with sodium in diglyme or with lithium phosphide in THF. It is noteworthy that the tetraphospholide anion, P_4CH^- , was observed by Baudler in the same reaction mixture but it was not isolated. The crystallographic characterization of the tetraphospholide anion P_4CMes^* (**B**) was subsequently reported by Ionkin and co-workers.^[7] This anion was isolated as the cesium salt $\text{Cs}[\text{P}_4\text{CMes}^*]$ in a low yield by fractional crystallization from a three-component reaction involving $\text{P}(\text{SiMe}_3)_3$, CsF, and $\text{Mes}^*\text{C}(\text{O})\text{Cl}$ ($\text{Mes}^* = 2,4,6\text{-}i\text{Bu}_3\text{-C}_6\text{H}_2$).

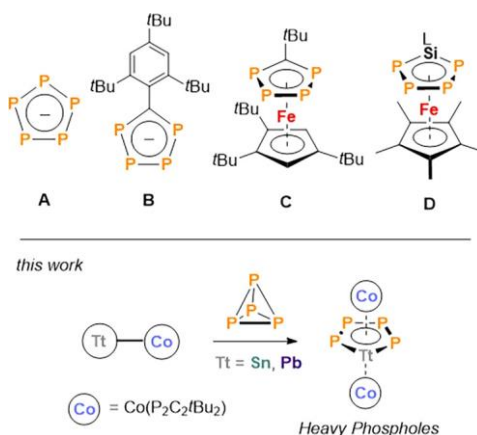


Figure 6.1: Previous examples of penta- and tetraphospholides (**A–D**, $L = \text{PhC}(\text{NtBu})_2$) and schematic strategy for the synthesis of heavy phospholes reported in this work.

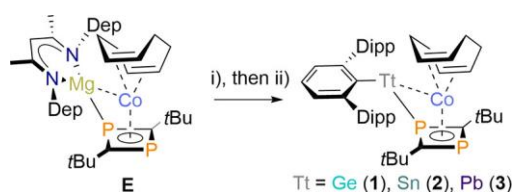
Similarly to Cp, the transition metal coordination chemistry of mono-, di-, tri-, and pentaphospholides is well developed. Notable examples are the pentaphosphaferrocenes $[(\text{C}_5\text{R}_5)\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{R} = \text{H}, \text{Me}$), which are outstanding synthons for the assembly of giant supramolecular fullerene analogues.^[4] However, there appears to be only a single example of a tetraphosphole complex in the literature (compound **C**, Figure 6.1).^[8,9] Tin- and lead-containing aromatic compounds are still scarce.^[10] Although heavier group 14 element analogues of the cyclopentadienyl anion, i.e., siloles, germoles, and stannoles, are of interest owing to their photophysical properties arising from $\sigma^*-\pi^*$ interactions,^[10f,g,i] analogues of such systems that additionally incorporate a heavier group 15 element such as phosphorus are exceedingly rare. The recently reported compound **D** is a solitary example for a tetraphosphasilole complex.^[11] Phospholes containing Ge, Sn, or Pb appear to be unknown.

A recent work from the Wolf group has successfully utilized the reaction of white phosphorus (P_4) with heterobimetallic complexes to prepare unusual polyphosphorus compounds.^[12,13] Using this strategy, we have now synthesized the heavy tetraphospholide anions SnP_4^{2-} and PbP_4^{2-} . These hitherto unknown π -aromatic molecules are stabilized by the coordination to two cobalt atoms in the triple-decker sandwich compounds $[(\eta^4\text{-}t\text{Bu}_2\text{C}_2\text{P}_2)_2\text{Co}_2(\mu, \eta^5: \eta^5\text{-P}_4\text{Tt})]$ [$\text{Tt} = \text{Sn}$ (**6**), Pb (**7**)]. We describe the structural and spectroscopic characterization of these complexes and analyze the electronic structure of the P_4Tt^{2-} ligands with quantum chemical methods.

6.3 Results and Discussion

Our study commenced with the preparation of the bimetallic tetrel cobaltate complexes $[\text{Ar}'\text{TtCo}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)(\eta^4\text{-COD})]$ [$\text{Tt} = \text{Ge}$ (**1**), Sn (**2**), Pb (**3**)] used as precursors to our target complexes. Compound **1–3** were prepared by reacting the recently reported magnesium cobaltate salt $[(^{\text{Dep}}\text{nacnac})\text{-MgCo}(\eta^4\text{-P}_2\text{C}_2t\text{Bu}_2)(\eta^4\text{-COD})]$ (**E**, $^{\text{Dep}}\text{nacnac} = \text{CH}(\text{DepNCMe})_2$, $\text{Dep} = 2,6\text{-Et}_2\text{-C}_6\text{H}_3$) with terphenyl tetrel halides, $[\text{Ar}'\text{Tt}(\mu\text{-X})_2]$ ($\text{Tt} = \text{Ge}$, $\text{X} = \text{Cl}$; Sn, Pb , $\text{X} = \text{Br}$) (Scheme 6.1). Low temperatures (-80°C) are required for clean formation of the germanium compound **1**, while for tin and lead, the reactions are selective at ambient temperature. Addition of either $\text{Li}(^{\text{Dep}}\text{nacnac})$ or $\text{Li}(\text{acac})$ ($\text{acac} = \text{acetyl acetonate}$) to the reaction mixtures is necessary during workup to convert $[(^{\text{Dep}}\text{nacnac})\text{MgX}]$ into the n -hexane soluble complexes $[\text{Mg}(^{\text{Dep}}\text{nacnac})_2]$ or $[\text{Mg}(^{\text{Dep}}\text{nacnac})(\text{acac})]$. Using this procedure, it is possible to isolate **1–3** in moderate yields as a dark green crystalline powder from concentrated n -hexane solutions.

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions



Scheme 6.1: Synthesis of Compounds **1–3**: Reagents and conditions: (i) +0.5 [Ar'TtX]₂ (Tt = Ge, X = Cl; Sn, Pb, X = Br; Ar' = 2,6-Dipp₂-C₆H₃, Dipp = 2,6-*i*Pr₂-C₆H₃), toluene, -78 °C to r.t., 12 h; (ii) +Li(Depnacnac)/-Mg(Depnacnac)₂, -LiX, toluene/THF, -78 °C to r.t. (Depnacnac = CH(DepNCMe)₂, Dep = 2,6-Et₂-C₆H₃), 12 h.

The molecular structures of **1–3** were determined by single crystal X-ray diffraction. Since all three structures share the same motif, only the molecular structure of **2** is displayed in Figure 6.2, while those of **1** and **3** are shown in the full Supporting Information (SI) (Figures S1 and S3). The cobalt atoms feature η^4 -coordinated 1,5-cyclooctadiene and 1,3-diphosphacyclobutadiene ligands, while the tetrel atom (Ge, Sn, or Pb) is in a pseudo-two-coordinate environment by terphenyl-substituent and one of the P atoms of the diphosphacyclobutadiene ligand. The Tt–P bond lengths in **1–3** (2.3946(8) Å, 2.6442(7) Å, 2.7402(10) Å, respectively) are similar to those of tertiary phosphine adducts of tetrelenes.^[14]

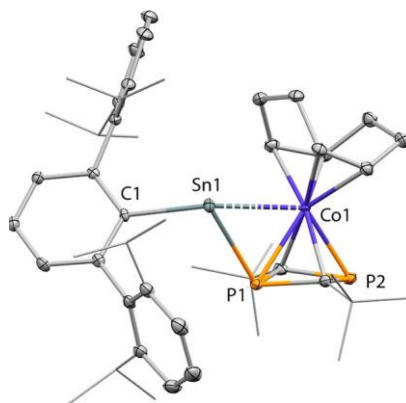


Figure 6.2: Molecular structure of **2**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted and the *t*Bu and *i*Pr groups drawn in the wire frame model for clarity. Selected bond lengths (Å) and angles (deg): Sn1–Co1 2.9534(5), Sn1–P1 2.6442(7), Sn1–C1 2.252(3), Co1–P1 2.3472(8), Co1–P2 2.2833(8), $\angle$ (C1–Sn1–Co1) 128.08(6), $\angle$ (C1–Sn1–P1) 102.17(7).

The Tt–Co distances in **1–3** (Ge–Co 2.8434(6) Å, Sn–Co 2.9534(5) Å, Pb–Co: 3.0318(6) Å) are longer than the sum of their covalent radii (Σr_{GeCo} 2.70 Å, Σr_{SnCo} 2.89 Å, Σr_{PbCo} 2.96 Å).^[15] These parameters suggest the absence of a covalent metal–metal bond, which is in line with quantum chemical calculations (vide infra). By contrast, the previously reported, related cluster compound (Ar'SnCo)₂ features strong covalent Sn–Co bonds, which even have partial multiple bond character.^[12] The P–C bonds of the diphosphacyclobutadiene ligands are in a close range. It thus appears that the coordination of the tetrel element only has a minor influence on the ligand structure (see full SI for a more detailed discussion).

It is noteworthy that although the Tt–Co and Tt–P distances for **1–3** increase down the group, the bond angles are approximately the same (C1–Tt–Co1 127°–129°, $\angle$ (C1–Tt–P1) 102°–103°). As a consequence of the relatively short atomic radius of germanium, the terphenyl substituent and the Co(P₂C₂tBu₂)(COD) unit in **1** are very close to each other resulting in a restricted rotation of the terphenyl ligand around the Tt–P/Tt–C bonds as evidenced by

variable temperature (VT) NMR experiments. At room temperature, the NMR spectra of **1** show inequivalence in the ^1H and ^{13}C signals for the COD ligand and the tBu groups in agreement with the molecular structure (see full SI, Figures S9–15, for details). The ^1H NMR spectra for **2** and **3** are far simpler, showing only six signals for the COD ligand and one singlet for the tBu moiety, indicating a C_s symmetry on the NMR time scale. At lower temperatures, the ^1H NMR signals of **2** and **3** resemble that of **1**. The VT NMR spectrum of **1** at higher temperatures shows only signals corresponding to several decomposition products (at $T > 60\text{ }^\circ\text{C}$) but not signals corresponding to a C_s symmetric **1**. In contrast, **2** and **3** show no appreciable decomposition up to $110\text{ }^\circ\text{C}$.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for **1–3** are in agreement with the molecular structures. In each case, two doublet signals are observed. Coordination of the P atom to the tetrel center results in a high-field shift of the $^{31}\text{P}\{^1\text{H}\}$ NMR signals ($\delta = -43.5$, -62.3 , and -56.1 ppm for **1**, **2**, and **3**, respectively; see Figure 6.10, Figure 6.15 and full SI) with respect to the signal for the uncoordinated P atom ($\delta = 57.4$, 59.1 , and 59.5 ppm for **1**, **2**, and **3**, respectively). In the case of **2** and **3**, Sn and Pb satellites are present for the signals of the Tt-coordinated P atom ($^1J_{\text{SnP}} = 1050$ Hz, and $^1J_{\text{PbP}} = 1192$ Hz, respectively, see Figure 6.10 and Figure 6.15). The corresponding ^{119}Sn and ^{207}Pb NMR signals were observed at 298 K as broad doublets at 1899.7 ppm for **2** (Figure 6.11) and at 8592 ppm for **3** (Figure 6.16) and could be unambiguously assigned via the scalar coupling values ($^1J_{\text{PSn}} = 1053$ Hz and $^1J_{\text{PPb}} = 1200$ Hz). At lower temperature (233 K), a significant broadening of the ^{119}Sn NMR signal of **2** was observed (Figure 6.12), while the ^{207}Pb NMR signal of **3** could not be detected anymore.

Intrinsic bond orbital (IBO), natural bond orbital (NBO) and atoms in molecules (AIM) analyses of DFT calculated electron densities were employed to analyze the bonding situation in **1–3**.^[16,17] The IBO analyses show the expected bond-like localized molecular orbitals. In addition, substantial π -bonding interactions are apparent between the cobalt atom and the π -orbitals of the diphosphacyclobutadiene ligand, which should result in a significant amount of charge transfer (see SI for a more detailed discussion and graphical representations of relevant IBOs). Additionally, there is a delocalized IBO between the tetrel, coordinating phosphorus and cobalt centers, but with low contributions from Co (**1**: Ge (24%) Co (8%) P (59%), **2**: Sn (14%) Co (10%) P (59%), **3**: Pb (13%) Co (10%) P (59%)). The Wiberg bond indices for Ge–Co, Sn–Co, and Pb–Co linkages in **1–3** (0.20, 0.15 and 0.13, respectively) are lower than expected for a covalent bond. In line with the results from DFT, the AIM analysis shows bond critical points (BCPs) between cobalt and phosphorus as well as the tetrel atoms and phosphorus (see Figure 6.3 and SI). However, no BCPs were found between the tetrel atoms and the cobalt center. All these results indicate the presence of only a weak interaction between Tt and Co.

It was also possible to synthesize the homoleptic tin(II) complex $\text{Sn}[\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)(\text{COD})]_2$ (**4**) by reacting **E** with commercially available $\text{Sn}(\text{acac})_2$ (Figure 6.4). Single-crystal X-ray diffraction on **4** revealed that the tin atom is coordinated by the two P atoms of the diphosphacyclobutadiene ligands with Sn–P distances (Sn1–P1 2.6490(10) Å, Sn1–P2 2.6484(10) Å) similar to **2** and a $\angle(\text{P}–\text{Sn}–\text{P})$ angle of $102.17(7)^\circ$. Similar to the structures of **1–3** discussed above, the Sn–Co distances (Sn1–Co 2 2.9682(6) Å and Sn1–Co2 2.9649(7) Å) suggest that there is only a weak interaction between the cobalt atom and tin. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for **4** is comparable to that of **2**, showing two doublet signals ($\delta = 77.2$ and -83.3 ppm, $^2J_{\text{PP}} = 17.4$ Hz). The high-field shifted signal can be assigned to the P atoms coordinated to tin due to the observation of ^{119}Sn satellites ($^1J_{\text{SnP}} = 1067$ Hz; see Figure S32).

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions

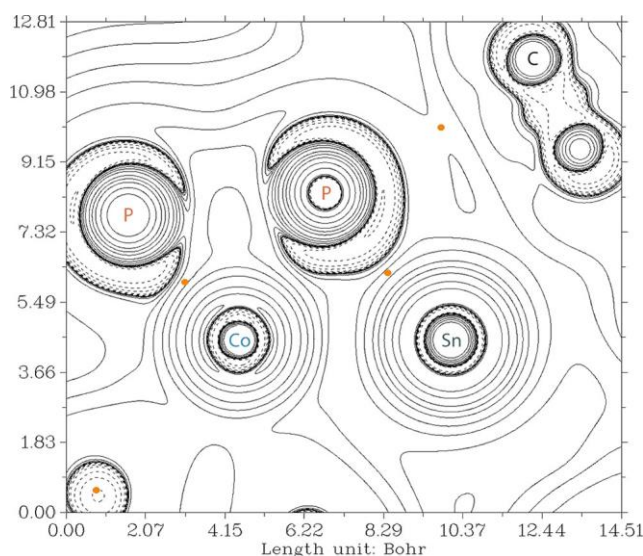


Figure 6.3: Laplacian contour plot in the P1, P2, Co1, Sn1 plane of **2**; bond critical points are shown as orange dots.

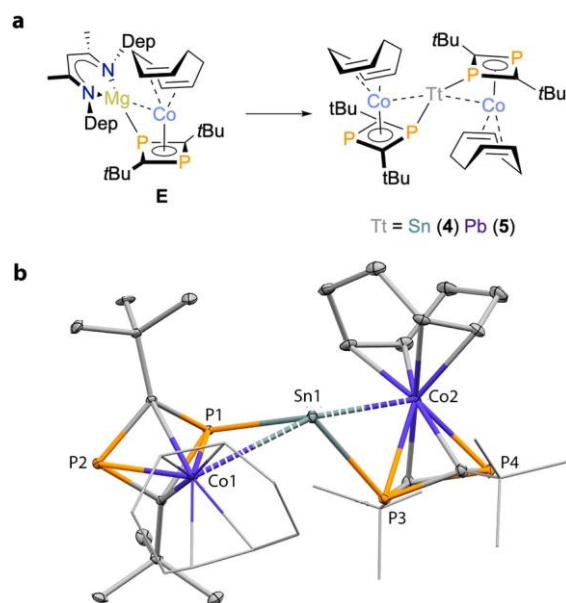


Figure 6.4: (a) Synthesis of compounds **4** and **5**; reagents and conditions: Tt = Sn: +Sn(acac)₂ (0.5 equiv)/ -Mg(^{Dep}nacnac)(acac), toluene, r.t., 12 h; Tt = Pb: +Pb(acac)₂ (0.5 equiv)/-Mg(^{Dep}nacnac)(acac), toluene, -30 °C to r.t., 16 h; (b) molecular structure of **4**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted and two *t*Bu groups and the COD ligand drawn in the wire frame model for clarity. Selected bond lengths (Å) and angles (deg): Sn1–Co1 2.9682(6), Sn1–Co2 2.9649(7), Sn1–P1 2.6490(10), Sn1–P3 2.6484(10), ∠(Co1–Sn1–Co2) 149.374(19), P1–Sn1–P3 100.24(3).

³¹P{¹H} NMR analysis of the related reaction of **E** (two equiv) with Pb(acac)₂ indicates the formation of analogous dimetalloplumbylene, Pb[Co(η⁴-P₂C₂*t*Bu₂)(η⁴-COD)]₂ (**5**, see Figure S36). Two doublet signals (δ = -65.9 and 74.1 ppm) are detected of which the high-field shifted signal possesses ²⁰⁷Pb satellites (¹J_{PbP} = 1004 Hz, ²J_{PP} = 19 Hz). Unfortunately, it was not possible to isolate **5** due to the low thermal stability of the compound. Any isolation attempt resulted in the deposition of a black precipitate (presumably metallic lead). Having compounds **1–4** in hand, we studied their reactivity toward P₄ to ascertain whether they can be used as precursors to novel

polyphosphorus compounds. Reactions between **1** and P_4 were unsuccessful. While no reaction occurs at ambient temperature, heating to 55 °C affords an intractable mixture of products according to $^{31}P\{^1H\}$ NMR spectra (see Figure S15). By contrast, reactions of **2** or **4** with P_4 at elevated temperatures afford the dark red, crystalline compound $[(tBu_2C_2P_2)_2Co_2(\mu,\eta^5:\eta^5-SnP_4)]$ (**6**) in each case (Figure 6.5a).^[18] When using **2**, separation of **6** from the unknown terphenyl containing byproducts proved difficult. Fortunately, the reaction of **4** with P_4 forms **6** selectively at ambient temperature, with 1,5-cyclooctadiene being the only byproduct, making isolation facile and allowing the crystallographic characterization of **6** by single-crystal X-ray diffraction (Figure 6.5b). The crystallographic analysis reveals the formation of a triple decker complex of two $(\eta^4-P_2C_2tBu_2)Co$ units and a planar cyclo- SnP_4 middle deck, for which a pronounced alternation of the P–P bond lengths is observed. The P–P bonds adjacent to the Sn atom (P1–P2 2.1101(12) Å and P3–P4 2.094(4) Å) approach the range for a P=P double bond.^[19] The P2–P3 bond length (2.2296(11) Å) suggests the presence of a single bond. The bond lengths between phosphorus and tin (av. P–Sn 2.52865(9) Å) are comparable to the single bonds found in diphosphastannylenes.^[20]

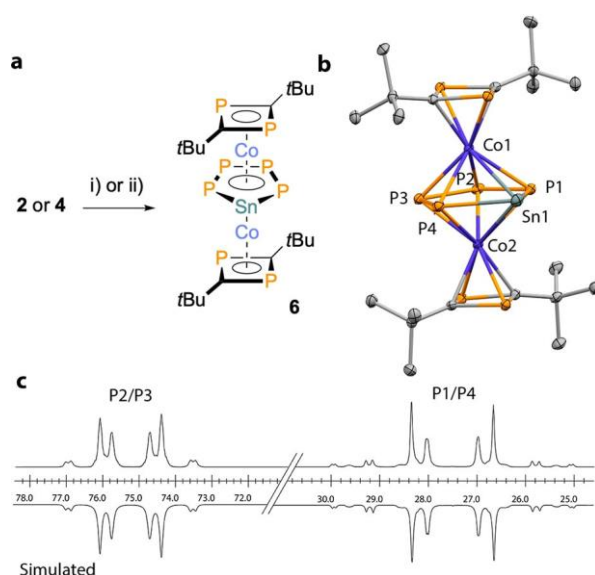


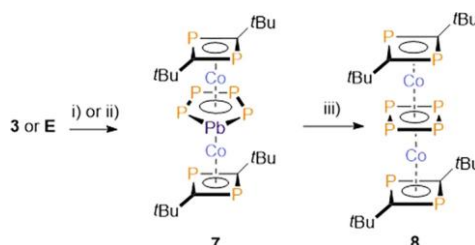
Figure 6.5: (a) Synthesis of compound **6** via **2** or **4**. Reagents and conditions: (i) **2** (1 equiv), $+P_4$ (1.4 equiv)/ -COD, “-Ar’P”, THF, 65 °C, 16 h; (ii) **4** (1 equiv), $+P_4$ (1.2 equiv)/ -COD, toluene, 55 °C, 16 h, toluene, r.t., 16 h; (b) molecular structure of **6**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1–P1 2.5198(8), Sn1–P4 2.5375(9), P1–P2 2.1101(12), P2–P3 2.2296(11), P3–P4 2.1104(12), Co1–Co2 3.050, $\angle(P1-Sn1-P4)$ 88.17(3), $\angle(Sn1-P1-P2)$ 118.23(4), $\angle(P1-P2-P3)$ 107.96(5), $\angle(P2-P3-P4)$ 107.60(5), $\angle(P3-P4-Sn1)$ 118.02(4); (c) sections of the measured (upward) and simulated (downward) $^{31}P\{^1H\}$ NMR spectrum of **6**.

The $^{31}P\{^1H\}$ spectrum of **6** shows one singlet and two multiplets with an integral ratio of 4:2:2. The singlet at $\delta = 67.1$ ppm can be assigned to the P atoms within the $P_2C_2tBu_2$ rings. One of the two multiplet signals ($\delta = 29.6$ and 77.0 ppm), the high-field shifted signal shows coupling to $^{117/119}Sn$, allowing for its definitive assignment to the P atoms adjacent to the Sn atom (P1 and P4). Simulation of the $^{31}P\{^1H\}$ spectrum by an iterative fitting procedure gave a $^1J_{PP}$ coupling constant of -434.7 Hz for the P1–P2/P3–P4 pairs, whereas the $^1J_{PP}$ coupling for P2–P3 (magnetically not equivalent) was -289.0 Hz (see Figures S39–S41, Figure 6.5c). A ^{119}Sn NMR spectrum of **6** shows a broad triplet at $\delta = 339.7$ ppm with a $^1J_{SnP}$ coupling constant of 797 Hz, which is in agreement with the

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions

simulated $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (see Figure 6.5c and S41 and Table S1). The line broadening of the ^{119}Sn NMR is likely due to interactions with the quadrupolar ^{59}Co nuclei.^[21]

It is noteworthy that the analogous lead compound $[(t\text{Bu}_2\text{C}_2\text{P}_2)_2\text{Co}_2(\mu, \eta^5: \eta^5\text{-PbP}_4)]$ (**7**) is formed by reacting **3** with P_4 (Scheme 6.2). In solution, **7** shows a similar $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum as **6** (see the SI for details). However, in contrast to **6**, **7** is unstable at ambient temperature, depositing lead metal and affording a new species, which was identified as $[\text{Co}_2(\text{P}_2\text{C}_2t\text{Bu}_2)_2(\mu, \eta^4: \eta^4\text{-P}_4)]$ (**8**).



Scheme 6.2: Synthesis of Compounds **7** and **8**: Reagents and conditions: (i) **3** (1 equiv), $+\text{P}_4$ (1 equiv)/ $-\text{COD}$, $-\text{P}_4\text{Ar}'_2$, $-\text{Ar}'\text{P}$, toluene, 55°C , 16 h; (ii) **E** (2 equiv), $+\text{Pb}(\text{acac})_2$ (1 equiv), P_4 (1 equiv)/ $-\text{Mg}(\text{Depnacnac})(\text{acac})$ (2 equiv), $-\text{COD}$ (2 equiv), toluene, -30°C to r.t., 16 h; (iii) $-\text{Pb}$, toluene, storage at r.t.

Since no intermediates en route to **6** or **7** were detected by ^{31}P NMR spectroscopy, any mechanistic proposal remains speculative at this point. However, in principle, two distinct scenarios are plausible (i) an initial oxidative addition of P_4 to the group 14 atom (tin or lead) followed by substitution of the COD ligand on cobalt or (ii) the substitution of the COD ligand by P_4 , which would be followed by an insertion of tin(II) or lead(II) into a P–P bond of the resulting tetraphosphido ligand (see SI, Schemes S1 and S2).^[13, 22]

While the isolation of **7** and **8** as pure compounds has so far not been possible, their identity was firmly established by single-crystal X-ray analysis and multinuclear NMR spectroscopy (vide infra). Additionally, the resonances for the terphenyl- P_4 butterfly compound $\text{DippAr}_2\text{P}_4$ were observed, confirming the fate of the terphenyl ligand attached to the lead center (see Figure S46).^[23] Note that these resonances are not present in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the reaction of **2** with P_4 ; in this case, the fate of the terphenyl substituent remains presently unclear. It should be noted that the one-pot reaction of **E**, $\text{Pb}(\text{acac})_2$, and P_4 also forms **7**, as observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, but only small amounts of crystalline material could be isolated, which were contaminated with $\text{Mg}(\text{Depnacnac})(\text{acac})$.

Similar to complex **6**, the molecular structure of **7** (Figure S6) features a triple-decker structure with a planar cyclo- PbP_4 middle deck. The bond lengths are similar to those observed for **6**, with two short P–P bonds adjacent to the Pb atom (P1-P2 2.1104(12) Å and P3-P4 2.083(4) Å), and a longer P2-P3 bond in the typical range for P–P single bonds. The P–Pb distances (av. P–Pb 2.625(3) Å) are in the typical range expected for P–Pb single bonds.^[20] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for **7** is in line with the molecular structure, showing a singlet at $\delta = 67.9$ ppm and multiplet signals at $\delta = 18.5$ and 64.9 ppm (Figure S50).

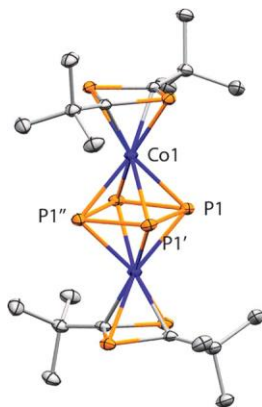


Figure 6.6: Molecular structure of **8**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–P1' 2.2411(7), Co1–P1 2.3015(6), Co1–Co2 3.377, $\angle$ (P1–P1'–P1'') 89.981(1).

The molecular structure of **8** (Figure 6.6) shows the same η^4 -1,3-diphosphacyclobutadiene cobalt moieties as observed in **6** and **7**, while the middle deck of the triple-decker structure is a square planar tetraphosphorus ring with equal P–P bond lengths (2.2411(7) Å) and $\angle$ (P–P) bond angles of 90°. The P–P bond length is longer than that found in Cs_2P_4 (2.146(1)/2.1484(9) Å), which also possesses a square planar cyclo- P_4 ring.^[24] Triple-decker sandwich complexes with a cyclo- P_4 middle deck have rarely been reported. To our knowledge, the only other examples are $[(\text{Cp}^{\text{R}}\text{Fe})_2(\mu, \eta^4: \eta^4\text{-P}_4)]^{[25]}$ and $[(\text{Cp}^{\text{R}}\text{Co})_2(\mu, \eta^4: \eta^4\text{-P}_4)]^{2+}$ ($\text{Cp}^{\text{R}} = 1,2,4\text{-}t\text{Bu}_3\text{-C}_5\text{H}_2$).^[26] Notably, the structure of the iron complex is distinct, featuring a highly distorted, “kite-like” P_4 ring.^[25] Tripledecker sandwich complexes with a middle deck composed of two separate P_2 units are much more common, such as in $[(\text{Cp}''\text{Co})_2(\mu, \eta^2: \eta^2\text{-P}_2)_2]$ ($\text{Cp}'' = 1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3$).^[27,28]

The presence of a triple-decker structure for **8** in solution is confirmed by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which shows a broad singlet at $\delta = 80.8$ ppm for the $\text{P}_2\text{C}_2\text{tBu}_2$ ring and a quintet at $\delta = 302.6$ ppm corresponding to the cyclo- P_4 middle deck. The splitting pattern of the latter signal indicates that the P_4 ring is coupled with the P atoms within the phosphacyclobutadiene rings. Due to the broadness of the singlet for the $\text{P}_2\text{C}_2\text{tBu}_2$ ring, the $^2J_{\text{PP}}$ coupling is not resolved. An iterative fit of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum gave a $^2J_{\text{PP}}$ coupling constant of 10.6 Hz (see the SI for details). The low field signal is in a similar range to Cs_2P_4 ($\delta = 330.3$ ppm) and vastly different from that of $[(\text{Cp}''\text{Co})_2(\mu, \eta^2: \eta^2\text{-P}_2)_2]$ ($\delta = -36.3$) showing two dumbbell P_2 units. The ^{31}P NMR spectroscopic data hence indicate that the P_4 ring of **8** remains intact in solution.

In order to gain insight into the electronic structures of the planar polyphosphorus ligands, quantum chemical calculations were performed on the free P_4^{2-} , P_5^- , and TiP_4^{2-} ($\text{Ti} = \text{Sn, Pb}$) anions and complexes **6–8** in the gas phase to analyze their electronic properties. The geometry optimization (TPSS-D3BJ/def2-SVP) of the lone dianionic tetraphosphametallol ring, TiP_4^{2-} gives a planar structure with almost identical P–P bond lengths. To analyze the degree of aromaticity or antiaromaticity, we have undertaken calculations of magnetic response properties. NICS(0) (nucleus independent chemical shifts) calculations indicate that the free molecules P_4Sn^{2-} (–16.0) and PbP_4^{2-} (–15.2) are aromatic. It is apparent that the introduction of the Co moieties in **6** and **7** greatly enhances the aromaticity of the TiP_4 ring. These findings compare well to what was found for the all phosphorus titanocene, $[\text{Ti}(\eta^5\text{-P}_5)_2]$ (–36.8) and P_5^- (**A**, Figure 6.1, –15.4).^[29] This trend continues for the P_4 ring within **8** (–3.5) and P_4^{2-} (4.0). Analogous results are obtained when calculating the NICS(1) values (see SI for

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions

further details). In addition, we have calculated total molecular currents for P_4^{2-} , P_5^- , and SnP_4^{2-} (at TPSS/def2-TZVP level of theory).

According to the magnetic criterium for aromaticity, aromatic molecules maintain a strongly diamagnetic response and antiaromatic molecules maintain a strongly paramagnetic response.^[29] For a homogeneous magnetic field of strength 1 T perpendicular to the molecular plane, we find total molecular currents of -6.6, 18.9, and 20.2 nA/T for P_4^{2-} , P_5^- , and SnP_4^{2-} , respectively. For comparison, molecular currents of 12.0 and -20.0 nA/T were calculated for benzene and cyclobutadiene (in D_{6h} and D_{2h} symmetry, respectively) at the same level of theory. This suggests that P_5^- and P_4Sn^{2-} are aromatic species, while P_4^{2-} is nonaromatic or antiaromatic at best.^[30] Indeed, the paramagnetic response in P_4^{2-} does not emerge from the π system alone but from magnetic $\pi \rightarrow \sigma^*$ (virtual) excitations (see SI for further details).^[31]

To investigate how the aromaticity of the $[TtP_4]^{2-}$ is affected by coordination to the cobalt atoms, we have performed a fragment orbital interaction analysis with AMS (formerly known as ADF), and also closely inspected the Kohn–Sham molecular orbitals of **6** and **7** (see SI for details). The two highest occupied π orbitals of $[SnP_4]^{2-}$ are nondegenerate and strongly interact with the empty p_x and p_y orbitals on the cobalt atoms perpendicular to the Co–Co axis. In the complex, the two relevant π orbitals of the $[TtP_4]^{2-}$ ring (the donor orbitals) become almost degenerate. An interesting consequence of this energetic approximation of the π orbitals is that the P–P distances ring become more different in the complex in comparison with the free $[TtP_4]^{2-}$ species. These results are corroborated by IBO analyses (TPSS-D3BJ/def2-SVP level) of the lone dianionic tetraphosphametallole ring, P_4Tt^{2-} , which show a delocalized π -system involving the Tt, P1/P3, P2/P4 centers. Figure 6.7 depicts the multicentered IBOs of SnP_4^{2-} and shows the typical interaction of an aromatic π -system with transition metal atoms. The bonding situation of **7** (Figures S74 and S75) and **8** appears to be similar, except the bonding orbitals appear to be more delocalized for **8** (see Figure S76).

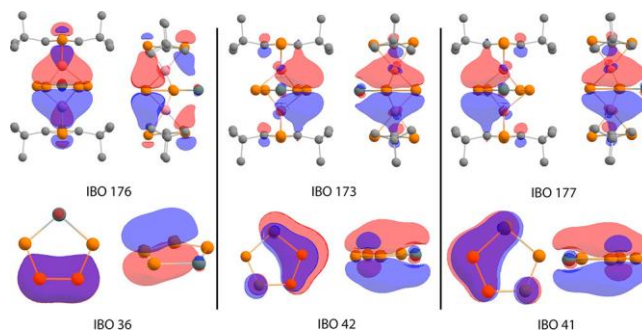


Figure 6.7: Selected IBOs for compound **6** (above) and the corresponding orbitals for SnP_4^{2-} (below, TPSS-D3BJ/def2-SVP, contour value = 0.03); each IBO is shown from two different perspectives.

6.4 Conclusion

We have synthesized the first metal complexes of the heavy tetraphospholide anions, SnP_4^{2-} and PbP_4^{2-} . These ligands are of fundamental interest as group 14 analogues of the wellknown P_5^- anion. A substantial aromatic character was deduced for P_5^- and SnP_4^{2-} using quantum chemical calculations. The observation of SnP_4^{2-} and PbP_4^{2-} is a milestone in the chemistry of phospholides, while it also bodes well for the preparation of further elusive group 14/group 15 element anions.^[32] A rich organometallic chemistry is anticipated for these anions, which may offer access to further unusual compounds as shown by the preparation of the phosphorus-rich triple-decker complex **8**. More generally, our work also demonstrates that the activation of P_4 by heterobimetallic complexes

has a high utility for the preparation of previously inaccessible (poly-)phosphorus species. We are continuing to explore these avenues.

6.5 Acknowledgements

We thank Marco Fritz for experimental assistance. Financial support by the Deutsche Forschungsgemeinschaft (RTG IonPairs in Reaction Project 426795949) and the European Research Council (ERC CoG 772299) is gratefully acknowledged. Maria Dimitrova, thanks the Finnish Cultural Foundation for the research grant as well as the Finnish IT-centre for science (CSC) for the computational resources. This paper is dedicated to Oliver Reiser on the occasion of his 60th birthday.

6.6 Conflict of Interest

The authors declare no competing financial interest.

6.7 Supporting Information

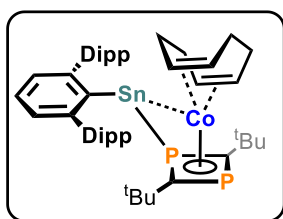
Figures, schemes, tables, etc. referenced in the chapter with a “S” are available in the full Supporting Information available under pubs.acs.org/doi/10.1021/jacs.2c08754, which further contains: Synthesis and characterization of all compounds by single-crystal XRD, NMR- and UV-Vis spectroscopy, a proposed mechanism for the formation of 6 and 7, details on computational studies and additional references.

6.7.1 General Considerations

All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H₂O and O₂). Solvents were purified, dried, and degassed with an MBraun SPS800 solvent purification system and then stored under argon over activated 3 Å molecular sieves or a potassium mirror in gas-tight ampules. Measurements were conducted on Bruker Avance III HD 400 MHz spectrometers equipped with a double resonance broad band probe (BBO) and on a Bruker Avance NEO 600 MHz spectrometer equipped with a double resonance broad band Prodigy probe (BBO). NMR frequencies were referenced externally and are given in parts per million (ppm). ¹H and ¹³C frequencies are referenced to TMS (tetramethylsilane), ³¹P to H₃PO₄ (85 wt.% in H₂O), ¹¹⁹Sn to Me₄Sn and ²⁰⁷Pb to Me₄Pb. For all NMR measurements, the system was locked on the corresponding deuterium signal of the deuterated solvents. C₆D₆ (99.6%), toluene-d₈ (99%) and THF-d₈ (99.5%) were stored over activated 3 Å molecular sieves. ¹H- and ¹³C-NMR spectra were calibrated on the solvent residual peaks. UV/vis spectra were recorded on an Ocean Optics Flame Spectrometer. Elemental analyses were determined by the analytical department of Regensburg University. {(Ar')GeCl}₂,^[33] [(Ar')Sn(μ-Cl)]₂,^[33] [(Ar')Pb(μ-Br)]₂^[34] and [(^{Dep}nacnac)MgCo(P₂C₂tBu₂)₂(COD)]^[13] were all prepared according to literature procedure. All other reagents were used as received.

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions

6.7.2 $[\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{SnAr}')(\eta^4\text{-COD})]$ (**2**)



To a Schlenk flask cooled to $-78\text{ }^{\circ}\text{C}$ containing $[(\text{Ar}')\text{Sn}(\mu\text{-Cl})_2]$ (0.22 g, 0.39 mmol) and $[(^{\text{Dep}}\text{nacnac})\text{MgCo}(\text{P}_2\text{C}_2\text{tBu}_2)_2(\text{COD})]$ (0.3 g, 0.39 mmol) was added toluene. This was left to stir at room temperature overnight. The reaction mixture was again cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of $(^{\text{Dep}}\text{nacnac})\text{Li}$ (0.14 g, 0.39 mmol) in THF was added dropwise and left to stir at room temperature for 4 hours. Subsequently all volatiles were removed in vacuo and the residue was extracted with *n*-hexane. The filtrate was concentrated under reduced pressure and stored at $-30\text{ }^{\circ}\text{C}$ to yield dark green crystals of **2**. A second crop of **2** was obtained by concentrating the mother liquor and storing at $-30\text{ }^{\circ}\text{C}$ (0.19 g, 54%).

UV/vis (toluene, λ_{max} / nm, ϵ_{max} / $\text{L mol}^{-1} \text{ cm}^{-1}$): 287 (11000), 354 (5500), 428 (2000).

^1H NMR (400 MHz, C_6D_6 , 298 K): δ/ppm = 0.87 (s, 18H, $\text{C}(\text{CH}_3)_3$), 0.91–1.08 (br m, 1H, COD-*H*), 1.13 (d, 12H, $\text{CH}(\text{CH}_3)_2$), 1.17–1.40 (br m, 3H, COD-*H*), 1.49 (br d, 12H, $\text{CH}(\text{CH}_3)_2$), 1.66 (m, 2H, COD-*H*), 2.53 (m, 2H, COD-*H*), 3.00 (br m, 2H, COD-*H*), 3.30 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 4.36 (br m, 2H COD-*H*), 7.22 (dd, 1H, Ar-*H*), 7.26 (br m, 6H, Ar-*H*), 7.31 (d, 2H, Ar-*H*).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 298K): δ/ppm = 24.0, 27.0, 29.7, 31.3, 31.8, 33.6, 36.8, 76.6, 123.8, 125.4, 129.2, 132.5, 141.1, 146.2, 147.9.

$^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, C_6D_6 , 298 K): δ/ppm = -62.3 (d, $^2J_{\text{PP}}$ = 13.4 Hz, $^1J_{\text{SnP}}$ = 1050 Hz, 1P, Sn-*P*), 59.0 (d, $^2J_{\text{PP}}$ = 13.6 Hz, 1P).

^{119}Sn NMR (224 MHz, toluene- d_8 , 298 K): δ/ppm = 1899.7 (br d, $^1J_{\text{PSn}}$ = 1053 Hz).

Elemental analysis (%) calcd. for $\text{C}_{42}\text{H}_{55}\text{SnCoP}_2$ (Mw: 883.65 g mol^{-1}) C 65.24, H 7.64; found C 65.77, H 7.34.

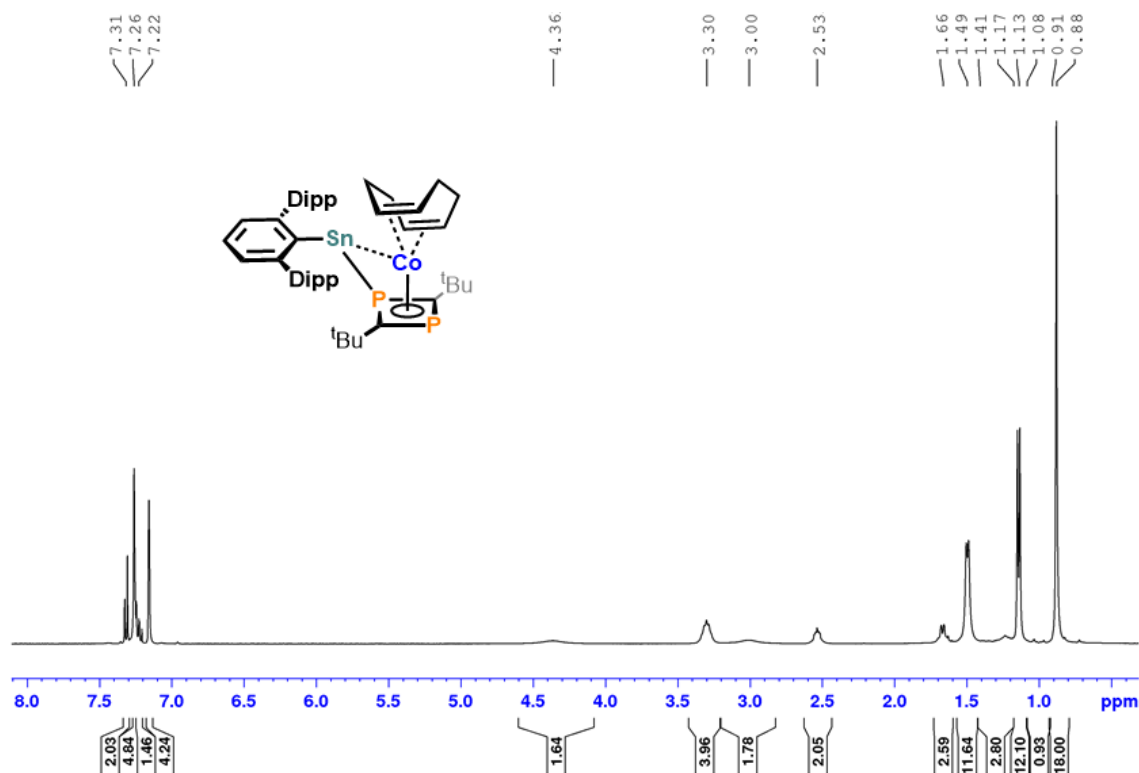


Figure 6.8: ^1H NMR spectrum of $[\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2\text{SnAr}')(\eta^4\text{-COD})]$ (**2**) in C_6D_6 at ambient temperature.

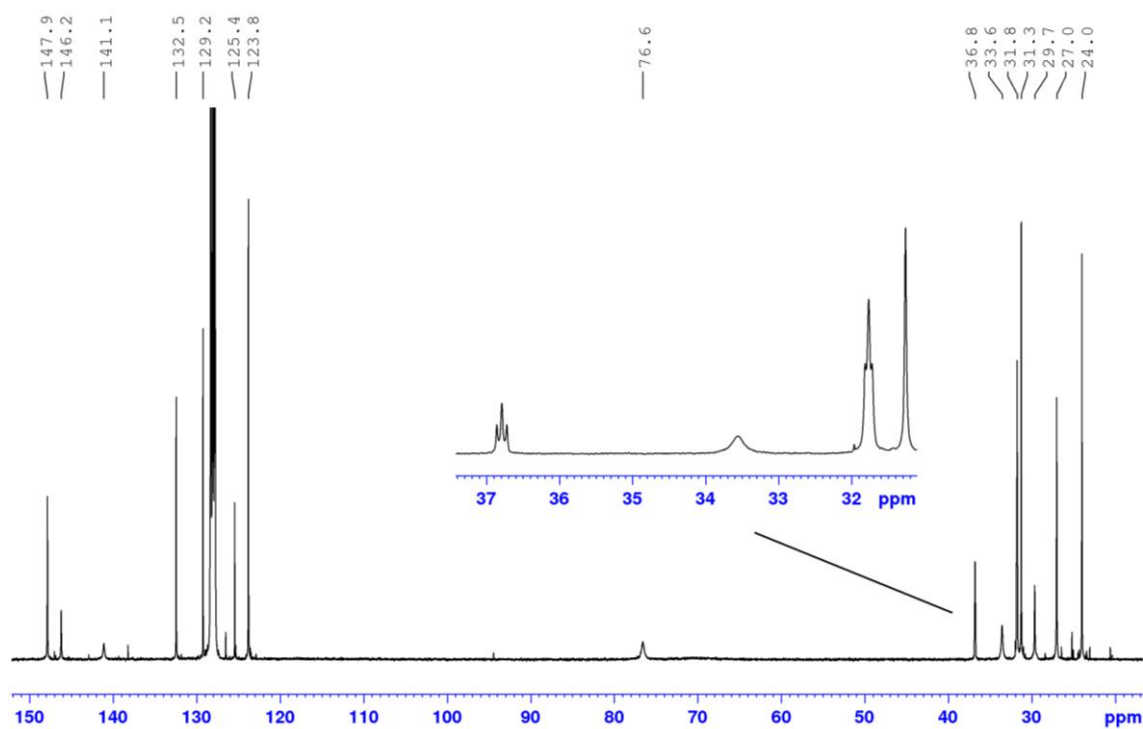


Figure 6.9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** in C_6D_6 at ambient temperature.

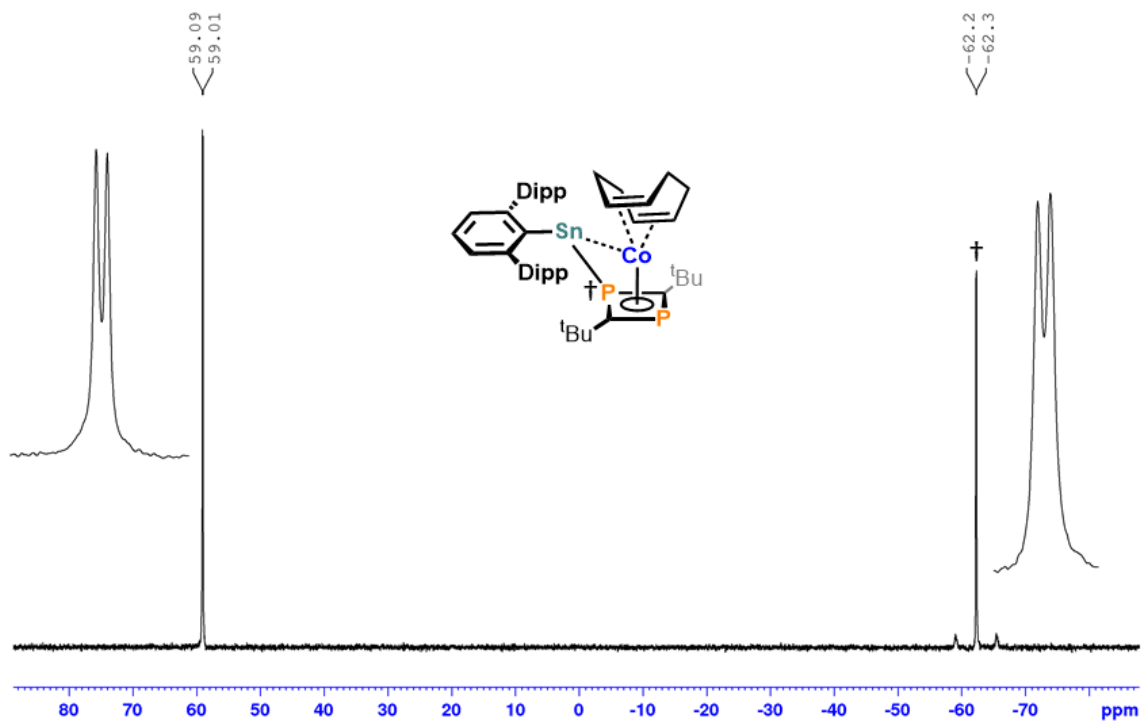


Figure 6.10: $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of **2** in C_6D_6 at ambient temperature.

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions

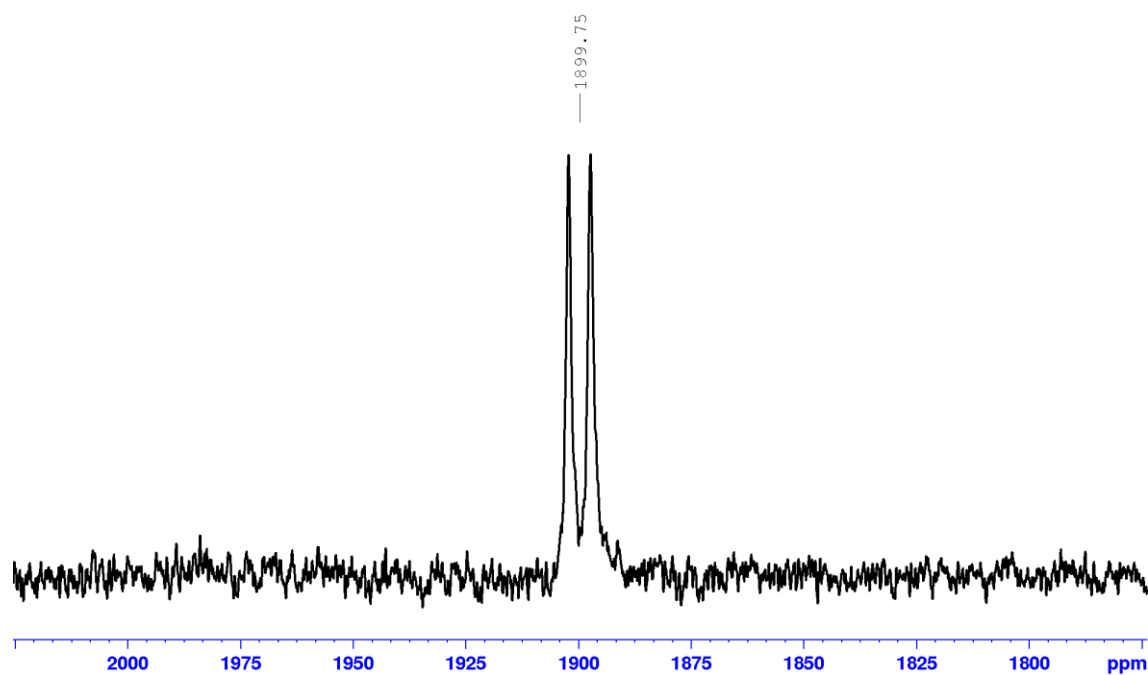


Figure 6.11: ^{119}Sn NMR Spectrum of **2** in toluene- d_8 at ambient temperature.

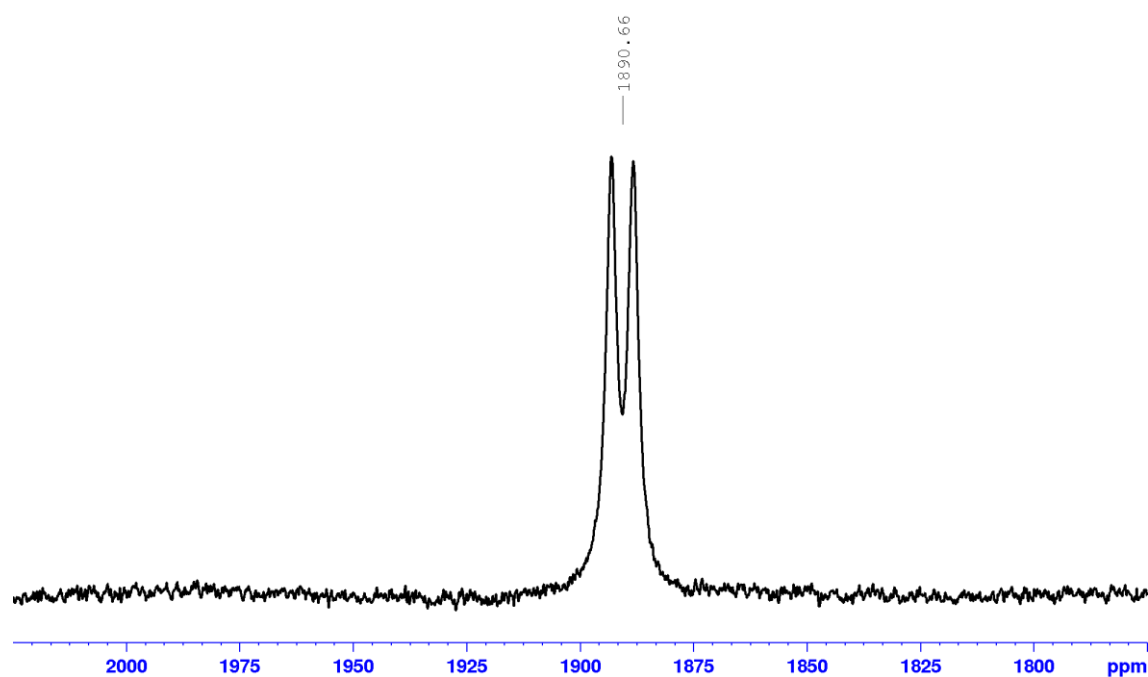
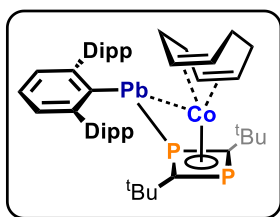


Figure 6.12: ^{119}Sn NMR Spectrum of **2** in toluene- d_8 at 233 K.

6.7.3 [Co(η^4 -P₂C₂tBu₂PbAr')(η^4 -COD)] (**3**)



The same procedure as for **2** except using [(Ar')Pb(μ -Br)]₂ (0.27 g, 0.39 mmol), [(^{Dep}nacnac)MgCo(P₂C₂tBu₂)₂(COD)] (0.3 g, 0.39 mmol) and (^{Dep}nacnac)Li (0.14 g, 0.39 mmol). This yields dark green crystals of **3** (0.25 g, 65%).

UV/vis (toluene, λ_{max} / nm, ϵ_{max} / L mol⁻¹ cm⁻¹): 286 (18000), 348 (8500), 417 (4000).

¹H NMR (400 MHz, C₆D₆, 298 K): δ /ppm = 0.87 (s, 18H, C(CH₃)₃), 0.97 (m, 2H, COD-*H*), 1.11 (d, 12H, CH(CH₃)₂), 1.47 (d, 12H, CH(CH₃)₂), 1.48–1.64 (br m, 2H, COD-*H*), 1.72 (m, 2H, COD-*H*), 2.58 (m, 2H, COD-*H*), 3.03 (br m, 2H, COD-*H*), 3.26 (m, 4H, CH(CH₃)₂), 4.45 (br m, 2H, COD-*H*), 7.26 (s, 6H, Ar-*H*), 7.38 (t, 1H, Ar-*H*), 7.80 (d, 2H, Ar-*H*).

¹³C{¹H} NMR (150 MHz, C₆D₆, 298 K): δ /ppm = 24.0, 27.1, 27.5, 31.0, 31.3, 34.9, 36.9, 71.5, 74.7, 123.7, 123.9, 129.0, 139.3, 141.1, 147.4, 147.7.

³¹P{¹H} NMR (161 MHz, C₆D₆, 298 K): δ /ppm = -56.1 (d, ²*J*_{PP} = 15.4 Hz, ¹*J*_{PbP} = 1192 Hz, 1P, Pb-*P*), 59.5 (d, ²*J*_{PP} = 15.2 Hz, 1P).

²⁰⁷Pb NMR (126 MHz, toluene-*d*₈, 298 K): δ /ppm = 8592.8 (br d, ¹*J*_{PPb} = 1200 Hz).

Elemental analysis (%) calcd. for C₄₂H₅₅PbCoP₂ (Mw: 972.14 g mol⁻¹) C 59.30, H 6.95; found C 59.5, H 6.79.

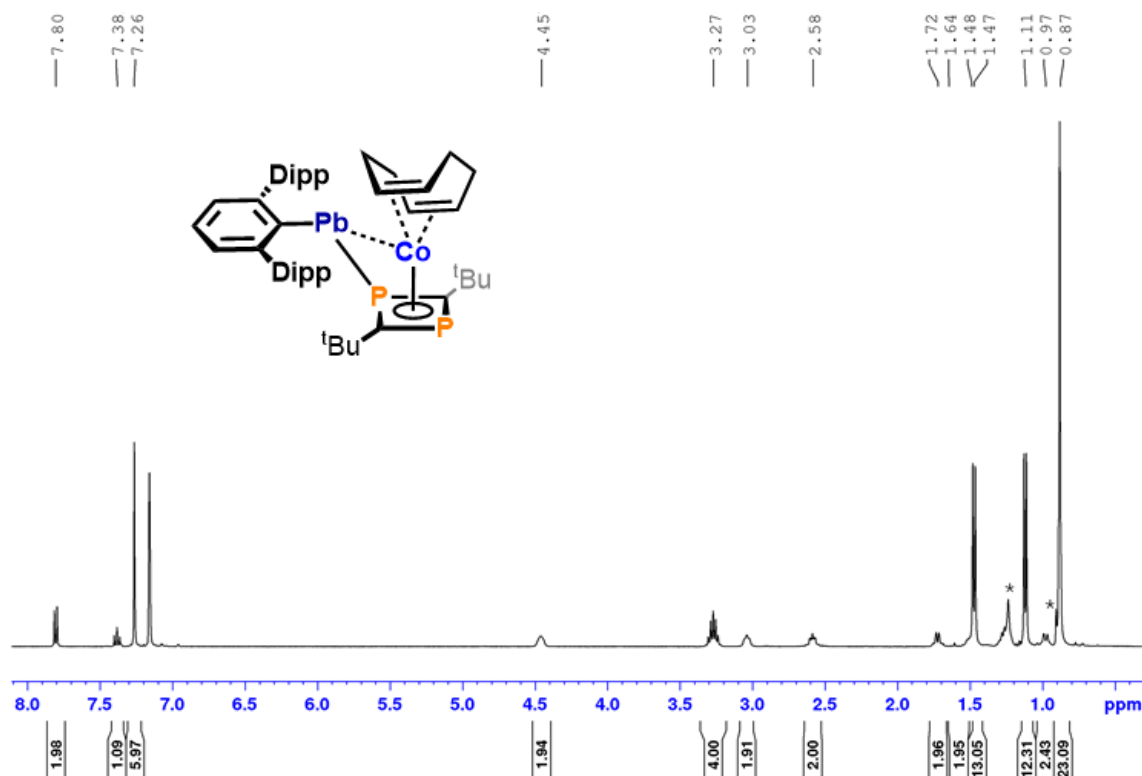


Figure 6.13: ¹H NMR spectrum of [Co(η^4 -P₂C₂tBu₂PbAr')(η^4 -COD)] (**3**) in C₆D₆ at ambient temperature (* = *n*-hexane).

6 Transition–Metal–Stabilized Heavy Tetraphospholide Anions

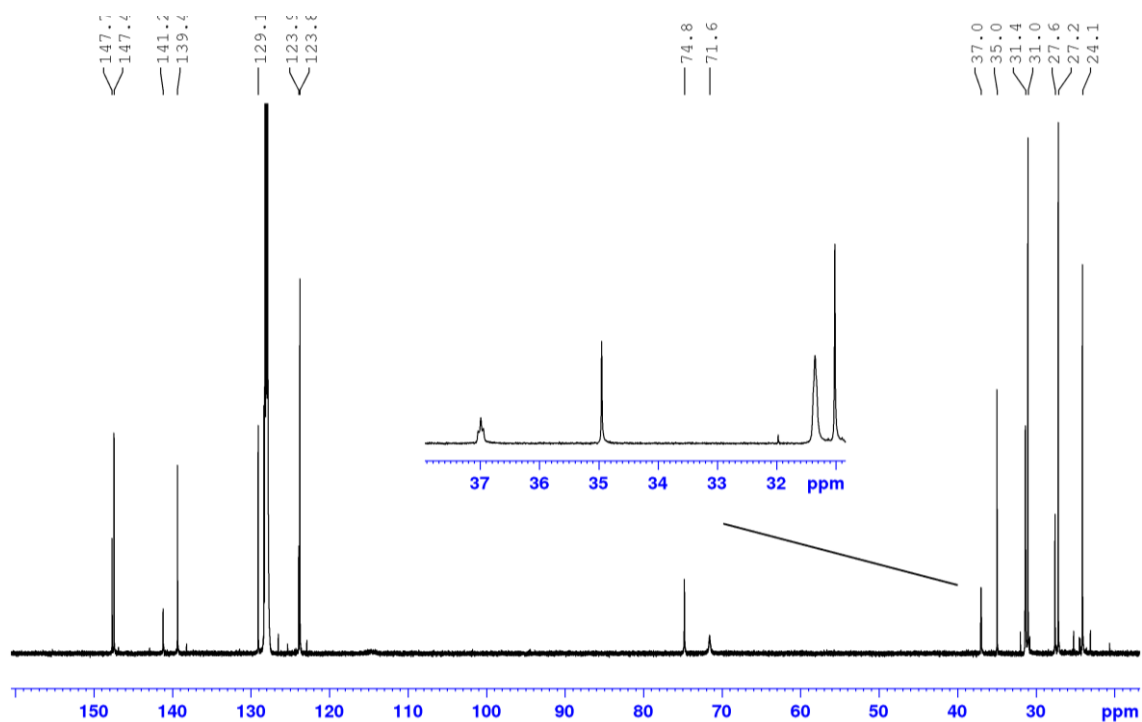


Figure 6.14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** in C_6D_6 at ambient temperature.

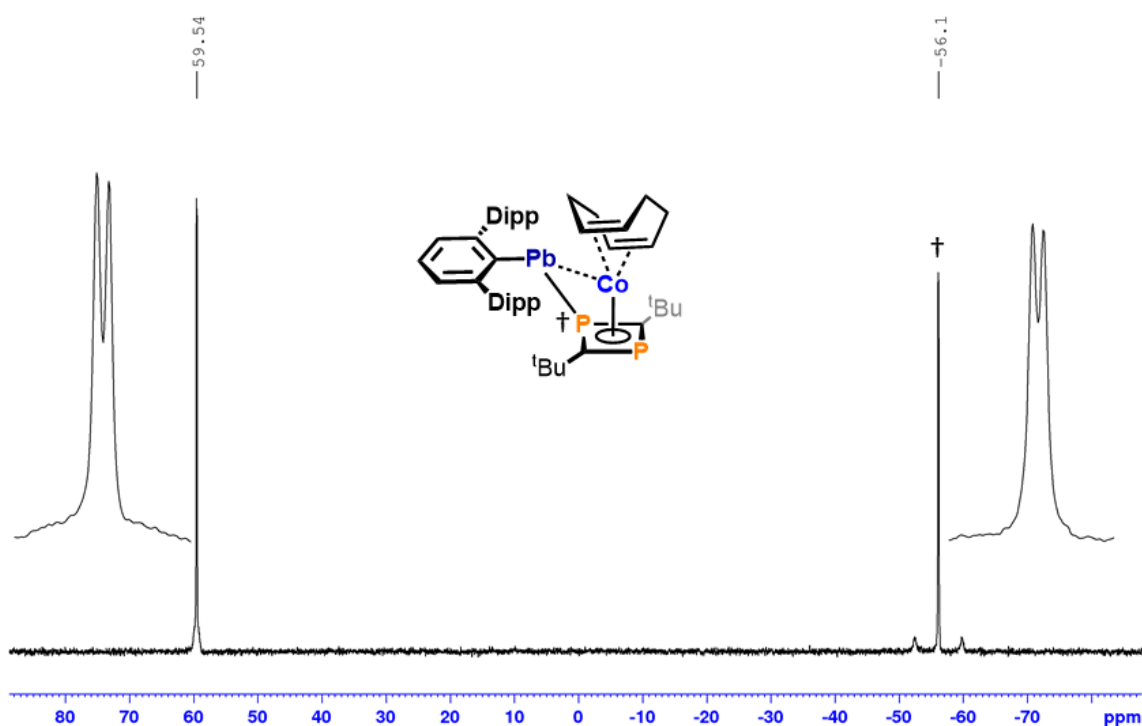


Figure 6.15: $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of **3** in C_6D_6 at ambient temperature.

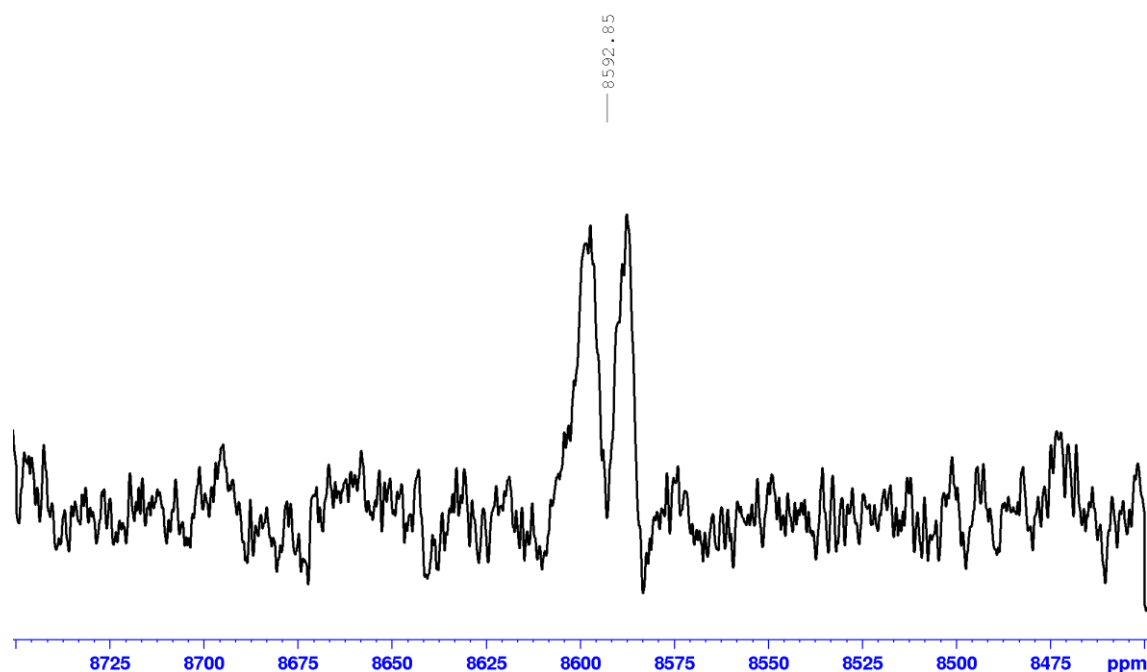


Figure 6.16: ^{207}Pb NMR Spectrum of **3** in toluene- d_8 at ambient temperature.

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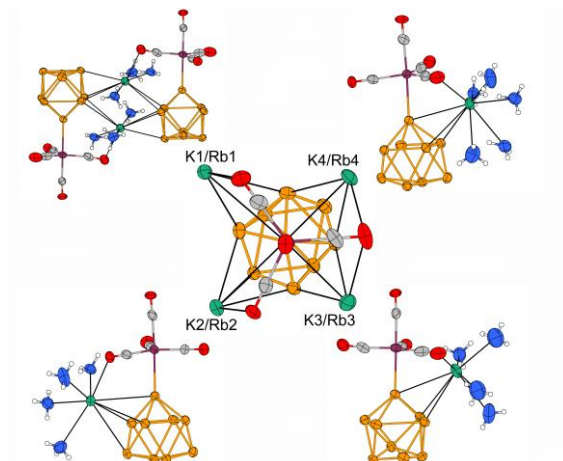
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7 [(K,Rb)@([2.2.2]CRYPT)]₂(K,Rb)₄[Si₉W(CO)₄]·13.4 NH₃ – THE FIRST TUNGSTEN FUNCTIONALIZED SILICON ZINTL CLUSTER



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Z. Anorg. Allg. Chem. **2023**, e202300117

DOI: 10/1002/zaac.202300117

On the occasion of the 125th birthday of Prof. Dr. Eduard Zintl.

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Paul Braun performed all experimental work, including preparation of flame-sealed NMR-samples and measurement of XRD crystal structures and performed quantum chemical calculations. NMR spectroscopic investigations were carried out by **Franz F. Westermair**. The project was overseen by Ruth M. Gschwind and Nikolaus Korber. The manuscript was prepared by Paul Braun, with assistance from all authors.

7 The First Tungsten Functionalized Silicon Zintl Cluster

7.1 Abstract

The reaction between the heteroleptic metal carbonyl complex $[\text{W}(\text{CO})_4(\text{tmeda})]$ ((tmeda) = *N,N,N',N'*-Tetramethylene-1,2-diamine) with $[\text{Si}_9]^+$ silicon Zintl clusters in presence of [2.2.2]crypt ([2.2.2]crypt = 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) in liquid ammonia yielded the compound $[(\text{K,Rb})@([2.2.2]\text{crypt})]_2(\text{K,Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$. The compound was analyzed by single crystal X-ray diffraction and crystallizes in the space group $P\bar{1}$ ($a = 11.48390(10) \text{ \AA}$, $b = 19.7383(2) \text{ \AA}$, $c = 19.8983(2) \text{ \AA}$, $\alpha = 12.5760(10)^\circ$, $\beta = 97.4210(10)^\circ$, $\gamma = 95.3760(10)^\circ$, $V = 4079.01(7) \text{ \AA}^3$). The compound represents the first group 6 carbonylate-functionalized silicon Zintl cluster. The central moiety is composed of a tricapped trigonal prismatic nine-atom silicon species which coordinates with the lone pair of one capping atom to the tungsten tetracarbonylate cluster anion $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$. The chemical bonding in the new cluster entity is analyzed using theoretical calculations and subsequent analysis using QTAIM and NBO.

7.2 Introduction

The highly charged group 14 Zintl ions are a topic of research since their discovery by Joannis in 1891^[1]. Especially the cluster anions of the lighter group 14 elements silicon and germanium are interesting in terms of materials science.^[2] Fässler et al. recently published a paper investigating the quantum chemical mixing behavior of Si and Ge within $(\text{Si}_{9-x}\text{Ge}_x)^{4-}$ ($x = 0, 1, 2$) Zintl anions.^[3] A current focus in research is set on the derivatization of these molecular building blocks with silanes and / or transition metal complexes.^[4,5] Two families of organometallic reagents which yield a large variety of interesting, functionalized clusters are NHC (*N*-heterocyclic carbene) metal complexes.^[6] Since the homoleptic carbonyl complexes hardly show any reactivity towards the Zintl clusters, labile ligands like mesitylene, toluene, PPh_3 , etc. were introduced.^[7] The reactions with heteroleptic complexes like e.g. $[\text{Cr}(\text{CO})_3(\text{tol})]$, $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ and $[\text{M}(\text{CO})_3(\text{mes})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{mes} = \eta^6\text{-1,3,5-C}_6\text{Me}_3\text{H}_3$) resulted in the first metal carbonyl-functionalized Zintl clusters: $[\text{Sn}_9\text{M}(\text{CO})_3]^{4-}$ and $[\text{Pb}_9\text{M}(\text{CO})_3]^{4-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).^[8-10] The transition metals typically tetra-coordinate the square plane of the monocapped square antiprismatic cluster, and even new clusters involving the $\{\text{M}(\text{CO})_3\}$ fragment in a penta-coordination can be observed.^[9,10] A few years later the group 6 metal carbonyl functionalization of germanium clusters could be achieved via a gas phase deposition route, leading to the characterization of $[\text{Ge}_9(\text{Si}(\text{SiMe}_3)_3)\text{M}(\text{CO})_3]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[\text{Ge}_9(\text{Si}(\text{SiMe}_3)_3)\text{Cr}(\text{CO})_5]^-$.^[11]

Also to mention is the chemistry of group 15 Zintl clusters with group 6 transition metal carbonyls which results in a wide variety of functionalized clusters like $[\text{E}_7\text{M}(\text{CO})_3]^{3-}$ ($\text{E} = \text{P}, \text{As}, \text{Sb}$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$), $[\text{Bi}_3\text{M}_2(\text{CO})_6]^{3-}$ ($\text{M} = \text{Cr}, \text{Mo}$), $[\text{Bi}_3\text{Mo}_2(\text{CO})_9]^{4-}$ and $[\eta^3\text{-Bi}_3\text{W}(\text{CO})_3]^{3-}$.^[5,7,12]

Especially for germanium, a multitude of different structure motifs is known. For group 6 there are further examples like $[\text{Ge}_9\{\text{M}(\text{CO})_5\}_3]^{4-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) with the $\{\text{M}(\text{CO})_5\}$ fragments coordinating the three capping Ge atoms of the nine atom cluster in its tricapped prismatic shape.^[13] Further examples for transition-metal-carbonyl-functionalized germanium clusters are $[\text{Ge}_8\{\text{Mo}(\text{CO})_3\}_2]^{4-}$ with a intermolecular Mo–Mo interaction, $[\{(\text{CO})_5\text{M}\}_6\text{Tt}_6]^{2-}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{Tt} = \text{Ge}, \text{Sn}$) as a derivative of the unknown $[\text{Ge}_6]^{2-}$ anion,^[14] and $[\text{Ge}_{10}\text{Mn}(\text{CO})_4]^{3-}$.^[15] Very recently also the cluster $[(\text{CrGe}_9)\text{Cr}_2(\text{CO})_{13}]^{4-}$ was published showing a combination of a penta- and a monocoordination of the carbonyl fragment.^[16] Outside of group 6, the anion $[\text{Ge}_8\text{Fe}(\text{CO})_3]^{3-}$ was reported with a replaced vertex of a $[\text{Ge}_9]^{4-}$.^[17] Notable is also $[\text{Ge}_5\text{Ni}_2(\text{CO})_3]^{2-}$ which shows a functionalized $[\text{Ge}_5]^{2-}$ anion.^[18] The reaction of germanium or tin Zintl ions with $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$ even results in endohedral or

The First Tungsten Functionalized Silicon Zintl Cluster 7

fused clusters. Examples for Ni functionalized clusters are $[\text{Ni}@\text{Sn}_9\text{Ni}(\text{CO})]^{3-}$, $[\text{Ni}_6\text{Ge}_{13}(\text{CO})_5]^{4+}$, $[\text{Co}@\text{Sn}_9\text{Ni}(\text{CO})]^{3-}$ and $[\text{Sn}_5\text{Ni}_6(\text{CO})_9]^{4+}$.^[19] In contrast to the rich coordination chemistry of germanium clusters, for bare silicon clusters, only few transition-metal-coordinated clusters have been reported to date. The first structure $[\text{Si}_9\text{ZnPh}]^{3-}$ was published by Sevov et al. in 2006.^[20] Since then, additions were $[(\text{MesCu})_2\text{Si}_4]^{4+}$, $[(\text{NHC}^{\text{tBu}}\text{Au})_6(\eta^2\text{-Si}_4)]^{2+}$, $[\text{NHC}^{\text{Dipp}}\text{Cu}(\eta^4\text{-Si}_9)]^{3-}$ and $[\{\text{Ni}(\text{CO})_2\}_2(\mu\text{-Si}_9)_2]^{8-}$.^[21,22] The latter represents the first metal-carbonyl-coordinated silicon cluster.

In general, solution studies in liquid ammonia by NMR spectroscopy provide the possibility of further investigation of silicon clusters by ^1H - and ^{29}Si -NMR. In past experiments, the protonated silicon Zintl anions $[\text{HSi}_9]^{3-}$, $[\text{H}_2\text{Si}_9]^{2-}$ and $[\text{HSi}_4]^{3-}$ could be detected.^[23,24] Recently, NMR spectroscopy allowed for the detection of the first protonated group 14 Zintl cluster coordinating to a coinage metal, the existence of $[\text{NHC}^{\text{Dipp}}\text{Cu}(\eta^4\text{-Si}_9)\text{H}]^{2-}$ was supported by crystallographic data and computational analyses.^[25]

We here report on the synthesis and characterisation of the first tungsten-functionalized silicon cluster anion $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ in the ammoniate $[(\text{K,Rb})@([2.2.2]\text{crypt})]_2(\text{K,Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$.

7.3 Results and Discussion

7.3.1 Crystal structure of $[(\text{K,Rb})@([2.2.2]\text{crypt})]_2(\text{K,Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$

The reaction of $\text{K}_6\text{Rb}_6\text{Si}_{17}$ with $\text{W}(\text{CO})_4(\text{tmeda})$ in the presence of $[2.2.2]\text{crypt}$ in liquid ammonia resulted in crystals of the compound $[(\text{K,Rb})@([2.2.2]\text{crypt})]_2(\text{K,Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$. The central moiety is represented by a $[\text{Si}_9]^{4-}$ cluster which coordinates via one vertex silicon atom to the tungsten tetracarbonylate $[\text{W}(\text{CO})_4]^{2-}$. The resulting complex $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ is directly coordinated by four alkali metal cations ($\text{A} = \text{K,Rb}$). The two remaining cations are found in the cavity of $[2.2.2]\text{cryptands}$. Therefore, the overall charge of the anions sums up to -6 .

The shape of this type of nine atom clusters can be evaluated using the h/e ratio (ideally $h/e = 1$ for the tricapped prism with point group D_{3h}) or the $d1/d2$ ratio (ideally $d1/d2 = 1$ for the monocapped square antiprism with point group C_{4v}).^[26] For the silicon cluster in $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ (Figure 7.1), a h/e ratio of 1.19 and a $d1/d2$ ratio of 1.39 is determined. An unequivocal assignment of the cluster symmetry is therefore not possible. The Si–Si distances range from 2.4328(18) Å to 3.191(2) Å, which corresponds well to literature values.^[27]

The tungsten tetracarbonylate fragment shows W–C distances in the range of 1.934(6) Å to 1.978(5) Å and C–O bonds in the range of 1.156(6) Å to 1.219(7) Å, which are both in agreement with literature.^[28,29] The CO group opposite to the $[\text{Si}_9]^{4-}$ cage shows a slightly prolonged W–C4 distance (1.978(2) Å) and accordingly shortened C4–O4 bond (1.156(6) Å). The W–Si1 distance is 2.6649(13) Å which fits well into the range of other W–Si distances.^[30] The equatorial C1O1, C2O2 and C3O3 groups show ($\angle\text{C–W–C}$) angles of 118.3(2)° to 121.7(3)°, the apical to equatorial ($\angle\text{C4–W–Cx}$, $x = 1\text{--}3$) angles are 84.12(15)° to 92.37(16)°, and the apical to apical ($\angle\text{C4–W–Si1}$) angle is 177.40(15)°. The structure can be compared to the structurally related metal pentacarbonylates which also preferentially form a trigonal bipyramid.^[28,31]

7 The First Tungsten Functionalized Silicon Zintl Cluster

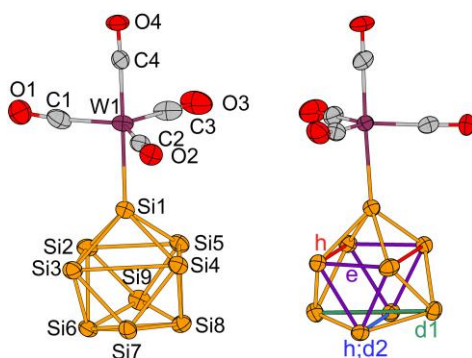


Figure 7.1: Asymmetric unit of the central moiety $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ in $[(\text{K},\text{Rb})@([2.2.2]\text{crypt})]_2(\text{K},\text{Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$ and representation of the d1/d2 diagonals and h/e bonds. The displacement ellipsoids are shown at 50% probability.

The chelated alkali metal positions A5 (=K5/Rb5) and A (=K6/Rb6) can be resolved as 91.5/8.5% and 91.0/9.0% K/Rb. A refinement model with fully occupied potassium resulted in significantly larger residual electron density (Figure 7.9), which indicated additional presence of a heavier alkali metal cation at this position. The non-chelated alkali metal positions (Figure 7.2) K1/Rb1 (=A1, 46.6/53.4%), K2/Rb2 (=A2, 31.8/68.2%), K3/Rb3 (=A3, 69.9/30.1%) and K4/Rb4 (=A4, 29.8/70.2%) are coordinated to the cluster. These four directly coordinating cations are instrumental for the stabilization of the unusually high charge of the cluster anion. The position of A1 additionally coordinates a triangular face of a second Si₉ cage, A2 is coordinated by four silicon atoms of the nonasilicide anion, A3 and A4 cap triangular faces of the Si₉ unit. The observed A–Si distances range from 3.4863(18) Å to 4.1783(18) Å, which is in accordance with literature.^[27] Additionally, the alkali metals are coordinated by one oxygen atom of the respective carbonyl groups at A–O distances from 2.725(6) Å to 3.089(4) Å, which are within the expected range.^[21]

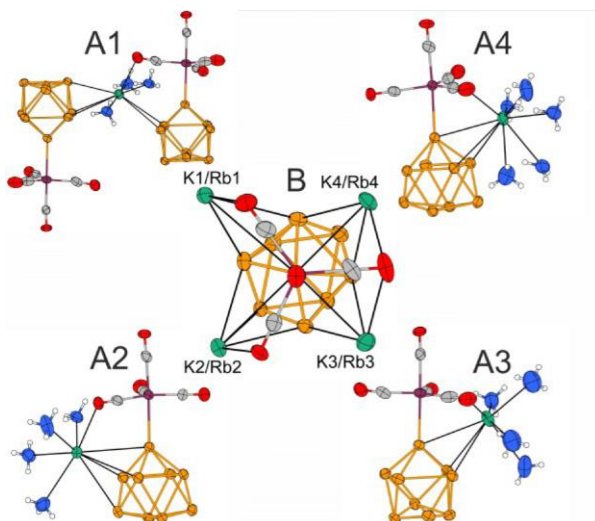


Figure 7.2: Alkali metal vicinity of the anion surrounding cations (**B**) and the coordination spheres of alkali metal position **A1** (K/Rb: 46.6/53.4 %), **A2** (31.8/68.2 %), **A3** (69.9/30.1%) and **A4** (29.8/70.2 %). The displacement ellipsoids are shown at 50% probability.

The coordination spheres of the positions A2–A4 are completed by ammonia molecules of solvation (A1: 3×NH₃; A2/A3: 4×NH₃; A4: 5×NH₃). This results in a coordination number of nine for A1/A2/A4 and eight for A3. This in turn corresponds to the alkali metal occupation, as the larger rubidium cation is predominantly present at

The First Tungsten Functionalized Silicon Zintl Cluster 7

A1/A2/A4, while the smaller volume of A3 favors the occupation by potassium. Regarding direct cation-anion interactions, $(K,Rb)_2[Si_9W(CO)_4]_2^{6-} \cdot 6 NH_3$ dimers are observed, resulting from the double cage coordination of A1. These dimers are connected by μ^2 -ammonia bridged alkali metals to form a 2D network. The $A@[2.2.2]$ crypt complexes separate these two-dimensional layers from each other.

7.3.2 Chemical Bonding

The complex anion $[Si_9W(CO)_4]^{6-}$ is structurally related to the tungsten pentacarbonylate $[W(CO)_5]^{2-}$, which from the point of view of organometallics can be described as an 18-valence electron cluster.^[28] The configuration is achieved by five CO ligands, six electrons from the metal center and two negative charges. One of the CO ligands is replaced by a $[Si_9]^{4-}$ cluster as ligand. Sevov et al. stated that $[Ge_{10}]^{2-}$ in the structure $[Ge_{10}Mn(CO)_4]^{3-}$ acts as a two-electron ligand via the coordination of a lone pair.^[15] The corresponding molecular orbitals HOMO-3 ($[Si_9]^{4-}$) and LUMO ($[W(CO)_4]^{2-}$) support the description of $[Si_9]^{4-}$ as a two electron donor ligand (Figure 7.3).

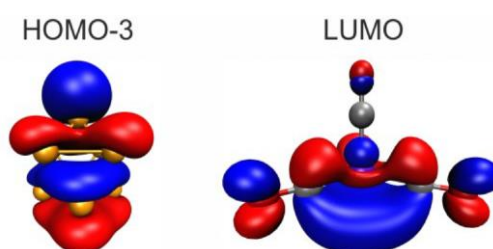


Figure 7.3: Molecular orbitals HOMO-3 of $[Si_9]^{4-}$ and LUMO of $[W(CO)_4]^{2-}$. The molecular orbitals were calculated on a ZORA-D3(BJ)-B3LYP/ma-ZORA-def2-TZVP (Si, C, O), ZORA-D3(BJ)-B3LYP/Sarc-ZORA-TZVP (W) level of theory.^[32–40]

To reinforce the similarity, theoretical calculations on a ZORA-D3(BJ)-B3LYP/ma-ZORA-def2-TZVP(Si, C, O) ZORA-D3(BJ)-B3LYP/Sarc-ZORA-TZVP (W) level of theory were carried out for the anion $[Si_9W(CO)_4]^{6-}$.^[32,33,35–41] The geometry optimized dimensions of the anion agree with the results of the X-Ray characterized compound and were confirmed as an energetic minimum by frequency analysis (Figure 7.4). The $\{Si_9\}$ unit of the calculated structure is described via a C_{4v} -symmetry with a d1/d2 ratio of 1.00 and a h/e ratio of 1.18. Compared to the calculated model, the strong distortion of the experimentally determined compound presumably is induced by the crystal packing effects. The converged W–Si distance is 2.684 Å and the silicon cage is coordinating with the apical atom which caps the square face.

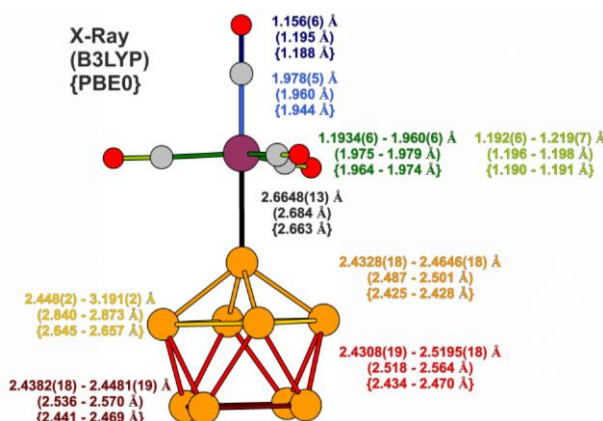


Figure 7.4: Representation of the atomic distances from the single crystal X-Ray diffraction model, ZORA-D3(BJ)-B3LYP/ma-ZORA-def2-TZVP (Si, C, O), ZORA-D3(BJ)-B3LYP/Sarc-ZORA-TZVP (W) level and

7 The First Tungsten Functionalized Silicon Zintl Cluster

ZORA-D3(BJ)-PBE0/ma-ZORA-def2-TZVP (Si, C, O), ZORA-D3(BJ)-PBE0/Sarc-ZORA-TZVP (W)
calculations on $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$.^[32,33,35–41]

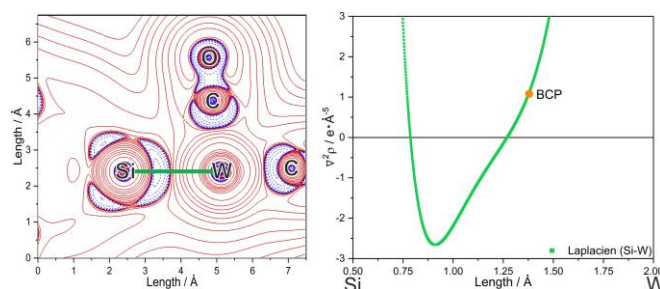


Figure 7.5: Contour line map showing the Laplacian of the electron density along the Si–W–C plane with positive values in red and negative values in blue and the Laplacian along the Si–W bond axis in green. The contour line map was plotted using Multiwfn.^[44]

Viewing the Laplacian electron density on the Si–W–(CO) plane and along the Si–W bond axis (Figure 7.5), it is strongly indicated that the Si lone pair is donating electrons to the W. Further evaluation of the bonding situation with a QTAIM analysis of the bond critical point (BCP) resulted in a positive ρ , $\nabla^2\rho$ and a negative virial potential energy density at the BCP. This can be, according to the criteria of Bianchi et al., interpreted as a dative bond.^[42,43] Comparing the NPA and Bader charges of $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ (NPA: C/O = 0.222 – 0.367/–0.699 – –0.718; Bader: C/O = 0.378 – 0.486/–1.311 – –1.319) to a neutral CO fragment (NPA: C/O = 0.489/–0.489; Bader: C/O = 1.193/–1.193) the CO groups in the complex show higher negative charges compared to the neutral fragment.^[34,43] Also, the delocalization index (DI) of the bound CO group is lower compared to the neutral fragment which indicates a weaker CO bonding. If the anion would be separated, the expected charges for the $\{\text{Si}_9\}$ ligand would be 4– and 2– for the $\{\text{W}(\text{CO})_4\}$ (Figure 7.6). The NPA/Bader charges suggest electron shift from the $\{\text{Si}_9\}$ ligand towards the metal carbonylate since the overall charges are –3.586/–3.595 for $\{\text{Si}_9\}$ and –2.414/–2.404 for $\{\text{W}(\text{CO})_4\}$. More specifically the capped square plane of the $\{\text{Si}_9\}$ antiprism shows a deficit of charge of 0.414 which is relocated mostly towards the W and partially towards the O atoms. This interpretation could be supported further by IR or Raman measurements, which were not successful until now because of the poor solubility of the compound and the lability of the solid ammoniate.

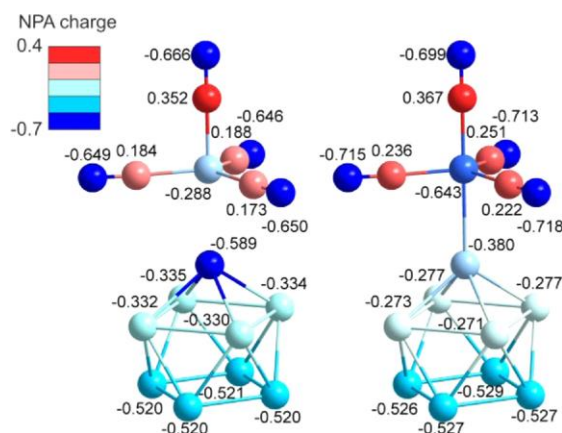


Figure 7.6: NPA charges of $[\text{Si}_9]^{4-}$, $[\text{W}(\text{CO})_4]^{2-}$ and $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ calculated on a ZORA-D3(BJ)-B3LYP/ma-ZORA-def2-TZVP (Si, C, O), ZORA-D3(BJ)-B3LYP/Sarc-ZORA-TZVP (W) level of theory.^[32–40]

7.3.3 NMR Spectroscopic Studies

Preliminary NMR measurements of samples containing $[\text{W}(\text{CO})_4(\text{tmeda})]$, 99.2% ^{29}Si -enriched $\text{K}_6\text{Rb}_6\text{Si}_{17}$ and $[\text{2.2.2}]\text{crypt}$ in a molar ratio of 1:1:2 in liquid ammonia were carried out at 203 K. ^{183}W is the only naturally occurring isotope of tungsten with nuclear spin quantum number $I = \frac{1}{2}$ and a natural abundance of 14.3% (All other natural isotopes have nuclear spin quantum number $I = 0$). While direct observation of ^{183}W -NMR is possible, it is usually not accessible with standard NMR hardware due to its very low resonance frequency (below ^{109}Ag). Surprisingly, alongside the known signal of $[\mu\text{-HSi}_4]^{3-}$ we were able to detect an unprecedented ^1H -NMR signal at -4.796 ppm six months after sample preparation (Figure 7.16).^[24] It had exotic satellite integrals (Figure 7.17), which were simulated and thus unambiguously assigned to originate from a ^1H - ^{183}W coupling with a presumably 1J -coupling constant of 53.3 Hz, in accordance with literature (Figure SI12).^[45] Since this signal is not observed in samples containing only $[\text{W}(\text{CO})_4(\text{tmeda})]$ in liquid ammonia, it can be assumed, that $\text{K}_6\text{Rb}_6\text{Si}_{17}$ plays a vital role in its formation (Figure 7.19) Unfortunately, unambiguous evidence for the presence of complex $[(\text{K},\text{Rb})@([\text{2.2.2}]\text{crypt})]_2(\text{K},\text{Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$ in solution by means of direct observation of a ^{29}Si -signal with ^{183}W satellites could not be generated yet.

On the other hand, the presence of the new ^1H -signal corroborates the statement that $[\text{W}(\text{CO})_4(\text{tmeda})]$ has labile ligands at the applied reaction conditions, while simultaneous observation of $[\mu\text{-HSi}_4]^{3-}$ indicates that silicides are still present in solution and could react as potential ligands towards tungsten without decomposition.

Further investigations concerning the protonated tungsten species and attempts of direct detection of $[(\text{K},\text{Rb})@([\text{2.2.2}]\text{crypt})]_2(\text{K},\text{Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$ are in progress.

7.4 Conclusions

The use of the heteroleptic tmeda carbonyl complex $[\text{W}(\text{CO})_4(\text{tmeda})]$ together with the nominal Zintl phase $\text{K}_6\text{Rb}_6\text{Si}_{17}$ in solution experiments in liquid ammonia allowed the crystallization of the compound $[(\text{K},\text{Rb})@([\text{2.2.2}]\text{crypt})]_2(\text{K},\text{Rb})_4[\text{Si}_9\text{W}(\text{CO})_4] \cdot 13.4 \text{ NH}_3$. The compound was analyzed via single crystal X-Ray diffraction and proved the presence of the pseudo pentagonal bipyramidal tungsten complex anion $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$. The highly charged anion is stabilized by direct ion interactions of the four cations around the W-Si bond. The structure represents the first tungsten functionalized nonasilicide Zintl anion and only the sixth transition metal functionalized bare silicon cluster. Theoretical calculations suggest dative Si-W bonding interaction is responsible for the formation of this new $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ complex anion.

7.5 Methods Section

All operations were conducted under argon atmosphere using standard glove box and Schlenk techniques. Liquid ammonia was dried and stored over sodium cooled by an ethanol/dry ice bath dewar for at least 96 h.

Synthesis of $\text{K}_6\text{Rb}_6\text{Si}_{17}$ and $\text{K}_6\text{Rb}_6^{29}\text{Si}_{17}$ (99.2% enriched):

Potassium (766.1 mg, 19.59 mmol), rubidium (1674.7 mg, 19.59 mmol) and silicon (1559.2 mg, 55.16 mmol) were weighed, filled into a tantalum ampoule, welded shut and enclosed into a quartz glass ampoule. The ampoule was heated up to 1223 K at a rate of 50 K/h and after 2 h cooled to room temperature at a rate of 20 K/h.^[46] $\text{K}_6\text{Rb}_6^{29}\text{Si}_{17}$ was synthesised according to the method described by Streitferdt et al.^[25]

7 The First Tungsten Functionalized Silicon Zintl Cluster

Synthesis of $\text{W(CO)}_4(\text{tmeda})$:

The compound was synthesized via an adapted method reported by King and Fronzaglia.^[47] The solvents used were degassed beforehand. In a two-neck flask a mixture of $[\text{W(CO)}_6]$ (5 g, 14.2 mmol), tetramethylethylenediamine (5 mL, 39.0 mmol), 80 mL *n*-decane and a few mL *n*-hexane are refluxed for 27 h. The reaction mixture was left for crystallization at 253 K overnight. The solvent was removed, the crystals were washed three times with *n*-hexane and once with dichloromethane. ^{13}C -NMR (400 MHz, CDCl_3): δ =61.94 ppm (s, 2 C), δ =57.73 ppm (s, 4 C).

Synthesis of $[(\text{K,Rb})@([2.2.2]\text{crypt})]_2(\text{K,Rb})_4[\text{Si}_9\text{W(CO)}_4] \cdot 13.4 \text{ NH}_3$:

$\text{K}_6\text{Rb}_6\text{Si}_{17}$, $\text{W(CO)}_4(\text{tmeda})$ and $[2.2.2]\text{crypt}$ were weighed into a flame-dried Schlenk vessel (1 : 1 : 1.5) and ammonia (10 mL) was condensed into the reaction vessel forming a brown-red solution. After storage for 12 weeks at 203 K, an abundance of dark red crystals could be observed and analyzed via X-ray single crystal diffraction.

X-ray diffraction studies:

The compound was found to be highly moisture-, air- and temperature-sensitive. Due to these circumstances the crystals were transferred directly from the cooled Schlenk vessel into a nitrogen stream cooled perfluoroether oil. Suitable crystals were picked up using a MiTeGen loop and transported to the diffractometer using liquid nitrogen for cooling. The diffractometer used was a Rigaku Synergy DW with a photon Jet-DW VHF Cu X-ray source and a HyPix Arc 150° detector. Data collection was performed at a temperature of 123 K. For data reduction and absorption correction the software *CrysAlisPro* (version 171.43.36a^[48]) was used. The structure solution (*ShelXT*^[49]) and refinement (*ShelXL*^[50]) was performed in Olex² 1.5 alpha.^[51] The figures were created in Diamond 4 using displacement ellipsoids at 50% probability level.^[52]

All atoms (except H) could be located in the electron density map. H atoms of the ammonia molecules of solvation were constructed using a riding restraint (Afix 137). The H atoms of the ammonia molecule N15 could not be constructed in a meaningful way. The occupancy of the ammonia molecule N4 was refined to a value of 0.369(17).

Crystal data for $[(\text{K,Rb})@([2.2.2]\text{crypt})]_2(\text{K,Rb})_4[\text{Si}_9\text{W(CO)}_4] \cdot 13.4 \text{ NH}_3$:

$M_r = 1870.72$, space group $P\bar{1}$, $\mu = 7.791 \text{ mm}^{-1}$, $\rho_{\text{calc}} = 1.523 \text{ g cm}^{-3}$, $a = 11.48390(10) \text{ \AA}$, $b = 19.7383(2) \text{ \AA}$, $c = 19.8983(2) \text{ \AA}$, $\alpha = 112.5760(10)^\circ$, $\beta = 97.4210(10)^\circ$, $\gamma = 95.3760(10)^\circ$, $V = 4079.01(7) \text{ \AA}^3$, $Z = 2$, 72249 measured reflections, 16465 independent reflections, $R_{\text{int}} = 0.0555$, $R_1 = 0.0482/wR_2 = 0.1263$ ($I \geq 2\sigma(I)$), $R_1 = 0.0596/wR_2 = 0.1325$ (all data), $\text{GOOF} = 1.055$, $\Delta\rho_{\text{max}} = 1.44 \text{ \AA}^{-3}$, $\Delta\rho_{\text{min}} = -1.61 \text{ \AA}^{-3}$.

Crystallographic data for the structure has been deposited in the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-2260797 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Sample preparation for NMR studies:

$\text{K}_6\text{Rb}_6^{29}\text{Si}_{17}$ (99.2% enriched, 6.3 mg, 0.005 mmol), $[\text{W(CO)}_4(\text{tmeda})]$ (2.1 mg, 0.005 mmol) and $[2.2.2]\text{crypt}$ (3.8 mg, 0.010 mmol) were weighed into a flame-dried heavy wall precision NMR tube (Pyrex) under argon atmosphere. Ammonia was condensed into the tube, yielding a light red solution and it was sealed shut under ammonia atmosphere. The sample was stored at 195 K until NMR examination.

NMR studies:

NMR-Spectroscopic measurements in liquid NH_3 were recorded on a Bruker Avance III 600 MHz spectrometer equipped with a 5 mm TBI-P probe (^1H , ^{31}P , X) with z-gradient without using ^2H -lock. A N_2 evaporator unit was used for measurements at 203 K. ^1H -NMR measurements without presaturation were performed using a standard Bruker pulse program (zg) with 32 scans, relaxation delay of 3 seconds and acquisition time of 1.81 seconds. If not noted otherwise, optimized ^1H -NMR measurements with presaturation of the ammonia signal were performed using a standard Bruker pulse program (zgpgpr) with 512 scans, relaxation delay of 3 seconds and acquisition time of 2.5 seconds. Data were processed with the Bruker software TopSpin 4.2.0 using the parameters SI = 131072, WDW = "EM", LB = 2 (Hz). Baselines of integrated spectra were corrected using cubic splines ("sab" command in TopSpin). ^1H -NMR chemical shifts are reported relative to center of the solvent signal of NH_3 at 1.21 ppm.

Quantum chemical calculations:

The calculations on $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$, $[\text{Si}_9]^{4-}$ and $[\text{W}(\text{CO})_4]^{2-}$ were performed using Orca 5.0.3 employing a ZORA-D3(BJ)-B3LYP/ma-ZORA-def2-TZVP (Si, C, O), ZORA-D3(BJ)-B3LYP/Sarc-ZORA-TZVP (W) level of theory using a CPCM model of ammonia.^[32,35–40] For $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ also a ZORA-D3(BJ)-PBE0/ma-ZORA-def2-TZVP (Si, C, O), ZORA-D3(BJ)-PBE0/Sarc-ZORA-TZVP (W) level of theory (CPCM: ammonia) calculation was performed.^[41] The NPA charges were calculated using NBO 7.0.9^[34] and the QTAIM charges using AIMAll.^[43] The Laplacian was plotted using Multiwfn^[44] and the line graph was made in Origin 9.9.0.225.^[53] The molecular orbitals were plotted in orca plot and visualized using VMD.^[38,54]

7.6 Acknowledgements

Funded in the RTG2620 by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 426795949. We would like to thank Dr. Florian Kleemiß for the assistance with the theoretical calculations and Dr. Stefanie Gärtner for very valuable discussions. Open Access funding enabled and organized by Projekt DEAL.

7.7 Conflict of Interest

The authors declare no conflict of interest.

7.8 Supporting information

7.8.1 X-Ray Diffraction

Table 7.1: Crystallographic data for [(K,Rb)@([2.2.2]crypt)]₂(K,Rb)₄[Si₉W(CO)₄]·13.4 NH₃

CCDC number	CCDC-2260797
Compound	[(K,Rb)@([2.2.2]crypt)] ₂ (K,Rb) ₄ [Si ₉ W(CO) ₄]·13.4 NH ₃
Empirical formulat	C ₄₀ H _{107.72} K _{3.6} N _{17.38} O ₁₆ Rb _{2.4} Si ₉ W
Formula weight	1870.72
Temperature / K	123.00(10)
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
a / Å	11.48390(10)
b / Å	19.7383(2)
c / Å	19.8983(2)
α / °	112.5760(10)
β / °	97.4210(10)
γ / °	95.3760(10)
Volume / Å ³	4079.01(7)
Z	2
ρ_{calc} / g cm ⁻³	1.523
μ / mm ⁻¹	7.791
F(000)	1909.0
Crystal size / mm ³	0.14 × 0.12 × 0.09
Radiation	Cu K α (λ = 1.54184 Å)
2 Θ range for data collection / °	4.89 to 150.53
Index ranges	-14 ≤ h ≤ 14, -24 ≤ k ≤ 24, -21 ≤ l ≤ 24
Reflections collected	72249
Independent reflections	16465 [<i>R</i> _{int} = 0.0555, <i>R</i> _{sigma} = 0.0468]
Data / restraints / parameters	16465 / 0 / 824
Goodness-of-fit on F ²	1.055
Final R indexes (<i>I</i> ≥ 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0482, <i>wR</i> ₂ = 0.1263
Final R indexes (all data)	<i>R</i> ₁ = 0.0596, <i>wR</i> ₂ = 0.1325
Largest diff. peak / hole / e Å ⁻³	1.44/-1.61

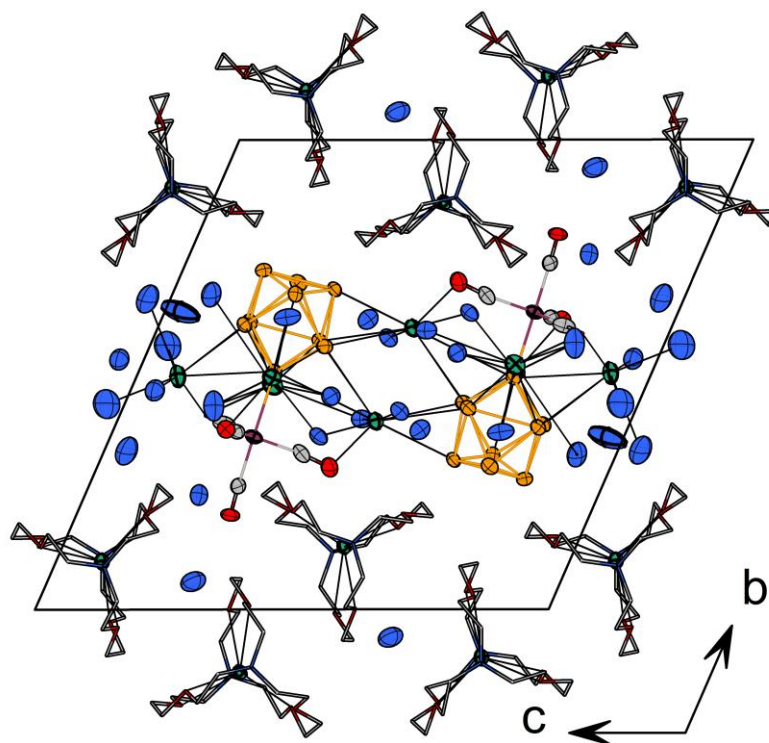


Figure 7.7: Unit cell of $[(K,Rb)@([2.2.2]crypt)]_2(K,Rb)_4[Si_9W(CO)_4] \cdot 13.4 NH_3$ along the crystallographic c-axis shows dimers of $[((K,Rb)[Si_9W(CO)_4]_2)]^{6-} \cdot 6 NH_3$ interconnected by ion-dipole interaction by ammonia molecules to form 2D layers.

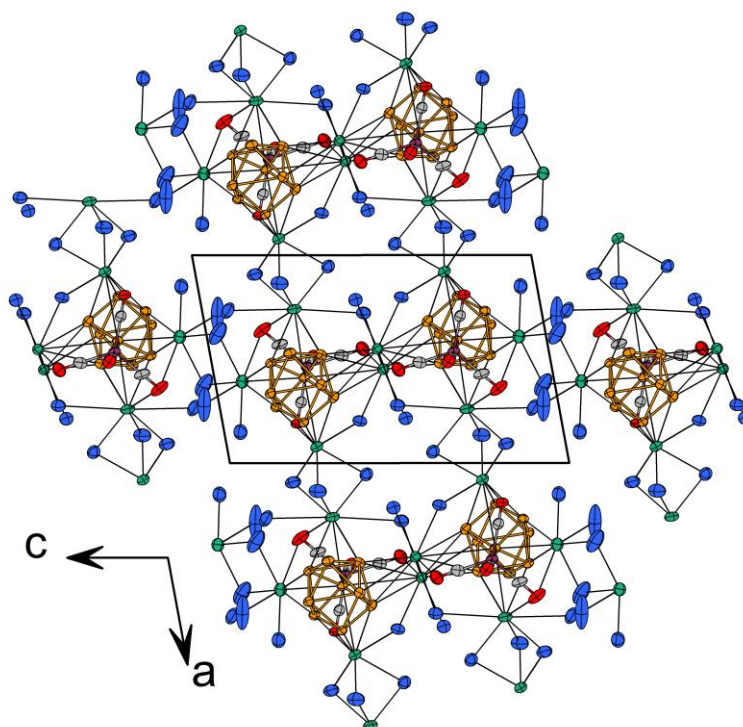
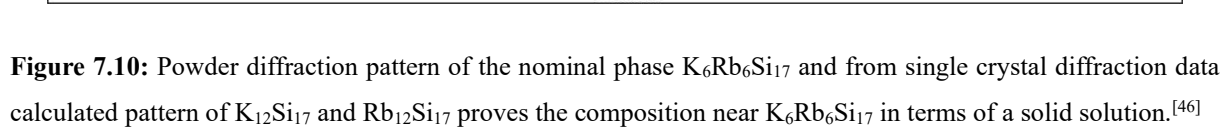
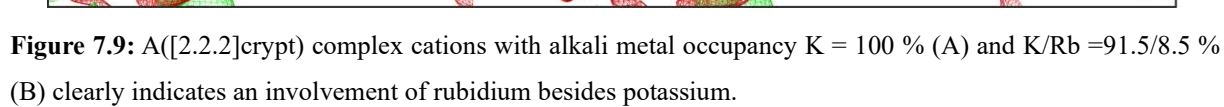


Figure 7.8: Unit cell of $[(K,Rb)@([2.2.2]crypt)]_2(K,Rb)_4[Si_9W(CO)_4] \cdot 13.4 NH_3$ along the crystallographic b-axis shows the top view on the 2D layers formed by the $[((K,Rb)[Si_9W(CO)_4]_2)]^{6-} \cdot 6 NH_3$ dimers, cations and ammonia molecules. The $A@([2.2.2]crypt)$ are omitted for clarity.



7.8.2 Theoretical Calculations

Table 7.2: Coordinates (Å), NPA and QTAIM charges of the optimized $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ on a B3LYP/ma-ZORA-def2-TZVP (Si, C, O) B3LYP/Sarc-ZORA-TZVP (W) level.

Atom No.	X	Y	Z	NPA charge	QTAIM charge
W1	3.61734	1.46102	12.99463	-0.64258	1.18628
Si2	3.79648	4.11755	13.33052	-0.37992	-0.22829
Si3	5.9055	7.36527	14.12798	-0.52925	-0.51872
Si4	5.0151	5.23884	15.1857	-0.27710	-0.32545
Si5	2.24143	5.59004	14.61695	-0.27331	-0.32235
Si6	3.76102	7.39279	15.54427	-0.52612	-0.51792
Si7	4.51213	7.79211	12.02511	-0.52600	-0.51673
Si8	2.84453	5.89048	11.84603	-0.27133	-0.32187
Si9	5.61037	5.54676	12.39189	-0.27679	-0.32653
Si10	2.36901	7.81919	13.43274	-0.52663	-0.51674
O11	6.70071	1.50006	13.73253	-0.71323	-1.31785
O12	3.53821	-1.68102	12.71825	-0.69946	-1.31074
O13	2.7038	1.96627	9.99463	-0.71844	-1.31872
O14	1.52669	1.39969	15.38301	-0.71515	-1.31846
C15	3.56495	-0.49002	12.813	0.36654	0.48612
C16	5.53818	1.49714	13.45352	0.25068	0.41454
C17	3.04735	1.79538	11.12942	0.22196	0.37811
C18	2.31578	1.44608	14.48437	0.23615	0.39655

Table 7.3: Coordinates (Å), NPA and QTAIM charges of the optimized Si_9^{4-} on a B3LYP/ma-ZORA-def2-TZVP (Si, C, O) B3LYP/Sarc-ZORA-TZVP (W) level.

Atom No.	X	Y	Z	NPA charge	QTAIM charge
Si1	3.79648	4.11755	13.33052	-0.58897	-0.52927
Si2	5.9055	7.36527	14.12798	-0.52058	-0.50404
Si3	5.0151	5.23884	15.1857	-0.33463	-0.36593
Si4	2.24143	5.59004	14.61695	-0.33216	-0.36359
Si5	3.76102	7.39279	15.54427	-0.51989	-0.50447
Si6	4.51213	7.79211	12.02511	-0.52022	-0.50325
Si7	2.84453	5.89048	11.84603	-0.32950	-0.36157
Si8	5.61037	5.54676	12.39189	-0.33381	-0.36506
Si9	2.36901	7.81919	13.43274	-0.52025	-0.50345

7 The First Tungsten Functionalized Silicon Zintl Cluster

Table 7.4: Coordinates (Å), NPA and QTAIM charges of the optimized $[\text{W}(\text{CO})_4]^{2-}$ on a B3LYP/ma-ZORA-def2-TZVP (Si, C, O) B3LYP/Sarc-ZORA-TZVP (W) level.

Atom No.	X	Y	Z	NPA charge	QTAIM charge
W1	3.61734	1.46102	12.99463	-0.28766	1.24927
O11	6.70071	1.50006	13.73253	-0.64622	-1.26674
O12	3.53821	-1.68102	12.71825	-0.66559	-1.26450
O13	2.7038	1.96627	9.99463	-0.64955	-1.26534
O14	1.52669	1.39969	15.38301	-0.64858	-1.26643
C15	3.56495	-0.49002	12.813	0.35244	0.56199
C16	5.53818	1.49714	13.45352	0.18757	0.42552
C17	3.04735	1.79538	11.12942	0.17320	0.40568
C18	2.31578	1.44608	14.48437	0.18438	0.42089

Table 7.5: Coordinates (Å) of the optimized $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ on a PBE0/ma-ZORA-def2-TZVP (Si, C, O) PBE0/Sarc-ZORA-TZVP (W) level.

Atom No.	X	Y	Z
W1	3.62977	1.4853	12.99803
Si2	3.81154	4.12169	13.32411
Si3	5.80434	7.43504	14.11144
Si4	4.95779	5.35562	15.06869
Si5	2.37109	5.64623	14.54804
Si6	3.74714	7.42753	15.47654
Si7	4.46321	7.81221	12.07719
Si8	2.91701	5.93261	11.97587
Si9	5.50055	5.64626	12.48416
Si10	2.40351	7.8141	13.44059
O11	6.68495	1.26066	13.74407
O12	3.47332	-1.62613	12.68337
O13	2.75076	1.88307	9.98548
O14	1.59058	1.32428	15.40478
C15	3.52964	-0.44516	12.79444
C16	5.53522	1.38312	13.46464
C17	3.08157	1.76891	11.12352
C18	2.35659	1.4223	14.49956

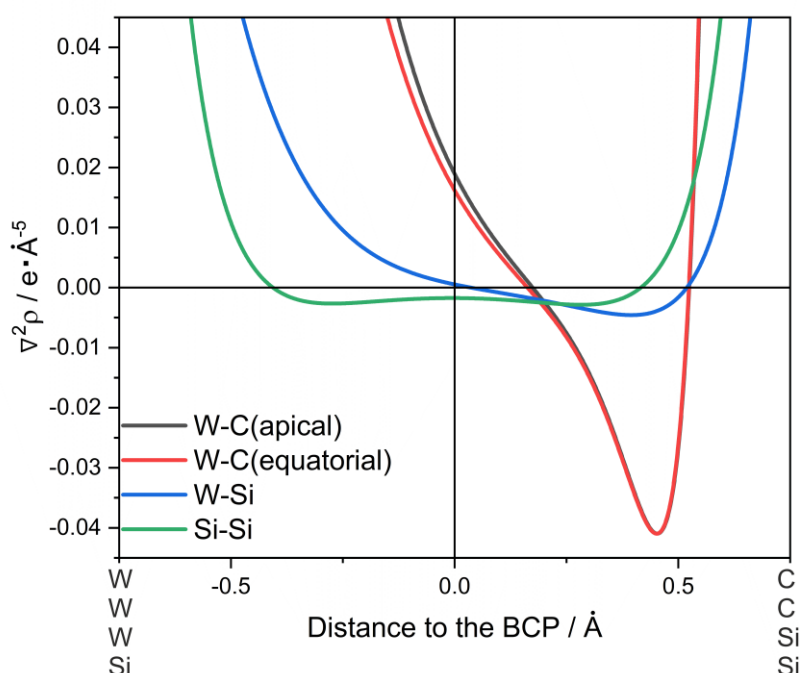


Figure 7.11: Representative Laplacians of the bonds in $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$. The W-Si bond can according to the criteria of Lepetit et al. be described as dative bond, the W-C bonds as donor-acceptor bonds and the Si-Si bond as covalent bond. ^[42b]

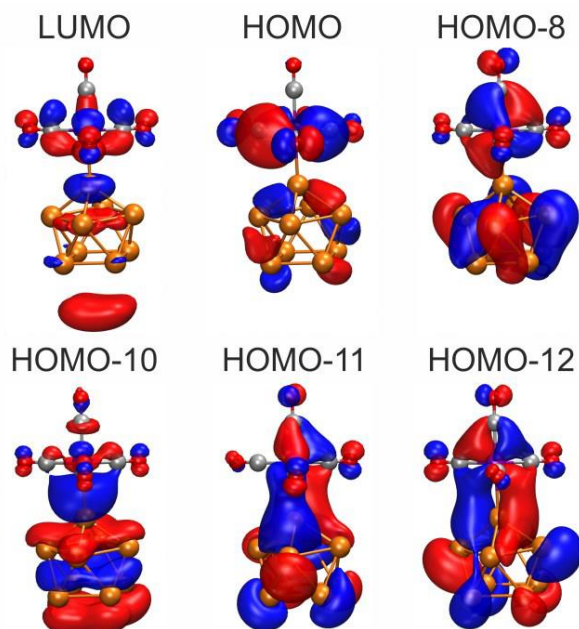


Figure 7.12: Relevant molecular orbitals of $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ showing the LUMO (0.474 eV), HOMO (-2.510 eV), HOMO-8 (-3.454 eV), HOMO-10 (-3.760 eV), HOMO-11 (-3.966 eV) and HOMO-12 (-3.970 eV). The molecular orbitals were generated using orca plot and rendered using VMD.^[38,54,55] The Si-W bonding is represented by the molecular orbitals HOMO-10 (-3.760 eV) and the degenerate orbitals HOMO-11 (-3.966 eV) and HOMO-12 (-3.970 eV). The HOMO-10 can be interpreted as a σ -bond and the HOMO-11/12 show delocalized π -systems along the W-Si bond.

7.8.3 NMR Investigations

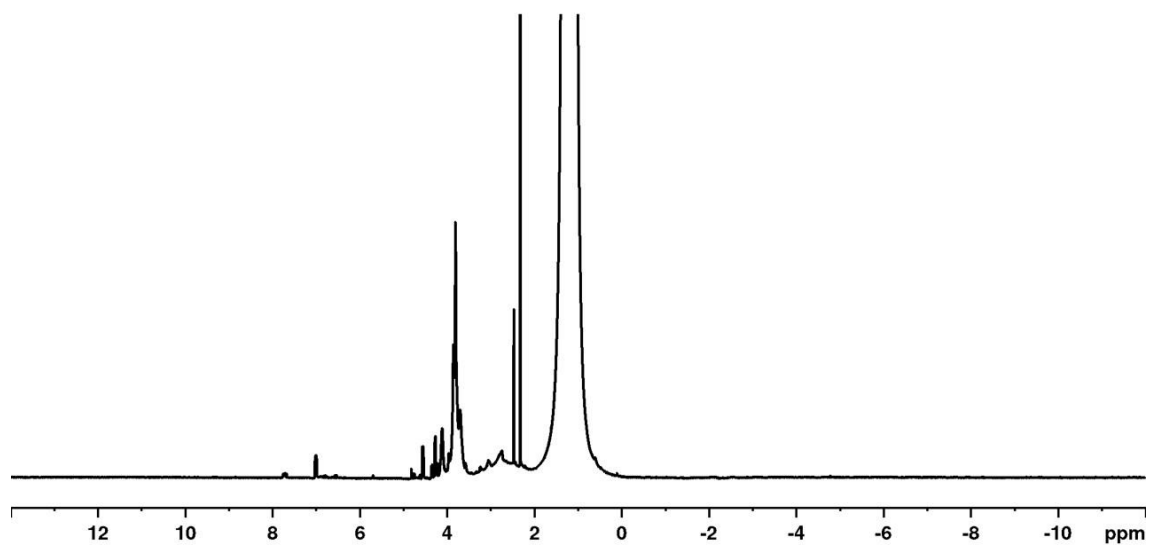


Figure 7.13: 600 MHz- ^1H -NMR Spectrum (no presaturation, “zg”) of $[\text{W}(\text{CO})_4(\text{tmeda})] + \text{K}_6\text{Rb}_6\text{Si}_{17} + [2.2.2]\text{crypt } 1:1:2$ in liquid NH_3 at 203 K.

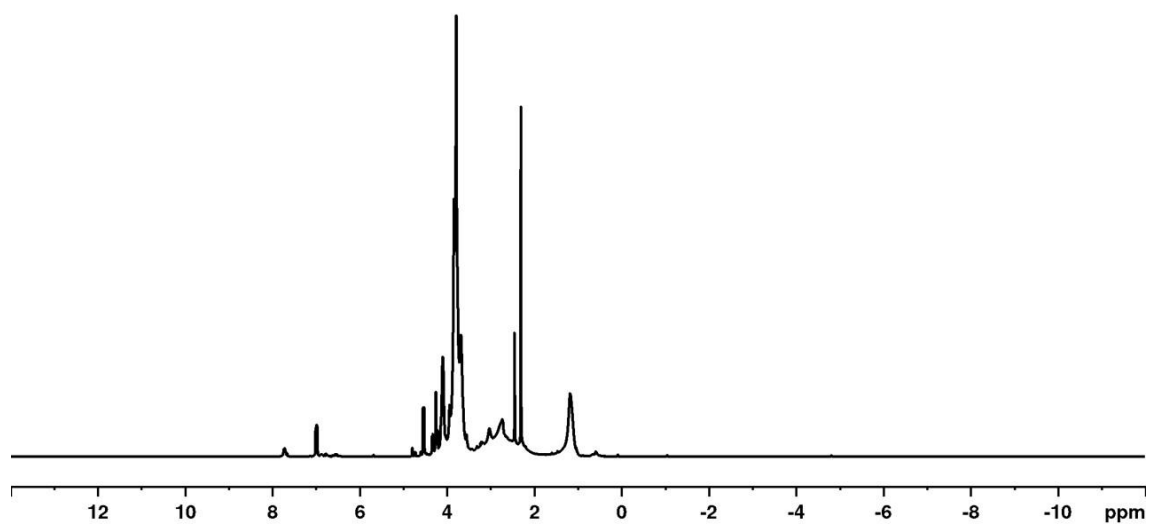


Figure 7.14: 600 MHz- ^1H -NMR Spectrum (with presaturation of the ammonia signal, “zgpgpr”) of $[\text{W}(\text{CO})_4(\text{tmeda})] + \text{K}_6\text{Rb}_6\text{Si}_{17} + [2.2.2]\text{crypt } 1:1:2$ in liquid NH_3 at 203 K. The dominating ammonia signal could be very well suppressed.

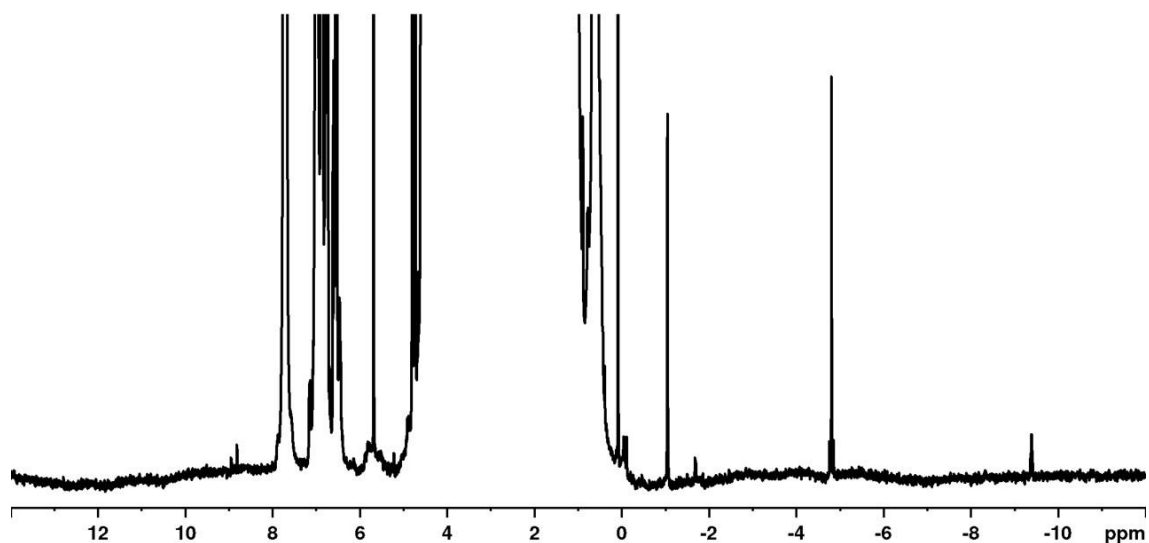


Figure 7.15: 600 MHz- ^1H -NMR Spectrum (with presaturation of the ammonia signal, "zgpgpr") of $[\text{W}(\text{CO})_4(\text{tmeda})] + \text{K}_6\text{Rb}_6\text{Si}_{17} + [2.2.2]\text{crypt}$ 1:1:2 in liquid NH_3 at 203 K. Enlarged version.

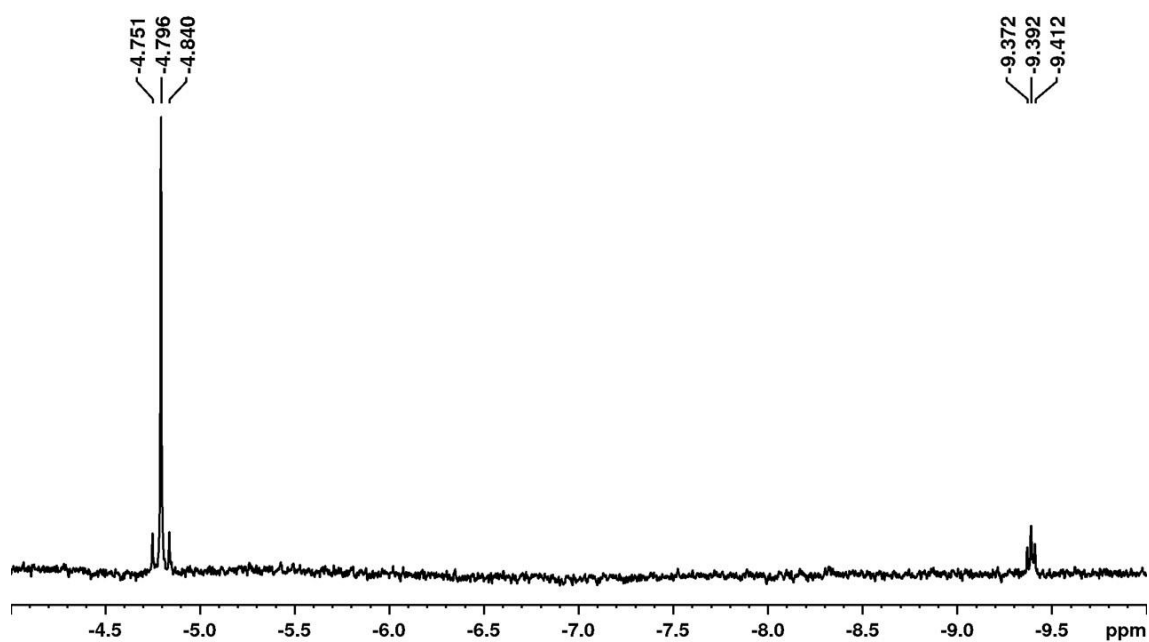


Figure 7.16: 600 MHz- ^1H -NMR Spectrum (with presaturation of the ammonia signal, "zgpgpr") of $[\text{W}(\text{CO})_4(\text{tmeda})] + \text{K}_6\text{Rb}_6\text{Si}_{17} + \text{crypt}$ 1:1:2 in liquid NH_3 at 203 K. Showing the supposed ^1H -Signal with ^{183}W coupling and the known signal of $[\text{Si}_4\text{H}]^{3-}$ next to each other.

7 The First Tungsten Functionalized Silicon Zintl Cluster

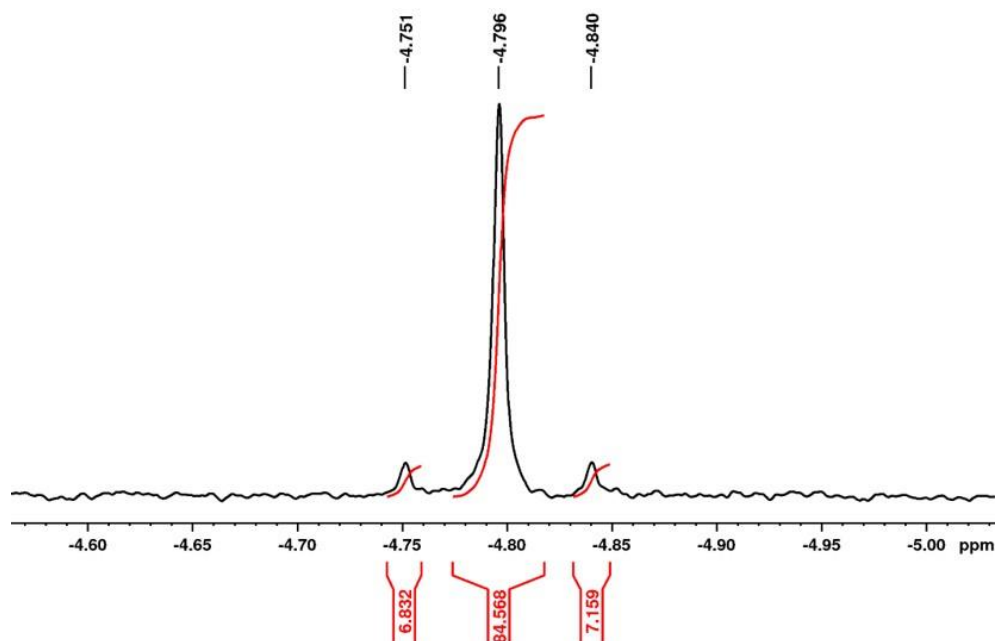


Figure 7.17: 600 MHz- ^1H -NMR Spectrum (with presaturation of the ammonia signal, “zggppr”) of $[\text{W}(\text{CO})_4(\text{tmeda})] + \text{K}_6\text{Rb}_6\text{Si}_{17} + [2.2.2]\text{crypt } 1:1:2$ in liquid NH_3 at 203 K. Showing the supposed ^1H -Signal with ^{183}W coupling. The $J(^1\text{H}-^{183}\text{W})$ was determined to be 53.3 Hz. Integrals are consistent with the natural abundance of ^{183}W of 14.3%. The baseline was corrected using cubic splines (“sab”).

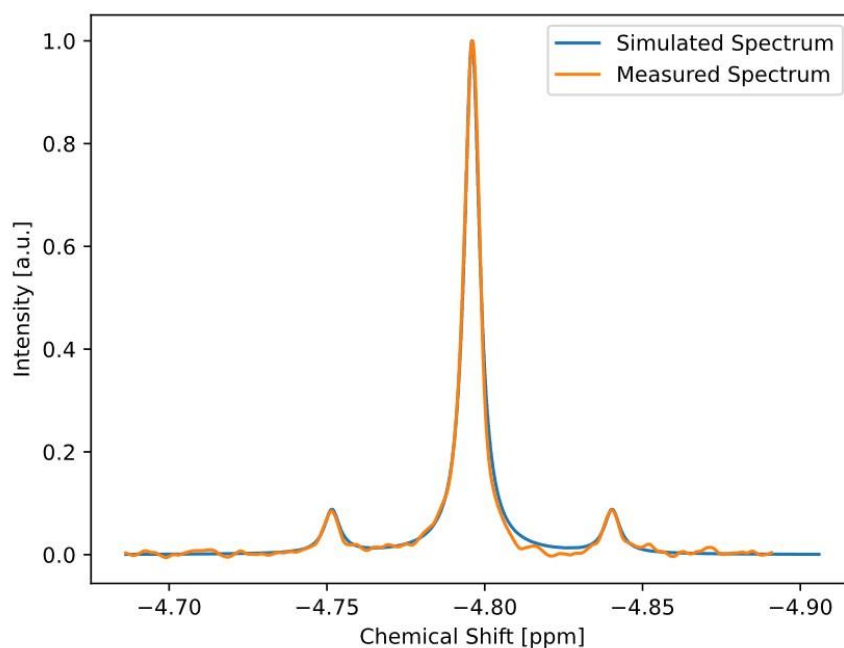


Figure 7.18: Overlay of the NMR-signal shown in Figure 7.17 (orange line) with the multiplet simulated with gNMR. Simulation parameters: $\delta_{\text{IH}} = -4.796$ ppm, $J(^1\text{H}-^{183}\text{W}) = 53.3$ Hz, linewidth = 3.594 Hz. The good overlap corroborates the assignment to a $^1\text{H}-^{183}\text{W}$ coupling. The spectrum was simulated using gNMR 5.0.6.0, the overlay figure was created with self-written Python scripts using the matplotlib module.

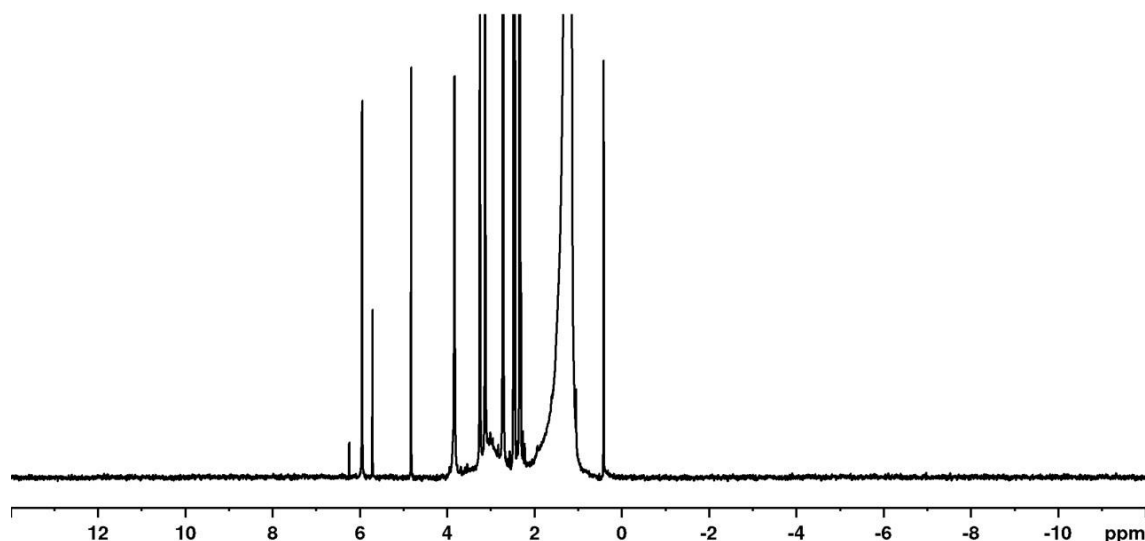


Figure 7.19: 600 MHz- ^1H -NMR Spectrum (with presaturation of the ammonia signal, “zgpgpr”) of $[\text{W}(\text{CO})_4(\text{tmeda})]$ in liquid NH_3 at 203 K. Recorded with 64 transients There are notably no signals upfield of 0 ppm.

7.9 References

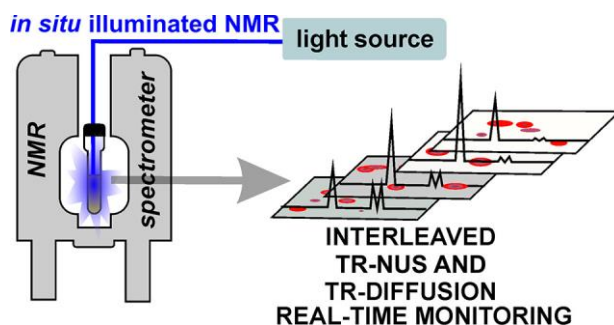
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8 DEEPER INSIGHT INTO PHOTOPOLYMERIZATION: THE SYNERGY OF TIME-RESOLVED NONUNIFORM SAMPLING AND DIFFUSION NMR



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J. Am. Chem. Soc., **2022**, *144*, 13938–13945

DOI: 10.1021/jacs.2c05944

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Kristina Kristinaityte, Adam Mames and Mariusz Pietrzak carried out synthesis and characterization of compounds and reaction monitoring by NMR spectroscopy **Franz F. Westermair** and Kristina Kristinaityte together conducted preliminary experiments of the project. Wagner Silva assisted in the implementation of the TR-acquisition scheme and NMR measurements. Ruth M. Gschwind supervised the initial investigations conducted at the University of Regensburg. Tomasz Ratajczyk and Mateusz Urbańczyk supervised the project. The manuscript was prepared by Kristina Kristinaityte with contributions from all authors.

8 Deeper Insight into Photopolymerization: TR–NUS and Diffusion NMR

8.1 Abstract

The comprehensive real-time in situ monitoring of chemical processes is a crucial requirement for the in-depth understanding of these processes. This monitoring facilitates an efficient design of chemicals and materials with the precise properties that are desired. This work presents the simultaneous utilization and synergy of two novel time-resolved NMR methods, i.e., time-resolved diffusion NMR and time-resolved nonuniform sampling. The first method allows the average diffusion coefficient of the products to be followed, while the second method enables the particular products to be monitored. Additionally, the average mass of the system is calculated with excellent resolution using both techniques. Employing both methods at the same time and comparing their results leads to the unequivocal validation of the assignment in the second method. Importantly, such validation is possible only via the simultaneous combination of both approaches. While the presented methodology was utilized for photopolymerization, it can also be employed for any other polymerization process, complexation, or, in general, chemical reactions in which the evolution of mass in time is of importance.

8.2 Introduction

The design of novel functional materials requires a comprehensive insight into the chemical reactions or processes in which these materials are synthesized, fabricated, or functionalized. The above statement is particularly valid in the case of polymerization processes, as tuning the polymerization toward the development of products would be significantly facilitated by the knowledge of what is happening during the reaction.^[1–3] One of the most important variants of polymerization is photopolymerization, which is even more challenging for the investigator, as the illumination conditions are often difficult to control. This often causes problems with the reproducibility of the data on different setups.^[4–7] Thus, the knowledge of the fate of the photoreaction as photopolymerization progresses would be of particular value.

One of the most comprehensive analytical methods is NMR spectroscopy, which can deliver in-depth insight into molecular structures.

In recent years, we have witnessed a rapid growth of new NMR-based reaction monitoring methods.^[8–16] In particular, two main concepts have recently made significant progress: ultrafast (UF)^[17,18] and time-resolved (TR) methods. Both methods arose concomitantly, and they possess somewhat orthogonal strengths and weaknesses.^[19] While the UF method allows much faster sampling leading to much better time resolution, the TR methods are more stable in out-of-equilibrium conditions. Therefore, the TR is a more optimal choice for photopolymerization monitoring, where the light source might cause additional disturbances in the system.

Time-resolved NMR was first introduced by Mayzel et al.^[20] for multidimensional nonuniform sampled NMR (TR–NUS). The concept of this method is based on a long nonuniform sampling schedule that covers the entire reaction time. Afterward, the data are separated into overlapping subsets from which spectra are reconstructed. As mentioned earlier, the overlapping subsets guarantee a high temporal resolution, while a single spectrum is time-averaged according to the size of the subset from which it was reconstructed. This method has been utilized widely to study many interesting systems.^[21–25] Interestingly, the method can be combined with an interleaved (IL) acquisition, where many different TRNUS experiments are acquired in a parallel mode by switching between pulse sequences after each registered NUS point.^[26]

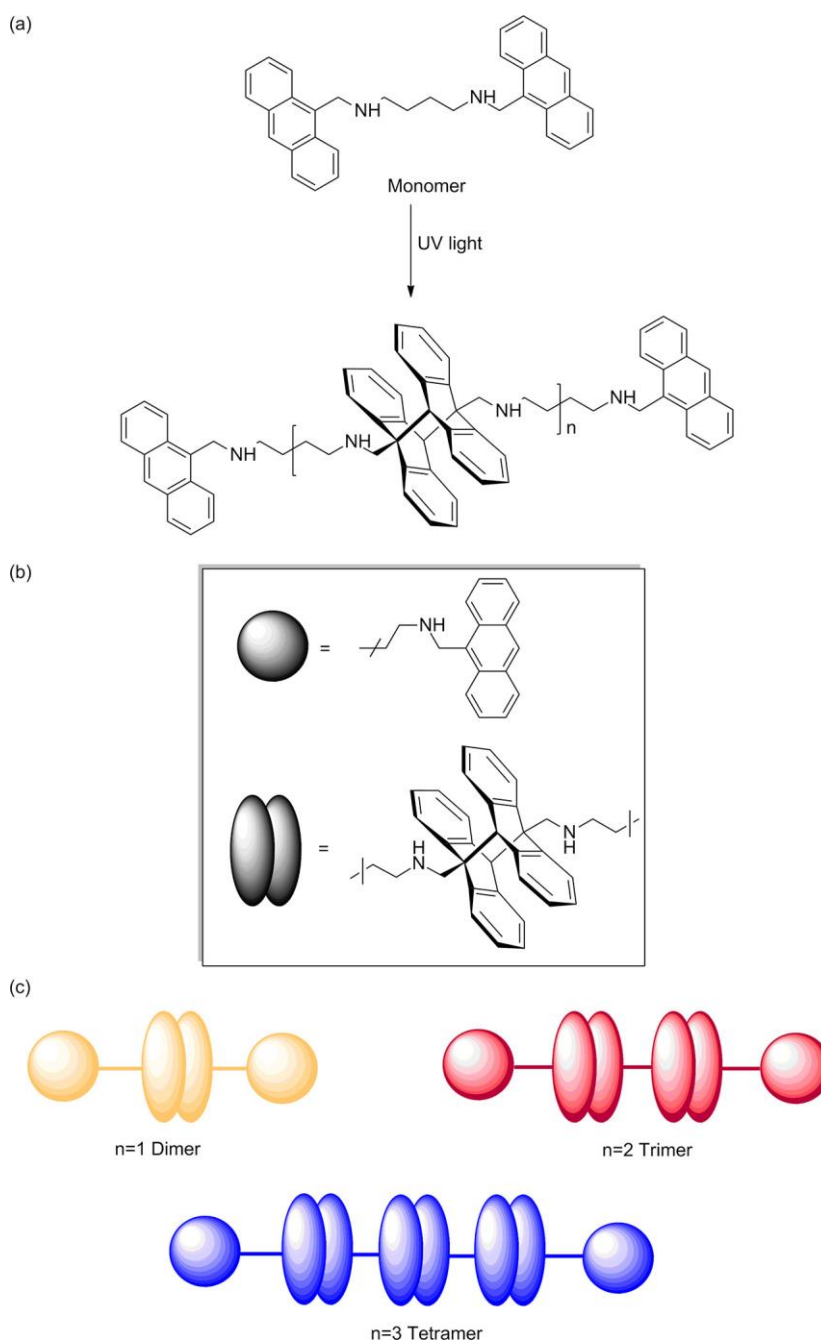


Figure 8.1: (a) General scheme of photopolymerization of H2banthbn. (b) Schematic representation of building blocks of n -mers. (c) Observed soluble products of the reaction.

A very useful progeny of TR-NUS is time-resolved diffusion ordered spectroscopy (TR-DOSY).^[27,28] This method combines the concept of the acquisition of TR-NUS data with the permuted DOSY (p-DOSY) approach^[29] by substituting the random sampling of the indirect dimension with randomly generated pulsed-field gradient strength in pulsed gradient stimulated echo (PGSTE) experiments. This method has recently been used by Fillbrook et al.^[30] to study the photoinduced electron/energy transfer reversible addition–fragmentation chain transfer (PET-RAFT) polymerization of methyl acrylate. This approach allowed the fate of the reaction and the evolution of the average molecular mass of the reactants to be followed. While the TR-NUS is related to the structure, the TR-DOSY offers information on how this structure behaves in time. A combination of analytical methods can often provide a

8 Deeper Insight into Photopolymerization: TR–NUS and Diffusion NMR

correlation between parameters delivered by these methods and information that cannot be obtained when employed separately.

Interestingly, the TR-NUS and TR-DOSY methods have never been used together to study a particular system. Here, we combined these methods into one tool. We demonstrated that this combination is an excellent methodology for the comprehensive monitoring of photopolymerization.

To avoid utilizing an overly simplified model as a system for monitoring, a photopolymerization of bis-anthracene-based systems was chosen. The system is very interesting, as photopolymerization of aromatic sheets, including anthracenes, is being employed as building blocks for the design of various photofunctional materials.^[31] Therefore, an in-depth understanding of the photopolymerization of this type of system is crucial.

In this work, we demonstrate the feasibility and advantages of the interleaved acquisition of both methods to study the photopolymerization of bis-anthracene derivatives, specifically *N,N*-bis(anthracen-9-ylmethyl)butane-1,4-diamine (H2banthbn).^[32–36]

8.3 Experimental Section

8.3.1 UV Illumination Setup

UV illumination was performed by a 365 nm (9 nm fwhm) fiber-coupled LED (M365FP1) purchased from Thorlabs. The maximum power of 15.5 mW at the end of the optical fiber was measured at a 1400 mA maximum current, using 1 m of FT400EMT Ø400 µm core, 0.39 NA multimode fiber. During all

experiments, 3 m length FT1000UMT (Thorlabs) Ø1000 µm core, 0.39 NA multimode fiber was used. The optical fiber tip was polished using sandpaper to illuminate the sample more homogeneously. The LED current was set to 500 mA using a T-cube LED driver (LEDD1B), also bought from Thorlabs. The optical fiber was fixed to the coaxial insert and placed in the Wilmad screw-cap NMR tube through the septum to avoid contact with oxygen after deoxygenating the sample. A 420 µL amount of the solution was chosen as optimal for the full illumination of the sample.

8.3.2 Sample Synthesis and Preparation

The synthesis of H2banthbn was carried out according to the literature protocols with some modifications.^[37,38] Antraldehyde (1 g, 4.85 mmol) was dissolved in fresh distilled tetrahydrofuran (THF)/methanol (v/v = 30 mL/20 mL) mixed solvents under an inert atmosphere. Butane-1,4-diamine (213 mg, 2.42 mmol) in 10 mL of methanol was added dropwise. The mixture was stirred for 24 h at room temperature. The resulting precipitate was filtered and washed with cold methanol to remove excess antraldehyde. The crude imine was dissolved in fresh distilled dichloromethane (DCM)/methanol (v/v = 60 mL/20 mL) mixed solvents, and sodium borohydride (189 mg, 5 mmol) was added. After stirring at room temperature for 12 h, the yellow crystals were filtered. The product was purified by recrystallization in THF/pentane. Obtained: 998 mg, yield = 88% of yellow crystals.

¹H NMR (400 MHz, CDCl₃): δ ppm 8.39 (s, 1H), 8.35–8.29 (m, 2H), 8.02–7.98 (m, 2H), 7.48 (ddd, *J* = 15.5, 8.5, 1.3 Hz, 4H), 4.71 (s, 2H), 2.90 (s, 2H), 1.66 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ ppm 131.9, 131.5, 130.2, 129.1, 127.1, 126.0, 124.9, 124.1, 50.4, 45.8, 28.0.

HRMS: *m/z* calcd for C₃₄H₃₂N₂ [M + H]⁺ 469.2644, obtained 469.2643.

For the measurements, the 3 mg (6.4 µmol, *c* = 4.8 mM) of the H2banthbn was dissolved in 0.75 mL of deuterated dichloromethane (99.6% D, ampules purchased from Deutero GmbH). Then, 420 µL of the solution was poured

into a Wilmad screw-cap NMR tube. Subsequently, the sample was degassed through three freeze–pump–thaw cycles to remove oxygen.

8.3.3 NMR

All NMR experiments were performed on a Bruker AVANCE II 300 MHz spectrometer equipped with a BBI 300 MHz W1 5 mm z-gradient probe with a BVT-3000 temperature controller. The spectrometer was controlled via the TOPSPIN 3.2 program.

The acquisition protocol was based on the TReNDS^[26] acquisition script modified by substituting the standard ¹H experiment with the stebpgp1s1d pulse sequence. The illumination was turned on during the entire acquisition. All experiments were performed with the temperature controller set to 298 K.

8.3.3.1 Time-Resolved Diffusion NMR

The stebpgp1s1d pulse sequence was used as a base for the acquisition of the TR-DOSY experiment. The acquisition parameters for interleaved acquisition were as follows:

Δ : 50 ms, δ : 3 ms, pulse length: 9.5 μ s, relaxation delay: 2.5 s, number of scans: 8. For the noninterleaved data sets, the parameters were slightly different: Δ : 50 ms, δ : 3 ms, pulse length: 9.5 μ s, relaxation delay: 3 s, number of scans: 4.

The pulsed-field gradient strength for all data sets was set as a shuffled logarithmically spaced array of 32 values from 5.63 to 35.47 G/cm. The range was optimized for the diffusion coefficient in the system. The resulting gradient array was repeated 17 times to cover the reaction's progress. This will guarantee that every frame used in the data processing will contain the same set of gradients.

8.3.4 Time-Resolved Nonuniform Sampling

The TR-NUS acquisition was based on the hsqcgpph pulse sequence. The acquisition parameters were as follows: relaxation delay: 2.5 s, number of scans: 32, indirect dimension spectral width: 8 ppm, centered at 127 ppm, maximum evolution points in indirect dimension: 64. The sampling schedule was generated using a sampling generator in the MDDNMR package^[39] with shuffle mode and the relaxation weighting parameter T2 set to 0.07. The effect of the choice of the nonuniform sampling scheme type (e.g., Poisson-gap or random) in the case of spectra of high sparsity (as in this work) should be negligible.^[40]

8.3.5 Data Analysis

The TR-NUS spectra were reconstructed by the TReNDS program using the IRLS algorithm^[41] with virtual echo.^[42] The frame size was set to 54 points with a 52-point overlap. We have applied exponential weighting for direct (5 Hz) and indirect (1 Hz) dimensions. To save time and memory, the spectrum was trimmed in the direct dimension to the region 9–6 ppm. Further, the analysis was performed in the Python 3.8 environment using the following packages: nmrglue,^[43] jupyter-lab,^[44] NumPy,^[45] SciPy,^[46] and Matplotlib.^[47]

The diffusion data were imported using nmrglue. Each spectrum was processed the same way: zero-filled to 131072 ($128 \cdot 2^{10}$ points, weighted exponentially by 2 Hz, and Fourier transformed. After that, the region 9–6 ppm (see the yellow rectangle in Figure 8.2a) was integrated and stored. The integrals were divided into subsets of 32 points that overlapped by 31 points. Each subset was used to fit the diffusion coefficient using the monoexponential model:

$$S(G) = Ie^{-D\delta^2 G^2 \gamma^2 (\Delta - \delta/3)} \quad (1)$$

8 Deeper Insight into Photopolymerization: TR–NUS and Diffusion NMR

where S is the integral of the peak intensity, G is the pulse field gradient strength, δ is the time of the G , Δ is diffusion mixing time, and γ is the gyromagnetic constant of ^1H .

In theory, by applying the inverse Laplace transform (ILT),^[48,49] we should be able to track individual reactant evolution in time. Unfortunately, the ILT could not distinguish separate peaks. Therefore, we have decided to use single-exponential fitting only (shown in Figure 8.2b).

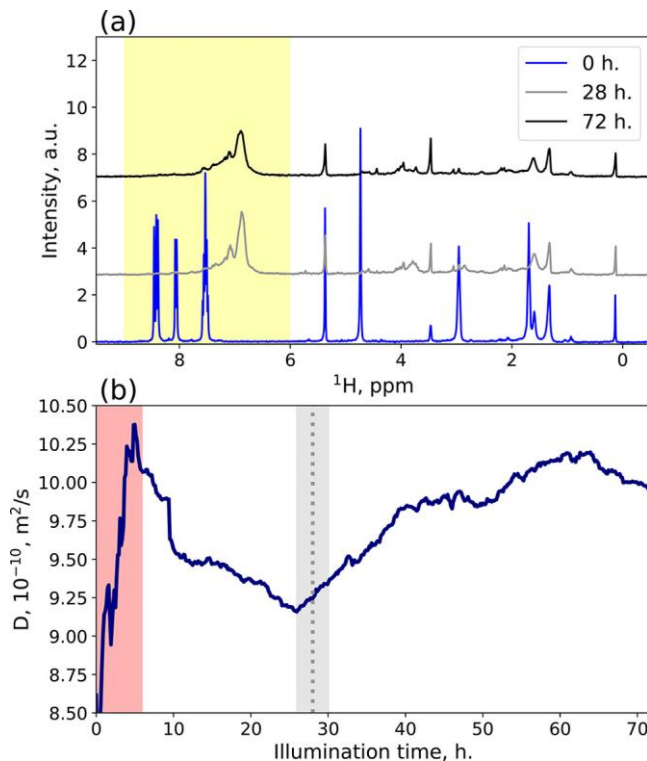


Figure 8.2: (a) ^1H spectra taken from the PGSTE experiment at the gradient strength equal to 7.32 G/cm. The blue line represents the start of the reaction, the gray line the spectrum closest to the moment when the average mass was the highest, and the black line the end of the reaction. The area highlighted in yellow shows the analysis region used for the diffusion fitting. (b) Average diffusion coefficient calculated from the highlighted area in (a). The red highlighted square shows the disturbance in the diffusion coefficient caused by heating of the sample from the switched-on light source. The dotted vertical line indicates the time of the middle spectrum from the (a) pane, while the gray area represents the time-averaging of a single frame.

After reconstruction, TR-NUS data were imported using nmrglue, and 11 regions were selected for integration (see boxes in Figure 8.3a–c). The regions were gathered into four groups, according to the same time-dependence profile. The groups were then assigned to the possible n -mers, and the signals' intensity from each group was summed up. The resulting time dependence of each reactant's peak intensity is shown in Figure 8.3d. The next step was to recalculate the average mass of the system. To do this, each time-dependent profile of reactant concentration was smoothed by applying the Savitzky–Golay filter,^[50] and then, for each frame, the intensities were normalized by the integral of the whole region. With this approach, we calculated the average mass of the system as a function of time ($\langle M \rangle_{\text{HSQC}}(t)$) using a simple equation:

$$\langle M \rangle_{\text{HSQC}}(t) = \sum_{\text{reactant}} I_{\text{reactant}}(t) \cdot M_{\text{reactant}} \quad (2)$$

where $I_{\text{reactant}}(t)$ is the normalized integral of each reactant, while M_{reactant} is its mass.

The diffusion coefficients (D) can be transformed into molecular mass $\langle M \rangle_D$ by following this equation:^[51]

$$D = k\langle M \rangle_D^\alpha \quad (3)$$

where k and α are empirical scaling coefficients. We calculated those coefficients by substituting $\langle M \rangle_D$ in eq 3 with $\langle M \rangle_{\text{HSQC}}$ and fitting the equation for $t > 6$ h (to avoid the disturbances from the switched-on light source). The resulting comparison between average molecular mass values calculated from both methods is presented in Figure 8.4. Additionally, the two additional TR-DOSY experiments were analyzed, to confirm the correctness of the approach. The first one was following the same reaction as the interleaved one, and the second one was monitoring the dimerization of anthracene in identical conditions. From those experiments, we determined diffusion coefficients of anthracene, dimer-anthracene, and the dimer of H2banthbn. With three diffusion coefficients of three molecules of known masses, we have calculated the parameters k and α from eq 3 and established the average mass of H2banthbn photopolymerization (as shown in Figure S1).

8.4 Results and Discussion

We have studied the photopolymerization of H2banthbn. The scheme of the reaction is shown in Figure 8.1. Photodimerization of amine-based anthracene derivatives is well known in the literature, and head/tail isomers of dimers are the preferred products.^[52–54]

We started our analysis with an approach similar to the one suggested by Fillbrook et al.^[30] We have monitored the reaction using the TR-DOSY method. After the processing, we obtained our system's average diffusion coefficient (see Figure S1).

For the reaction analysis, it is more convenient to use average mass than diffusion coefficients. We addressed this issue with different approaches for interleaved and sequential acquisitions. We have used the masses and diffusion coefficients of anthracene, the anthracene dimer, and H2banthbn for the calibration curve (the result is shown in Figure S1). The resulting time dependence of the average mass revealed interesting behavior. It steadily rose for the first 28 h until it achieved the highest average mass value: 1476 g/mol. Then the mass started to decrease slowly. Such behavior suggests that in the first 28 h of the reaction there is a mixture of products ranging from dimer to tetramer (the highest average mass is slightly larger than the mass of the trimer). After that, the higher mass polymers formed that precipitated from the solution (reducing the average mass of the reaction mixture). However, as the inverse Laplace transform analysis cannot distinguish separate forms in this data set, one cannot monitor the particular products.

We have combined TR-NUS HSQC and TR-DOSY into a single interleaved acquisition to overcome this limitation. The results from interleaved TR-DOSY were in significant agreement with the previous measurement. This time the TR-NUS HSQC experiment supported the data interpretation. In the TR-NUS HSQC, we have analyzed all the peaks in the region 9.0–6.0 ppm (see Figure 8.3). We found out that the time dependency of those peaks forms four distinct groups. Each group is highlighted with a different color in Figure 8.3. The first group's intensity was constantly decaying during the reaction. These regions were assigned as a monomer (black; $^{13}\text{C}/^1\text{H}$: 123.00/8.46 125.60/8.41 129.00/8.05 124.17/7.55 125.07/7.52 ppm). The other regions were trickier to assign. The peaks' intensity in the yellow regions ($^{13}\text{C}/^1\text{H}$: 124.75/ 6.86, 124.30/6.91 ppm) is rising the fastest at the beginning of the reaction, suggesting that they come from a dimer. The integral of the red regions ($^{13}\text{C}/^1\text{H}$: 124.00/7.06, 130.78/6.94 ppm) has a slower rise, and its maximum is at the moment when the monomer is depleted. We assume that this group corresponds to the trimer, as it needs both the dimer and the monomer in the reaction mixture to be formed. The peaks from the last groups (blue; $^{13}\text{C}/^1\text{H}$: 124.70/7.09, 130.29/6.95 ppm) are characterized by steady growth throughout the reaction, suggesting that they can be assigned to a tetramer. Additionally, we can see a

8 Deeper Insight into Photopolymerization: TR–NUS and Diffusion NMR

decline in the intensity of dimer and trimer signals. The first one is associated with the formation of the tetramer, while the second one forms insoluble higher n -mers. The precipitation was confirmed by the picture of the NMR tube after the reaction (see Figure S2) and the intensity loss of ^1H spectra (see Figure S3).

The diligent reader might notice that the peaks shown in Figure 8.3 are mostly the ones with a low signal-to-noise ratio (SNR). This is due to the low concentration of the reagent and the use of the spectrometer with a relatively low field (300 MHz) for such kind of investigations. These experimental conditions were chosen on purpose to demonstrate the behavior of the method at its sensitivity limit. Of course, higher fields would solve the high noise problem, but the data at 300 MHz are the real stress test to the method and in our opinion by far more impactful. The low SNR can also be noticed on the integrals shown in Figure 8.3d, where the noise influence manifests itself in the form of oscillations that are caused by the so-called intrinsic SNR.^[55]

Additionally, it is worth pointing out that the broadening of peaks typical for polymers has still allowed the separation of the peaks in HSQC spectra even at 300 MHz. Of course, in some cases of extreme broadening the peak overlap can cause additional problems in the analysis of the results. However, in our opinion the limits shown here on this example are especially promising for the broad applicability of the method presented.

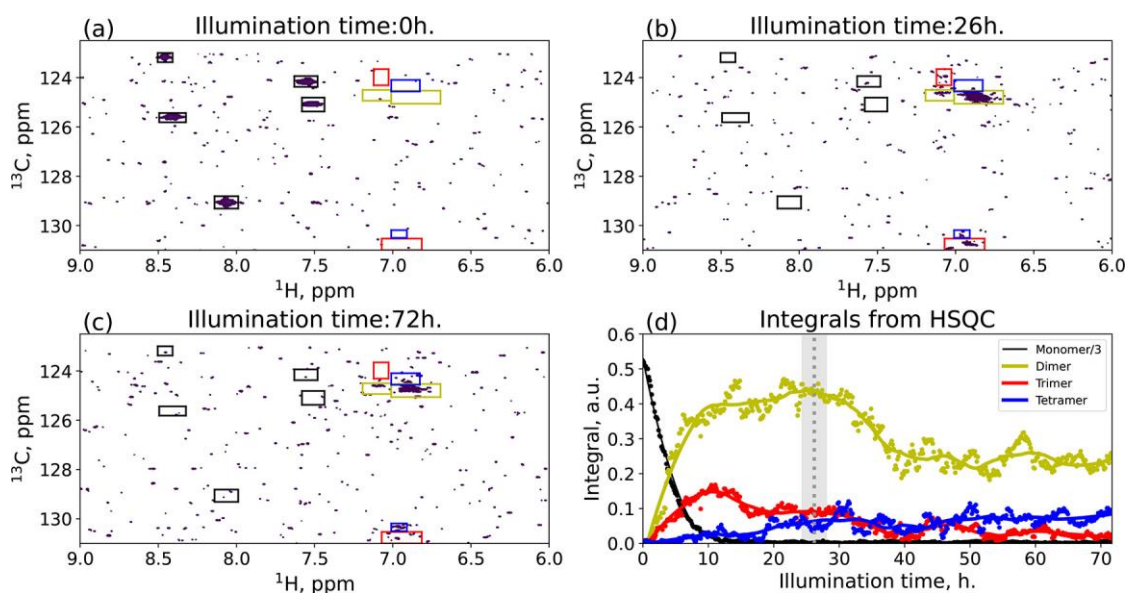


Figure 8.3: (a–c) HSQC spectra of the reacting mixture at three different time windows: (a) before illumination, (b) time at the maximum average weight, and (c) at the end of the reaction. The colored boxes represent the area where we have integrated the spectra. The color and label show the specific n -mer. The integrals from the boxes are shown in (d). The dots show the “raw” integrals, while the continuous lines are the data after the Savitzky–Golay filter. The dotted vertical line shows the time of the (b) pane, while the gray area represents the time-averaging of a single frame. To make the figure easier to read, the integral of the monomer is divided by a factor of 3.

The assigned integrals from HSQC have been used to calculate the average mass of the reactants, which was used later as reference data for calibration of the mass from the TR-DOSY experiments.

In Figure 8.4, we have presented the time dependence of the average mass calculated from TR-NUS peak intensities and from TR-DOSY diffusion coefficients. The curves are in substantial agreement. However, during the first 6 h of the reaction, the diffusion coefficient values are disturbed due to heating from the light source, which causes unstable temperature. This effect manifests itself in the deviation from the TR-NUS data. The

disturbance is extended in time due to interleaved acquisition, which causes a single frame to be averaged over 4.8 h. After that, the temperature stabilizes. Additionally, the similar curve obtained from the sequential TR-DOSY experiment proves that the assignment of peaks in the HSQC experiment was correct. Both curves show that maximum average mass is achieved at the 28th hour of our reaction. Later, the average mass drops due to precipitation of higher n -mers, which are insoluble. Overall, the presented data show that despite low concentrations of samples, broad NMR lines, and a relatively low field of 300 MHz, the combination of TR-NUS and TR-DOSY can be successfully applied. In the case of samples with higher SNR, of course, the assignment could be potentially confirmed using additional methods, such as spatially encoded 3D DOSY^[56,57] or TR adaptation of HSQC-iDOSY.^[58,59]

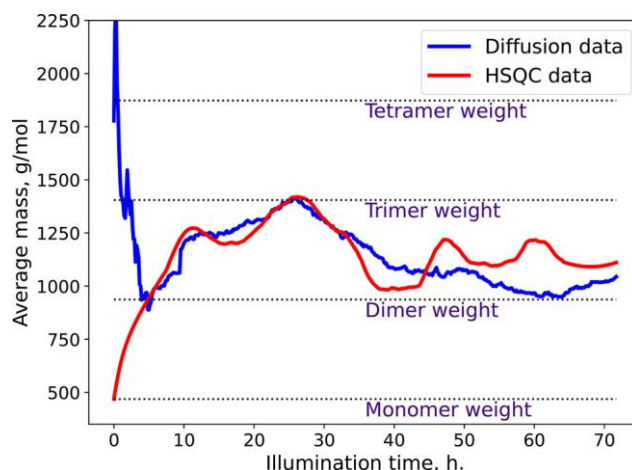


Figure 8.4: Time dependence of the average mass calculated by TR-DOSY (blue) and TR-NUS (red) methods.

8.5 Conclusion

The synergy between both time-resolved methods allows us to understand the photopolymerization process of H2banthbn. Using only diffusion methods, we would have only a crude idea about the average mass of the system, and obtaining the information about particular n -mers would be close to impossible. The HSQC data allow us to track the concentration changes of each n -mer, providing us with quite compelling information about the system. That being said, the assignment of the peaks without the confirmation from the diffusion data would be ambiguous. The use of both methods allows us to have certainty about the assignment and, therefore, to better understand the system. Finally, the presented comprehensive methodology was demonstrated on a challenging system in terms of concentration, line widths, and magnetic field. The presented approach is general and can be used for different types of chemical reactions, especially the polymerization reactions and photoreactions.

8.6 Acknowledgements

Mateusz Urbańczyk and Adam Mames would like to thank the National Science Centre, Poland, for its support in the form of an OPUS Grant (2021/41/B/ST4/01286). Kristina Kristinaityte and Tomasz Ratajczyk would like to thank the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 847413 and the international cofinanced project founded from the program of the Minister of Science and Higher Education entitled “PMW” in the years 2020–2024, agreement no. 5005/H2020-MSCA-COFUND/2019/2. Ruth M. Gschwind would like to thank the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) (TRR 325-444632635) for funding. Franz F. Westermair and Wagner Silva would like to

8 Deeper Insight into Photopolymerization: TR–NUS and Diffusion NMR

thank the DFG (German Research Foundation), RTG 2620-426795949, for funding. The authors would like to thank Prof. Krzysztof Kazimierczuk for the very helpful discussion about the noise behavior in TR-NUS.

8.7 Supporting Information

The full supporting information for this chapter can be found at <https://pubs.acs.org/doi/10.1021/jacs.2c05944>. The supporting information contains: Time dependent diffusion data, additional NMR kinetics data, HRMS of H2banthb, pulse sequences and source code for the TReNDS program.

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8 Deeper Insight into Photopolymerization: TR–NUS and Diffusion NMR

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9 CONCLUSION

In summary the results of two ongoing, and five finished projects are reported in this thesis. The (adapted) conclusions drawn in each chapter are collected here, to allow a quick overview of the works presented herein.

In chapter 2, the current state of development of a new, low-cost laser-based setup for in-situ illuminated NMR spectroscopy was presented. The overall cost for all parts in the assembly is approximately 1000 EUR. On average, six- to sevenfold higher illumination intensities were observed in the photoisomerization of 2,4-dinitrobenzaldehyde in dichloromethane, a known chemical actinometer, when compared to the established LED-based setup. As this project is not finished yet, it must be emphasized that more measurements are necessary. The focus will be put on optimizing the setup further and obtaining better data. I hope the device will prove to be valuable to the photo-NMR community, as its high illumination intensity should make previously not considered reactions feasible for in-situ NMR-monitoring and mechanistic investigations. With the increasing availability of 3D printing, it should be easy for persons skilled in the art to rebuild the setup and use it for their own research or further improve it.

In chapter 3, investigations on diamino-hydridosilanes with *N*-Dipp or *N*-*t*Bu moieties were carried out. It was found, that the starting materials react vastly different with triphenylsilanol in THF, as the former quantitatively yields a formal substitution product of Si–H by Si–OSiPh₃ under hydrogen elimination, while the latter is converted to formal addition products of HOSiPh₃ with cleaved Si–N bonds. Through extended ¹H and ²⁹Si NMR spectroscopic investigations, it was possible to identify pentacoordinate silicon species as key downstream intermediates in the dehydrogenative coupling of the *N*-Dipp substituted silane, quantify relative energies, rates and the activation barriers connecting them, thus providing a comprehensive picture of the reaction. Quantum chemical calculations corroborated the mechanistic proposal, as the populations of pentacoordinate, anionic Si–H_{ax} states were suggested as crucial factor for the hydrogen evolution reaction. Thus, it should be possible to predict the reaction outcomes of other *N*-substituted diamino-hydridosilanes based on calculations of relative energies. I hope that the findings serve as helpful guides in the understanding and development of reactions involving silanes, which are often employed across all fields of synthetic chemistry. Future investigations will be focused on isolation of enantiomerically pure silanes and assess their potentials as stereospecific mild reducing agents.

In chapter 4, the mechanism of the recently reported hydrostannylation of P₄ is described. This complex reaction can be used to facilitate the convenient transformation of P₄ directly into myriad useful P₁ products, but many aspects of its mechanism had previously remained unclear. Through a combination of computational and experimental study it was possible to identify a preferred sequence of elementary bond cleavage steps through which breakdown of the P₄ tetrahedron can occur, but also demonstrated that many competing pathways are available, all eventually leading to the same set of products (R₃Sn)_{*x*}PH_{3-*x*}. These conclusions are supported by DFT calculations and observation of intermediates that have been stabilized by increasing their steric bulk. From these results it has been possible to identify key, underpinning mechanistic factors that allow the hydrostannylation reaction to proceed so efficiently, and which can act as useful guidelines to aid in the development of future P₄ functionalization reactions. In particular, these studies suggest that it is beneficial for P₄ functionalization reactions to transform their substrate “one P–P bond at a time”, while ensuring that the remaining P–P bonds remain electronically similar. I believe that these insights will help to guide future research towards the goal of practical, direct P₄ functionalization.

9 Conclusion

In summary, the first complex to feature both ferriostannylene and stannylidyne functionalities was synthesized and characterized $[\text{Fe}(\text{SnAr}')_2]$. The combination of iron and two monosubstituted tin centers, along with the constrained ligand structure, forms an Fe–Sn single bond and an Fe=Sn double bond ($\sigma+\pi$). This arrangement results in a positively charged Sn center and an electron-rich Fe center. The unusual coordination environment effectively reduces the tendency of the two aryl-tin moieties to dimerize, thereby maintaining the high reactivity of the two-coordinate Sn centers. Additionally, the proximity of the metal centers enhances cooperative reactivity. Comprehensive spectroscopic characterization and theoretical calculations support the existence of an amphiphilic FeSn_2 core with multiple reactive sites. This was demonstrated in the reactions of $[\text{Fe}(\text{SnAr}')_2]$ with $\text{Ni}(\text{COD})_2$, AlBr_3 , CH_3I , and PMe_3 . The lone-pair electrons and vacant p-orbital of the two Sn atoms in $[\text{Fe}(\text{SnAr}')_2]$ create “push-pull” interactions with nickel due to their optimal distance and orientation. In the reaction with AlBr_3 , the cleavage of the Al–Br bonds was observed, accompanied by the migration of Ar' . The formation of a $[\text{Fe}(\text{SnAr}')_2]\cdot\text{AlBr}_3$ adduct may initiate this reaction. The oxidative addition of CH_3I leads to the formation of a Sn(IV) center, illustrating the amphiphilic nature of the ferriostannylene site. Interestingly, PMe_3 binds to the iron center, resulting in the cleavage of the Fe=Sn double bond and the formation of a Sn–Sn single bond. Notably, this process is reversible. Furthermore, compound $[\text{Fe}(\text{SnAr}')_2]$ activates CS_2 and CO_2 through different reaction pathways, and P_4 , which leads to the cleavage of multiple P–P bonds. The results emphasize the significant synthetic potential of complexes that feature multiple coordinatively unsaturated sites from group 14 elements. Complexes similar to $[\text{Fe}(\text{SnAr}')_2]$ should be easily obtainable using comparable strategies with other low-valent transition metalates and appropriate main group precursors. This bodes for future investigation pursuing further challenging synergistic bond activation reactions. Studies in this direction are in hand.

In chapter 6, the first metal complexes of the heavy tetraphospholide anions, SnP_4^{2-} and PbP_4^{2-} have been synthesized. These ligands are of fundamental interest as group 14 analogues of the well known P_5^- anion. A substantial aromatic character was deduced for P_5^- and SnP_4^{2-} using quantum chemical calculations. The observation of SnP_4^{2-} and PbP_4^{2-} is a milestone in the chemistry of phospholides, while it also bodes well for the preparation of further elusive group 14/group 15 element anions. A rich organometallic chemistry is anticipated for these anions, which may offer access to further unusual compounds as shown by the preparation of a phosphorus-rich triple-decker complex. More generally, the work also demonstrates that the activation of P_4 by heterobimetallic complexes has a high utility for the preparation of previously inaccessible (poly-)phosphorus species.

In chapter 7, it was found that the use of the heteroleptic *tmeda* carbonyl complex $[\text{W}(\text{CO})_4(\text{tmeda})]$ together with the nominal Zintl phase $\text{K}_6\text{Rb}_6\text{Si}_{17}$ in solution experiments in liquid ammonia allowed the crystallization of the compound $[(\text{K},\text{Rb})@([2.2.2]\text{crypt})]_2(\text{K},\text{Rb})_4[\text{Si}_9\text{W}(\text{CO})_4]\cdot 13.4\text{NH}_3$. The compound was analyzed via single crystal X-Ray diffraction and proved the presence of the pseudo pentagonal bipyramidal tungsten complex anion $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$. The highly charged anion is stabilized by direct ion interactions of the four cations around the W–Si bond. The structure represents the first tungsten functionalized nonasilicide Zintl anion and only the sixth transition metal functionalized bare silicon cluster. Theoretical calculations suggest dative Si–W bonding interaction is responsible for the formation of this new $[\text{Si}_9\text{W}(\text{CO})_4]^{6-}$ complex anion. The detection of the Zintl anion in solution via ^{29}Si NMR spectroscopy has not been successful to date and investigations are ongoing.

In chapter 8, the synergy between time resolved (TR) diffusion ordered spectroscopy and non uniform sampled (NUS) TR- ^1H - ^{13}C -HSQC allowed to understand the photopolymerization process of *N,N*-bis(anthracen-9-ylmethyl)butane-1,4-diamine. Using only diffusion methods, only a crude idea about the average mass of the

system would be given, and obtaining the information about particular n -mers would be close to impossible. The HSQC data allowed to track the concentration changes of each n -mer, providing quite compelling information about the system. That being said, the assignment of the peaks without the confirmation from the diffusion data would be ambiguous. The use of both methods allowed to have certainty about the assignment and, therefore, to better understand the system. Finally, the presented comprehensive methodology was demonstrated on a challenging system in terms of concentration, line widths, and magnetic field. The presented approach is general and can be used for different types of chemical reactions, especially the polymerization reactions and photoreactions.

10 Curriculum Vitae

Publications

- Kristina Kristinaityte, Adam Mames, Mariusz Pietrzak, Franz F. Westermair, Wagner Silva, Ruth M. Gschwind, Tomasz Ratajczyk, Mateusz Urbańczyk
Journal of the American Chemical Society, **2022**, *144*, 13938–13945
Deeper Insight into Photopolymerization: The Synergy of Time-Resolved Nonuniform Sampling and Diffusion NMR
DOI: 10.1021/jacs.2c05944
- John A. Kelly, Verena Streitferdt, Maria Dimitrova, Franz F. Westermair, Ruth M. Gschwind, Raphael J. F. Berger, Robert Wolf
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Transition-Metal-Stabilized Heavy Tetraphospholide Anions
DOI: 10.1021/jacs.2c08754
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[(K,Rb)@([2.2.2]crypt)]₂(K,Rb)₄[Si₉W(CO)₄]·13.4 NH₃ – The First Tungsten Functionalized Silicon Zintl Cluster
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Schrittweiser Abbau von weißem Phosphor: Experimentelle und computergestützte Studien zum Mechanismus der P₄-Hydrostannylierung
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- Yang Liu, Franz F. Westermair, Isabelle Becker, Sebastian Hauer, Michael Bodensteiner, Christoph Hennig, Gábor Balázs, Franc Meyer, Ruth M. Gschwind, and Robert Wolf
Journal of the American Chemical Society **2025** (accepted January 28, 2025)
Synthesis and Reactivity of an Iron–Tin Complex with Adjacent Stannylidene and Ferriostannylene Units
DOI: 10.1021/jacs.4c18423

11 DANKSAGUNG

An erster Stelle möchte ich mich herzlichst bei Frau Prof. Dr. Ruth. M. Gschwind bedanken, für die durchweg gute Zeit am Arbeitskreis, die vielen hilfreichen Diskussionen und Hilfe bei allen hoch interessanten Projekten die während der Dauer der Promotion und vorangegangener Masterarbeit zu bearbeiten waren. In der Zeit am AK wurde mein Interesse in die Forschung noch mehr gestärkt und ich habe nicht nur wissenschaftlich viel von Ihnen gelernt.

Bei Herrn Prof. Dr. Robert Wolf möchte ich mich zunächst für die gute Zusammenarbeit und vielen Kooperationen bedanken die im Lauf der Zeit entstanden sind. Besonders möchte ich mich für Ihre Anregung nach der AC Bachelorprüfung bedanken „der AC nicht verloren zu gehen“ die mich nachhaltig stark motiviert hat und ohne die ich vermutlich nicht das Interesse für Metall- und Anorganik, besonders Phosphor entwickelt hätte. Des Weiteren bedanke ich mich für die Übernahme des Amtes als Zweitgutachter.

Herrn Prof. Dr. Werner Kremer danke ich für die Übernahme der Rolle des Drittprüfers und für die Hilfestellungen bei Messproblemen an den Spektrometern in der Biophysik. Dabei konnte ich einiges lernen, das in keinem Lehrbuch steht.

Ich bedanke mich ebenso bei Herrn Prof. Dr. Rainer Müller für die Bereiterklärung, den Vorsitz des Prüfungsausschusses zu übernehmen.

Ich danke der Deutschen Forschungsgesellschaft für die finanzielle Förderung im Rahmen des Graduiertenkollegs RTG 2620 „Ion Pairs in Reaction“.

Pragnę serdecznie podziękować Panu Prof. Dr. Mateuszowi Urbańczykowi za przyjęcie mnie do zespołu badawczego w PAN – był to dla mnie cenny i pouczający czas. Ponadto chciałbym podziękować Prof. Dr. Tomaszowi Ratajczykowi oraz Dr. Adamowi Mamesowi za dobrą współpracę.

Ich danke den Mitarbeitern des AK Wolf, Dr. Jose Cammarata, Dr. Yang Liu, Dr. John Kelly und Dr. Daniel Scott für die Kooperationen. Ebenso möchte ich mich bei Dr. Tobias Götz, Manuel Kümper und PD Dr. Jonathan O. Bauer für das interessante Projekt bedanken. Besonders danke ich Dr. Stefanie Gärtner, Dr. Susanne Tiefenthaler, Dr. Franz Schmidt und Paul Braun vom AK Prof. Dr. Nikolaus Korber für die langjährige Zusammenarbeit. Allen ehemaligen und jetzigen Kolleginnen und Kollegen danke ich für die angenehme Zeit am Arbeitskreis. Insbesondere gilt mein Dank Dr. Verena Streitferdt, bei der ich Forschungspraktikant war und die mich an die NMR Spektroskopie herangeführt hat. Des Weiteren danke ich den jetzigen und ehemaligen Kollegen Dr. Wagner Silva, Dr. Julian Ilgen, Dr. Alexander Antonov, Dr. Matej Žabka, Dr. Kumar Motiram-Corral, Dr. Johnny Hioe, Dr. Nele Berg, Dr. Willibald Stockerl, Dr. Johannes Gramüller, Dr. Philipp Dullinger, Dr. Maximilian Franta, Kerstin Bauer, Patricia Albrecht, Cornelia Fischer, Ulrike Weck Nikola Kastner-Pustet, Michelle Brückner, Christian Scholtes, Johannes Eder, Sebastian Knapp, Markus Hecht, Maximilian Philipp, Anton Abramov, Bastian Dauth, Lea Müller, Dana Králová, Elias Wild und Ludwig Rütther, Thomas Walzl und Thomas Tiefel. Ich danke den Mitarbeitern der NMR-Abteilung, Dr. Ilya Shenderovich, Fritz Kastner, Tuanh Anh Nguyen, Annette Schramm und Sebastian Bock und Simon Grunert.

Meiner Familie und Freunden gilt mein allergrößter Dank, meinen Eltern Franz und Irmgard, meiner Schwester Veronika, meinem Bruder Simon und meiner Freundin Vera.

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- (1) Ich erkläre hiermit an Eides statt, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe des Literaturzitats gekennzeichnet.
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