Synthesis and Reactivity of Donor Stabilized Monomeric Pnictogenylalanes and –Gallanes

DISSERTATION

ZUR ERLANGUNG DES
DOKTORGRADES DER NATURWISSENSCHAFTEN
(DR. RER. NAT.)
DER FAKULTÄT FÜR CHEMIE UND PHARMAZIE
DER UNIVERSITÄT REGENSBURG

vorgelegt von
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aus Nittenau
im Jahr 2020

Diese Arbeit wurde angleitet von Prof. Dr. Manfred Scheer.

Promotionsgesuch eingereicht am: Dezember 2020

Tag der mündlichen Prüfung: Januar 2021

Vorsitzender:

Prüfungsausschuss: Prof. Dr. Manfred Scheer

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Michael Weinhart

This thesis was elaborated within the period from January 2017 till January 2021 in the Institute of Inorganic Chemistry at the University of Regensburg, under the supervision of Prof. Dr. Manfred Scheer.

Parts of this work have already been published or submitted:
(* = Co-First Authorship: These authors contributed equally to this work.)

A. Doddi, M. Weinhart, A. Hinz, D. Bockfeld, J.M. Goicoechea, M. Scheer, M. Tamm, *Chem. Commun.* **2017**, *53*, 6069-6072.

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„Geduld ist die Kunst,

nur langsam wütend zu werden.“

Japanische Weisheit

Preface

During the period of this thesis (January 2017 – January 2021) some results have already been published (*vide supra*). These results are also summarized in the present work and reprinted with the permission of the respective scientific publisher.

Each chapter contains the section 'author contributions', which describes the extent of involvement of every author contributing to the respective part. Here it is stated, if results from collaborations have been in part already discussed in other theses.

To ensure a uniform design of this work, all chapters are subdivided into 'Introduction', 'Results and Discussion', 'Conclusion', 'References', 'Supporting Information' and 'Author Contributions'. Furthermore, all chapters have the same text settings and the compound numeration begins anew. Due to different requirements of the journals and different article types, the presentation of figures for single crystal X-ray structures or the 'Supporting Information' may differ. In addition, a general introduction is given at the beginning and a comprehensive conclusion of all chapters is presented at the end of this thesis.

Table of Contents

1. Introduction

1.1. Semiconductors

Semiconductors are essential technology enablers that power most of the pioneering digital devices we use today. Once the fabrication of semiconductor devices became a viable business around 1960 the industry's annual semiconductor sales revenue has since grown to over $481 billion, as of 2018.[1] The developed semiconductors so far all involve elements from the central part of the main group elements in the periodic table of the elements (Table 1).

Table 1. Showing elements from group II through VI actively used in current semiconductor technology.

II	III	IV	V	VI
			N	
	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In		Sb	Te
Hg				

Silicon forms the backbone of modern electronics. Its use in electronic metallurgy can be compared to steel in structural metallurgy. But with the ongoing exploration of this technology new heterogeneous semiconducting compounds built from two or more elements are discovered. The most widely used compound is GaAs which excels the properties of silicon.[2] For example, these properties allow them to substitute germanium and silicon in light emitting diodes (LED), lasers and solar panels.[3] The 2000 Nobel Prize in Physics expresses the technological importance of lasers which was awarded for the research on binary and ternary layers of Al/Ga and P/As which provide a large wavelength variety depending on their chemical composition.[2, 4] Furthermore, it is possible to employ GaAs/InAs quantum dots into solar cells to bypass their electronical efficiency limit of 31%.[5] The most prominent applications of a semiconducting compound formed by a group 13 element (boron, aluminum, gallium, indium) and a group 15 element (nitrogen, phosphorus, arsenic, antimony) in everyday life are the white and blue LEDs which was awarded with the Nobel Prize in Physics in 2014.[6] They consist of GaN and InGaN, respectively coated with a phosphorescent layer and are standard components of torches and displays.[7]

1.2. 13/15 Compounds

Although the chemistry of group 13/15 compounds has dramatically increased in the last 20 years they are already known for more than two centuries. First reports on such compounds date back to 1809, when *Gay-Lussac* synthesized the ammonia-borane adduct $H_3N–BF_3$, the first Lewis acid-base (= LA/LB) adduct, by the reaction of BF_3 and NH_3.[8] In 1890 *Besson* reported the first phosphine-borane adduct $H_3P·BCl_3$.[9] Nevertheless, it was not until 1937 till the first amine-borane adduct $Me_3N·BH_3$ containing exclusively hydride substituents on the boron atom was reported by *Burg* and *Schlesinger*.[10] Since these first studies, numerous Lewis acid-base adducts of the type $R_3E'\leftarrow ER'_3$ (E' = B, Al, Ga, In; R, R' = F, Cl, Br, I, alkyl, aryl, H; E = N, P, As) (Figure 1, **A**) have been synthesized and characterized. Besides these 1:1 LA/LB adducts hypercoordinated adducts $E'R_3(ER'_3)_2$ (Figure 1, **B**) containing five-coordinated group 13 element centers have been studied in detail. Another thoroughly investigated class of group 13/15 organometallic compounds are monomeric, heterocyclic and cage-like compounds of the type $[R_2E'ER'_2]_x$ (Figure 1, **C–D**) and $[RE'ER']_x$ ($x \geq 2$) (Figure 1, **F–H**). These compounds contain regular *σ*-bonds consisting of 2-electron-2-center-bonds between the group 13 and the group 15 elements.[11]

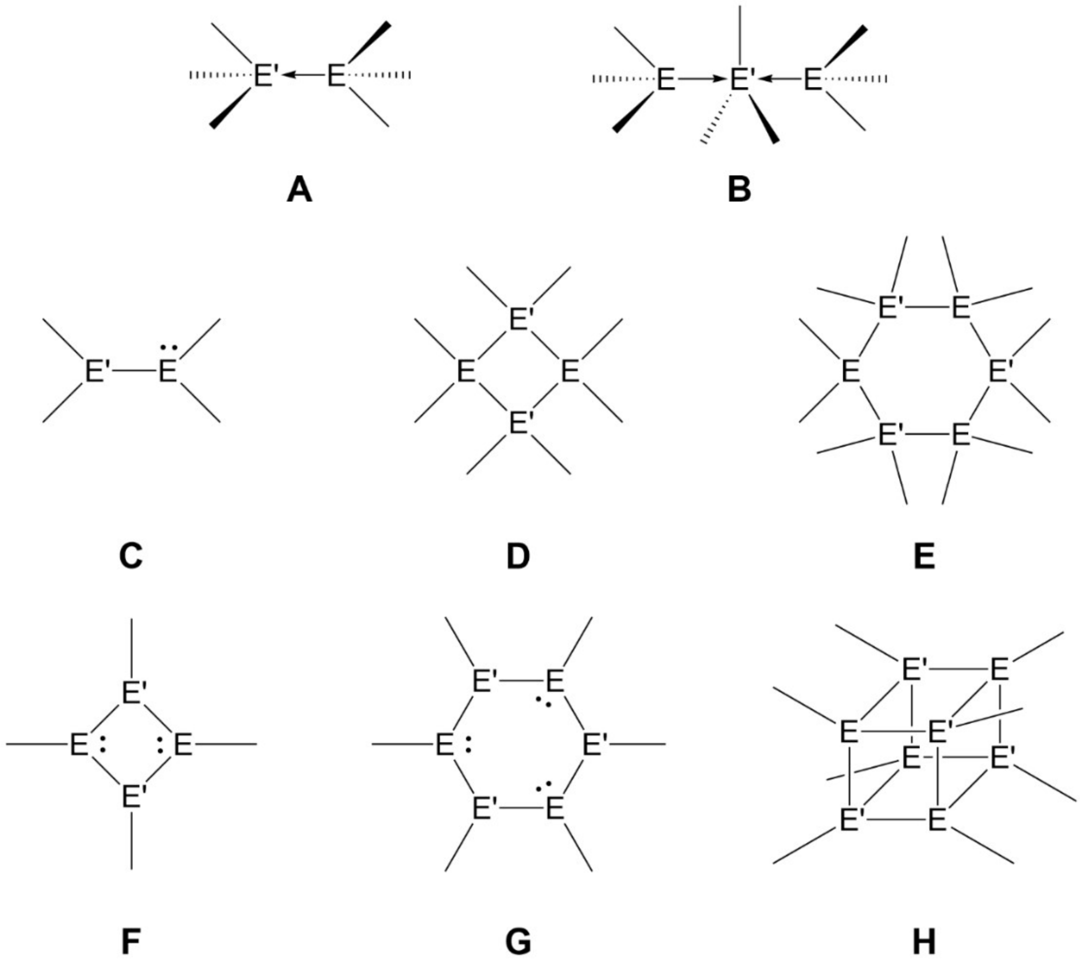
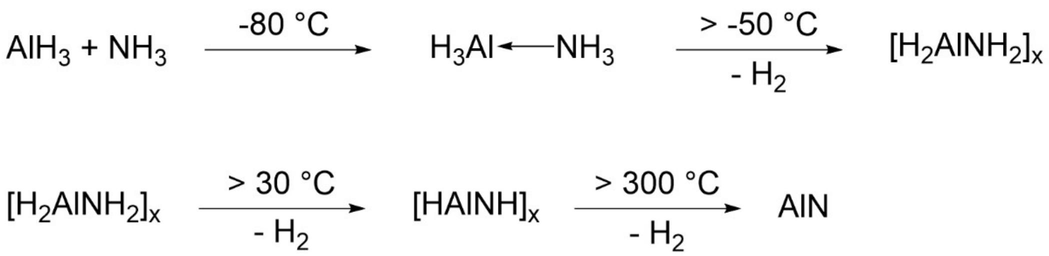


Figure 1: Different structural motifs of group 13/15 compounds.

In this field the studies by *Stock* and *Pohland* stick out with the synthesis of borazine $B_3N_3H_6$. Due to its electronic and structural analogy to C_6H_6 it is sometimes referred to as "*inorganic benzene*" (see Figure 2).[12] Another fundamental study was performed by *Wiberg*, who investigated the reaction of AlH_3 and NH_3 in detail and showed the complete range of H_2 elimination reactions possible in group 13/15 chemistry (Scheme 1).[13] Besides these academic studies involving the synthesis, structure and reactivity of group 13/15 compounds, material sciences had the most influence on their chemistry in the last three decades. As mentioned in the previous chapter binary group 13/15 materials, so called III–V materials, possess semiconducting properties and find their application in opto- and micro-electronic devices.[7a, 7b, 14]



Scheme 1: Reaction of AlH_3 and NH_3.

Thin films of these materials are required to exploit their properties. To form these needed coatings *Manasevit* introduced the MOCVD (**m**etal**o**rganic **c**hemical **v**apor **d**eposition) process in 1968, describing the deposition of thin GaAs films by thermolysis of $GaEt_3$ and AsH_3 on a substrate.[15] Today this process is one of the most advanced industrial process for the synthesis of semiconducting materials. In 1989 this two-source concept was extended by *Cowley, Jones* and others who introduced so called single-source precursors, containing both group 13 and group 15 elements in a single molecule connected by a stable bond.[16] The introduction of the single-source concept led to a tremendous increase in the synthesis of LA/LB adducts $R_3E'{\leftarrow}ER'_3$ and heterocycles of the type $[R_2E'ER'_2]_x$ and their use as precursors.[17]

Small group 13/15 compounds like parent B–N compounds are in the focus of current research as hydrogen storage materials. These compounds are well suited for hydrogen storage because both elements, boron and nitrogen, are lightweight elements and are capable of binding multiple hydrogen atoms. Additionally, B–H and N–H bonds are considered to be hydridic and protic, respectively, making facile hydrogen release possible.[18]

1.3. Bonding situation in 13/15 compounds and their relationship to CC-groups/units

Compounds with a direct bond between a group 13 element and a group 15 element are isoelectronic compared to a C–C bond, as both possess eight valence electrons, and are considered as inorganic analogues to hydrocarbon compounds. This relationship will be discussed in the following for the example of boron-nitrogen (BN) compounds.[3a] The structure of BN compounds is essentially identical to the corresponding C–C compounds. With the boron atom bearing one valence electron less than carbon and nitrogen bearing one more valence electron than carbon, they can form isoelectronic molecules, saturated as well as unsaturated ones (Figure 2). In all examples the hydrogen substituents stay in the same arrangement and slightly elongated B–N bond lengths, compared to the corresponding C–C bonds, can be observed.

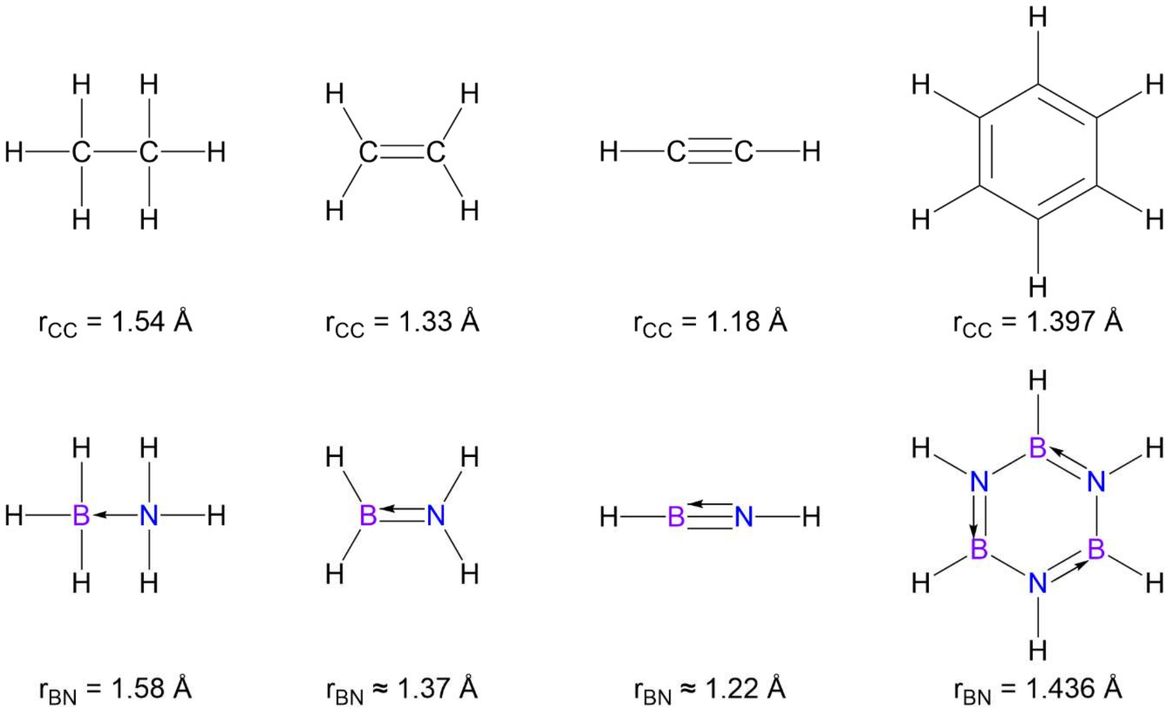


Figure 2: Isoelectronic analogy between BN- and CC-compounds.

The difference in electronegativity (EN_B = 2.0, EN_N = 3.0) leads to polarized bonds in BN compounds. According to calculations only about 0.2e^- are transferred to the boron atom and most of the electron density is localized at the nitrogen atom.[19] This polarization of the B–N bond leads to different properties and an altered chemical behavior compared to the isolobal CC compounds. For instance, ethane is a gas at ambient temperatures while $H_3N{\cdot}BH_3$ is a solid because of the ionicity in the molecule. Another example is the previously mentioned borazine which is a colorless liquid and exhibits a typical aromatic odor as benzene. However, borazine easily undergoes addition reactions with e.g. hydrochlorid, is sensitive towards hydrolysis and its aromaticity is lower. In solid state some BN compounds show the same physical properties as the CC compounds. *α*-boron nitride for example reveals a similar layered structure as graphene and is applied as a high temperature lubricant or as a coating for high temperature applications. In contrast, *β*-boron nitride exhibits a diamond type lattice, is known as one of the hardest materials and is used for the fabrication of abrasives. Compounds of formula [R_2E'–ER'_2] (R, R' = H or small organic substituent) reveal an interesting, different chemical behavior. The group 15 element possesses an accessible lone pair which can donate in a vacant *p*-orbital of the group 13 element. With this interaction these compounds may have a formal double bond through delocalization.[20] However, to obtain an efficient delocalization it requires planar geometries and co-planar coordination of both E–E' atoms. This is only given in R_2B–NR_2 species in which the inversion barrier of the nitrogen atom is low enough to enable a sufficient delocalization of the nitrogen lone pair. Heavier homologues have much higher barriers and preference for pyramidal geometries.[21] With this prevention of delocalization, the group 15 lone pair interacts intermolecular with the group 13 empty *p*-orbital of another molecule which leads to the formation of dimeric or trimeric structures and four coordinate E and E' centers for heavier homologues formed *via* a head to tail polymerization or oligomerization. This can be prevented by the introduction of sterically demanding substituents (e.g. Ph_2P–$BMes_2$) and by donor-acceptor- (LA/LB) or only LB-stabilization, which will be discussed in more detail in a later chapter. In the known aluminum, gallium, indium or thallium derivatives with the heavier pnictogens, a pyramidal coordination of the pnictogen atom can be observed even if electropositive substituents are used to promote *π* bonding. This leads to the generalization that except to B–N, B–P and B–As derivatives the *π* bonding is relatively weak in 13/15 compounds of aluminum, gallium, indium and thallium (ca. ≤ 10 kcal mol^{-1}). The reason for this weak bonding is the relatively large size and electropositive character of these group 13 elements which result in a substantial electronegativity and size difference across the bond.[22]

1.4. Synthesis of monomeric pnictogenyltrielanes $R_2E'ER'_2$

Different methods for the synthesis of monomeric 13/15 compounds with the general formula of $R_2E'ER'_2$ can be applied and will be discussed in the following for P/B containing compounds.[23] A viable and probably the most commonly used method for the synthesis of pnictogenyltrielanes, especially phosphanylboranes, is the salt metathesis (Figure 3). Most salt metathesis reactions start from haloboranes R_2BX (X = halogen) and metal phosphides R'_2PM (M = alkaline metal) (Figure 3, route **I**). This route has been applied to the synthesis of a great variety of bulky phosphanylboranes.[24] In 2014 *Gudat et al.* reported an alternative synthesis route utilizing a B-centered nucleophile in the reaction of a lithio-borane and a chlorophosphine (Figure 3, route **II**).[25] Another possible pathway is the elimination of Me_3SiCl (Figure 3, route **III**)[26] which was extended to the synthesis of diborylphosphines ($R'P(BR_2)_2$) and the first structurally characterized triborylphosphine ($R'P(BR_2)_3$).[27] Further synthetic routes are the Pd-catalysed cross-coupling (Pd-catalysed P–B coupling reaction)[28] and reductive coupling under 1,2-aryl migration,[29] although these reactions are not widely used. Additionally *Manners et al.* reported the synthesis of monomeric group 13/15 compounds by cleavage of oligomeric and polymeric species. The LB stabilized monomeric compound $H_2N–BH_2·NHC$ (NHC = N-heterocyclic carbene) could be obtained by the reaction of poly(aminoborane) with NHC but could only be characterized by mass spectrometry and NMR spectroscopy.[30] Likewise, preliminary results from *Adolf* in the *Scheer* group showed, that cleavage of poly(phenylphosphinoborane) can be achieved by strong LBs like dmap (4-dimethylaminopyridine) or NHCs.[31]

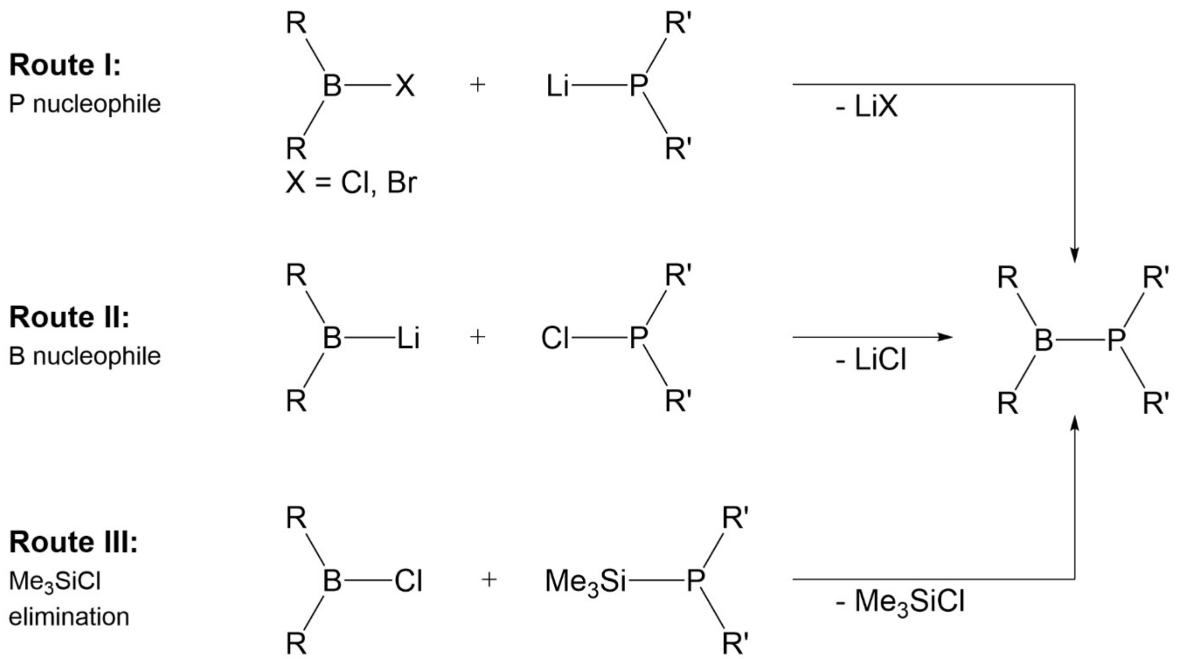


Figure 3: Different synthetic methods for the preparation of monomeric phosphanylboranes.

Moving to the heavier group 13 elements aluminum and gallium the formation of an E'–E bond can easily be achieved under elimination of H_2 (Figure 4, route **IV**),[32] $HSiMe_3$ (Figure 4, route **V**)[33] or alkanes (Figure 4, route **VI**).[34] Unfortunately 13/15 compounds carrying only hydrogen substituents are not stable as monomers and form different oligomeric structures. To prevent this oligomerization the use of LA/LB- or only LB-stabilization is inevitable, which will be discussed in the following chapter.

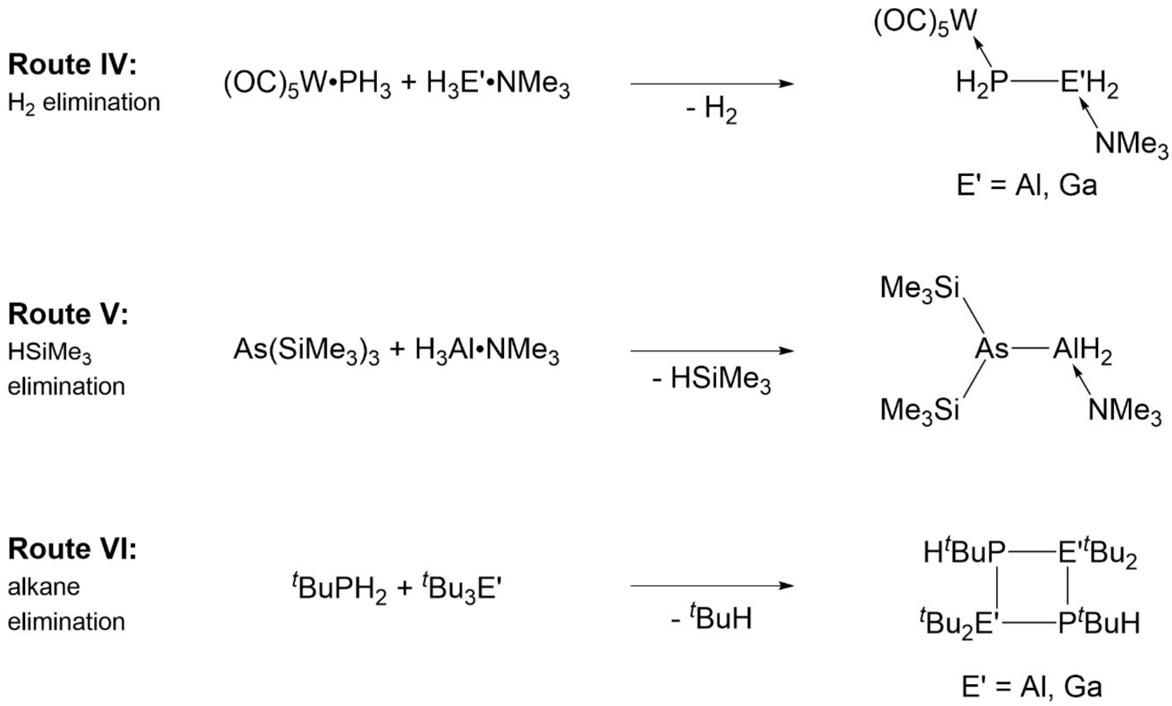


Figure 4: Synthesis of group 13/15 compounds via elimination reactions.

1.5. Synthesis and stabilization of parent Pnictogenyltrielanes

On account of the beforehand mentioned instability, exclusively hydrogen substituted parent compounds $H_2E'–EH_2$ (Figure 5, **I**) have only been studied theoretically.[35] The reason for this instability is the intermolecular interaction of the group 15 element free lone pair and the group 13 element vacant *p*-orbital, as discussed in previous chapters. However, a stabilization can be achieved by blocking the group 15 element with a Lewis acid (Figure 5, **J**, **L**) and the group 13 element with a Lewis base (Figure 5, **K**, **L**), respectively. By this method the oligomerization and polymerization of these compounds can be prohibited and monomeric only hydrogen substituted compounds are accessible.

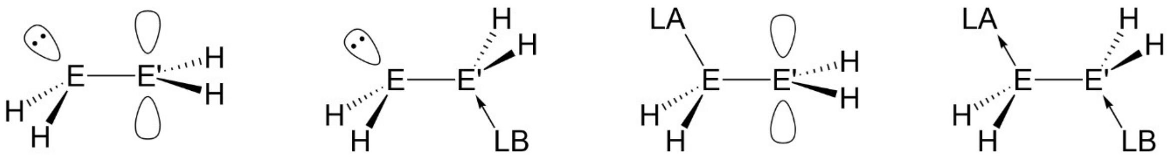


Figure 5: Different types of hydrogen substituted pnictogenyltrielanes.

Employing this concept, our group succeeded in 2001 to generate the highly sensitive and elusive monomeric parent compound of the phosphanylalanes and –gallanes by LA/LB stabilization in $(OC)_5W·H_2P–E'H_2·NMe_3$ by an H_2 elimination reaction of $(OC)_5W·PH_3$ and $NMe_3·E'H_3$ (E' = Al, Ga).[32] Furthermore, it was possible to transform the monomeric LA/LB stabilized phosphanylalanes into dimers, trimers and tetramers in a controlled manner *via* oligomerization.[36] A few years later the salt metathesis of $[(OC)_5W·EH_2Li]$ (E = P, As) and $ClH_2B·NMe_3$ led to the first monomeric parent compounds of phosphanyl– and arsanylboranes $(OC)_5W·H_2E–BH_2·NMe_3$.[37] Thereupon, several examples of different LA/LB stabilized phosphanylboranes were synthesized.[38] Finally, the only by a LB stabilized parent compound $H_2P–BH_2·NMe_3$ became accessible by photolytic treatment of a solution of $(OC)_5W·H_2P–BH_2·NMe_3$ and $P(OMe)_3$.[39] With the introduction of a new, convenient salt metathesis of $[(Me_3Si)_2ELi·2thf]$ and $ClH_2B·NMe_3$ the silylated compounds $(Me_3Si)_2E–BH_2·NMe_3$ (E = P, As) were generated. These compounds can easily be transferred into the only LB stabilized monomeric parent compounds by the reaction with MeOH and with this the access to the only LB stabilized arsanylborane $H_2E–BH_2·NMe_3$ has been achieved for the first time.[40] This new synthetic pathway realized the preparation of only LB stabilized pnictogenylboranes on a gram scale and with this the study of the reactivity of these compounds. With this even the heavy analogues $H_2Sb–BH_2·LB$ (LB = NMe_3, NHC) became possible to synthesize.[41] However, due to the strong hydridic behavior of H substituents on aluminum and gallium it was not possible to gain access to only LB stabilized monomeric parent pnictogenylalanes and –gallanes.

1.6. N-heterocyclic carbenes (NHCs)

As mentioned in previous chapters NHCs are promising Lewis bases for the stabilization of labile monomeric pnictogenyltrielanes and prevent their oligomerization and polymerization. In general, carbenes are defined as neutral compounds containing a divalent carbon atom with a six electron valence shell.[42] In 1988 *Bertrand et al.* reported the synthesis of the first isolable carbene stabilized by interactions with adjacent phosphorus and silicon substituents.[43] Three years later *Arduengo et al.* introduced the first NHC as an isolable and 'bottleable' carbene incorporated into a nitrogen heterocycle.[44] The inspiration for the structural features of these NHCs were already explored by *Wanzlick*[45] and *Öfele*[46] and their studies on metal-carbene complexes. The simple synthesis and exceptional stability of NHCs led to an immense increase of experimental and theoretical studies of novel NHCs concluding in a numerous library of different NHCs. Today NHCs find application mainly in coordination chemistry to transition metals and p-block elements and as organocatalysts.

Most of the time NHCs are defined as heterocyclic compounds containing a carbene carbon and at least one nitrogen atom within the ring structure.[47] Within this definition fall many different types of carbene compounds with different substitution patterns, ring sizes and degrees of heteroatom stabilization.[48] The inherent instability of carbenes because of their incomplete electron octet is kinetically stabilized in NHCs via bulky substituents adjacent to the carbene carbon and the electronical effects of the nitrogen atoms in the heterocycle. While most chain-like carbenes have a triplet ground state, NHCs exhibit a singlet ground state electronic configuration (Figure 6, **a**). The HOMO (**h**ighest **o**ccupied **m**olecular **o**rbital) and LUMO (**l**owest **u**noccupied **m**olecular **o**rbital) at the carbene carbon can best be described as a formally sp^2-hybridized lone pair and an unoccupied *p*-orbital, respectively. Further stabilization of the singlet ground state is realized by the *σ*-electron-withdrawing and *π*-electron-donating nitrogen atoms both inductively by lowering the energy of the occupied *σ*-orbital and mesomerically by donating electron density into the empty *p*-orbital (Figure 6, **b**). The cyclic structure of NHCs helps to favor the singlet state by forcing the carbene carbon into a bent arrangement.

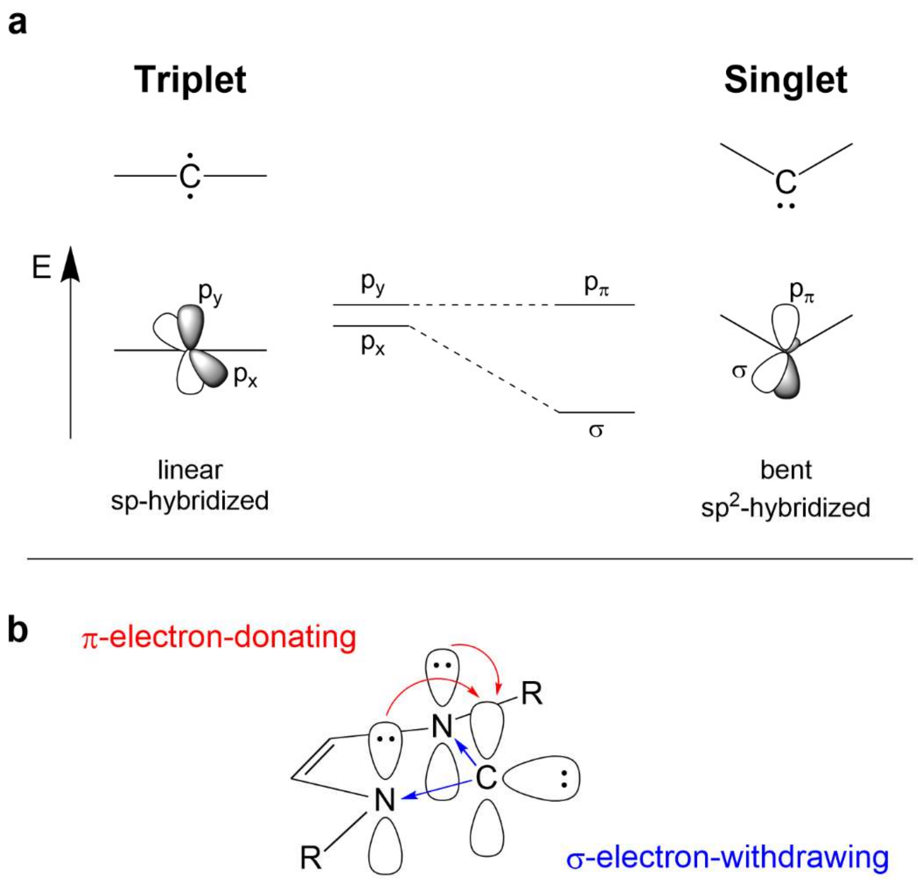


Figure 6: a) Electronic states of triplet and singlet carbenes. b) Ground-state electronic structure of imidazol-2-ylidenes.

Besides the general stabilization with bulky substituents and the interaction with the nitrogen atoms additional stabilization contributes to specific types of carbenes. NHCs derived from heteroaromatic compounds benefit from a partial aromaticity which provides extra stabilization that has been calculated in the range of 25 kcal mol^{-1} for imidazol-2-ylidenes (Figure 7, **M**).[49] This type of stabilization allows to reduce the steric bulk and smaller NHCs like the methyl substituted NHC 1,3-di(methyl)imidazole-2-ylidene (IMe) are persistent in solution.[50] However, many NHCs are stable without the benefit from aromaticity like the first example, 1,3-di(mesityl)imidazolin-2-ylidene (SIMes), reported by *Arduengo et al.* in 1995 (Figure 7, **N**).[51] Today, even NHCs with alternative heteroatoms within the ring motif like sulphur (**O**) and oxygen (**P**) instead of nitrogen are accessible.[52] In the last few years, cyclic(alkyl)(amino)carbenes (CAACs, **Q**) containing only one nitrogen substituent have also received considerable research attention.[53] Other species stabilized by only one nitrogen atom can be realized with the carbene center at alternative positions to C^2. For those carbenes a neutral, non-zwitterionic resonance structure cannot be drawn. These mesoionic or 'abnormal' NHCs (**R**) are generally more electron-donating compared to their 'normal' analogues and can exhibit different properties.[54]

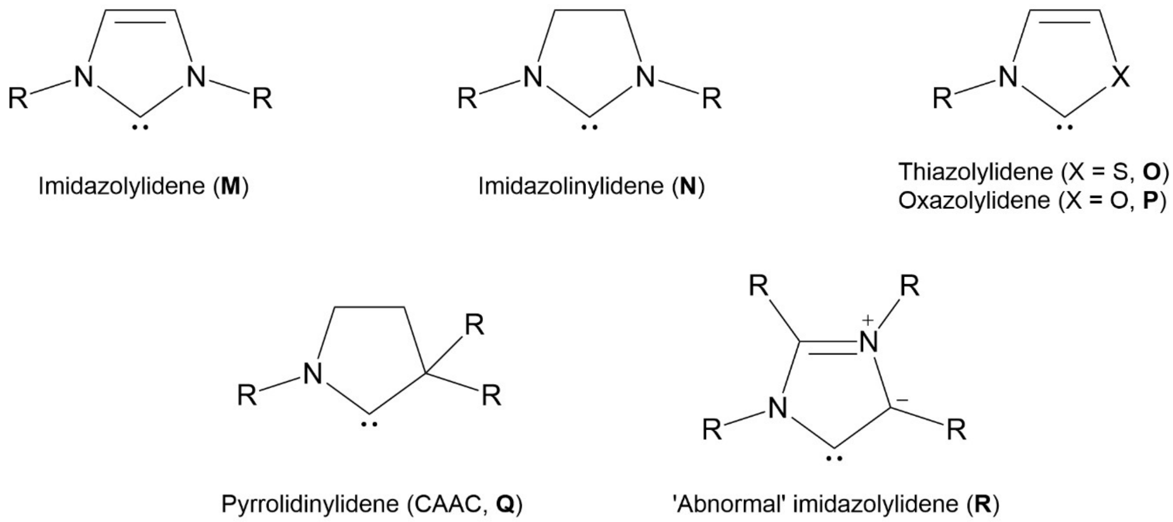


Figure 7: Structure motifs of some of the most commonly applied types of NHCs.

In contrast to the electrophilicity of most transient carbenes, the lone pair in NHCs is located in the plane on the heterocyclic ring which results in a nucleophilic behavior. This characteristic leads to NHCs acting as σ-donors and π-acceptors binding to a wide range of metallic and non-metallic species. The exceptional strength and distinct features of these interactions and their influence on the stability, structure and reactivity of the resulting complexes or adducts make NHCs perfect examples as Lewis bases to stabilize labile compounds like heavier pnictogenyltrielanes or hydride compounds like AlH_3.

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2. Research objectives

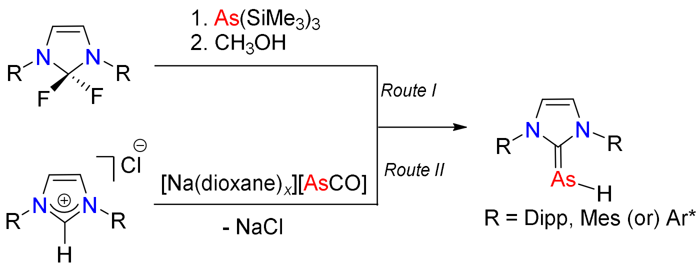
Since only LB stabilized monomeric parent pnictogenylboranes has been successfully synthesized with nearly every group 15 element (N, P, As, Sb), the focus in preparation of monomeric parent 13/15 compounds should shift towards heavier group 13 elements like aluminum and gallium. The known synthetic routes for pnictogenylalanes and –gallanes used H_2 elimination but either the elimination reaction could not be controlled and produced oligomers or monomers had to be stabilized with both Lewis bases and Lewis acids. The synthesis and reaction with MeOH of silylated compounds which was a prosperous pathway for numerous only LB stabilized monomeric parent pnictogenylborans could not be transferred to the aluminum and gallium analogues due to the strong hydridic character of the H substituents on the group 13 element. With these results the salt metathesis between a haloalane/halogallane and an alkali metal salt of the pnictogen element seems to be the most promising synthesis to achieve only LB stabilized monomeric parent pnictogenylalanes and –gallanes. To enable this reaction a suitable stabilization of the starting materials as well as the products is necessary. This stabilization needs to be both electronical and sterically to prohibit oligomerization *via* H_2 elimination and strengthen the E'–E bond to compensate the weaker π-bonding of pnictogenylalanes and –gallanes compared to the boron analogues. To accomplish this goal, following tasks arise:

- Synthesis of NHC stabilized haloalanes and halogallanes (NHC·E'H_2Cl and NHC·E'HCl_2, E' = Al, Ga) suitable for salt metathesis reactions with MEH_2 (M = Na, Li, K; E = P, As).
- Synthesis and characterization of only NHC stabilized pnictogenylalanes and –gallanes NHC·E'H_2–EH_2 (E' = Al, Ga; E = P, As).
- Exploration of a possible substitution limit by increasing the pnictogenyl substituents on the group 13 element (NHC·E'H(EH_2)$_2$; E' = Al, Ga; E = P, As).

With the synthesis of NHC stabilized haloalanes and –gallanes and gaining more knowledge about their stability, when stabilized by an NHC, the H_2 elimination became again a potential synthesis route for monomeric parent pnictogenylalanes and –gallanes and should be studied once more. Therefore another aspect of this work was:

- Synthesis of NHC stabilized hydride complexes of NHC·E'H_3 (E' = Al, Ga).
- Investigation of different reaction pathways and their conditions in the synthesis of NHC·E'H_2–EH_2 *via* H_2 elimination of NHC·E'H_3 and EH_3 (E' = Al, Ga; E = P, As)

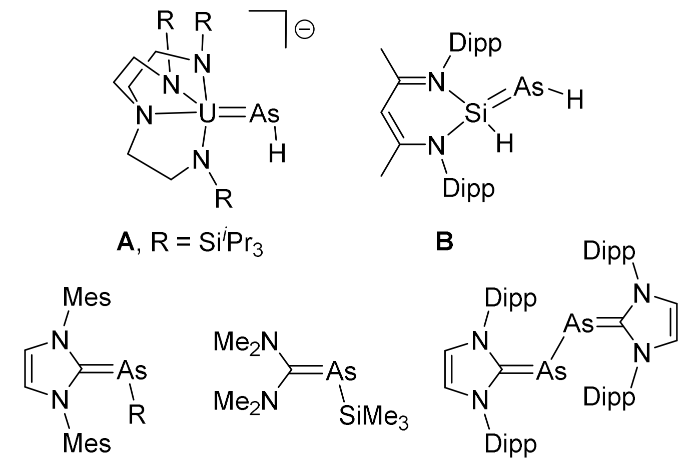
3. N-Heterocyclic Carbene-Stabilized Arsinidene (AsH)



Abstract: N-heterocyclic carbene adducts of the parent arsinidene (AsH) were prepared by two different synthetic routes, either by reaction of $As(SiMe_3)_3$ with 2,2-difluoroimidazolines followed by desilylation or by reaction of $[Na(dioxane)_{3.31}][AsCO]$ with imidazolium chlorides.

3.1. Introduction

Arsinidene (or arsanylidene, AsH) is a transient 6-electron triplet species that has been studied intensively by spectroscopic and theoretical methods because of its role in the epitaxial growth of gallium arsenide (GaAs) semiconductor films by metal-organic chemical vapour deposition (MOCVD).[1] Its stabilization in the condensed phase has been possible by complexation to a metal center in a handful of 3d-transition metal carbonyl complexes such as [(HAs){CpMn(CO)$_2$}$_2$] (Cp = C_5Me_5,[2] Cp = C_5H_4Me)[3] and [(HAs){M(CO)$_n$}$_3$]$^{2-}$ (M = Fe, n = 4;[4] M = Cr, n = 5),[5] in which the arsinidene ligand binds in a μ$_2$- or μ$_3$-bridging fashion, respectively. While metal complexes featuring terminal M = AsR functionalities (R = alkyl, aryl) are generally very rare,[6] terminal coordination of the parent AsH was only recently structurally authenticated in the anionic uranium(IV) complex [U(Tren^{TIPS})(AsH)]$^-$ [**A**, Tren^{TIPS} = N(CH$_2$CH$_2$NSi^{i}Pr$_3$)$_3$].[7] Isolation of elusive diarsene in [{U(Tren^{TIPS})}$_2$(μ-η^2:η^2-As$_2$H$_2$)] was also accomplished at the same uranium moiety.[8] In addition, matrix isolation and characterization by IR spectroscopy of the complexes HM=AsH (M = Ti, Zr, Hf) was reported recently by the reaction of laser-ablated group 4 metal atoms with AsH_3.[9] Interestingly, the related silaarsene unit HSi=AsH could be stabilised by a 1,3-diketiminate (NacNac) ligand, and to the best of our knowledge, the resulting complex **B** (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ = Dipp) represents the only structurally characterized example in which AsH is bound to a p-block element in a terminal fashion (Figure 1).[10]

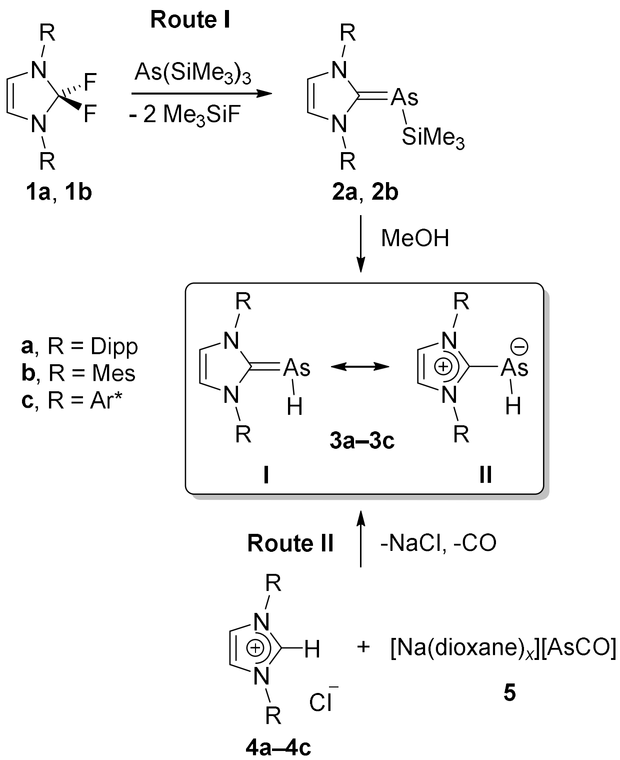


A, R = Si^{i}Pr$_3$ **B** **C**, R = Ph, C_6F_5 **D** **E**

Figure 1: Arsinidene complexes and carbene-arsinidene adducts.

N-Heterocyclic carbenes (NHC) have become particularly useful for the preparation of unusual main group element compounds,[11] and naturally, the first NHC-arsinidene adducts **C** were prepared by the reaction of 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) with cyclic oligoarsinidenes, *i.e.* hexameric (AsPh)$_6$ or tetrameric (AsC$_6$F$_5$)$_4$, respectively.[12] Related acyclic carbene adducts such as **D** were prepared by arsenide addition to formamidinium salts and can be employed as arsinidene-transfer reagents.[13]

Carbene stabilization of diarsenic [$(IPr)_2As_2$] [**E**, IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazolin-2-ylidene] was also accomplished (Figure 1).[14] However, no NHC adducts of the parent AsH are known to date, while several routes were recently reported independently for the preparation of NHC adducts of its lighter congener phosphinidene (PH). In our hands, (IPr)PH was prepared conveniently from the 2,2-difluoroimidazoline $IPrF_2$ (PhenoFluor™) by reaction with $P(SiMe_3)_3$, followed by desilylation.[15] The same compound was also synthesized from the imidazolium salt (IPrH)Cl by the use of sodium 2-phosphaethynolate, Na(OCP), or $P_7(TMS)_3$ (TMS = trimethylsilyl) as phosphorus-transfer reagents.[16] Na(OCP) can also serve as the phosphorus source for the synthesis of (IMes)PH[17] or the more bulky derivative (IAr*)PH with 2,6-bis(diphenylmethyl)-4-methylphenyl (Ar*) substituents.[18] Various (NHC)PH species, including (IMes)PH, could also be accessed directly from imidazolium salts and P_4 or Na_3P_7,[19] while the 4,5-dihydro form of (IPr)PH was obtained from PH_3 and the corresponding imidazol*in*ium chloride.[20] In view of the current tremendous interest in the use of the carbene-phosphinidene adducts in coordination chemistry,[15],[17],[18],[20],[21] we reasoned that also the heavier carbene-pnictinidene congeners (NHC)EH (E = As, Sb, Bi) might serve as suitable ligands in transition metal chemistry if they became available. Herein, we report on the development of two synthetic protocols by using $As(SiMe_3)_3$ (**route I**),[22] or the recently reported 2-arsaethynolate ion (**route II**),[23],[24] as starting materials for the syntheses of the novel parent N-heterocyclic carbene-arsinidene adducts (IPr)AsH (**3a**), (IMes)AsH (**3b**) and (IAr*)AsH (**3c**).



Scheme 1: Preparation of N-heterocyclic carbene-arsinidene adducts; Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl, Ar* = 2,6-bis(diphenylmethyl)-4-methylphenyl.

3.2. Results and Discussion

For the preparation of the carbene-arsinidene adduct **3a** (R = Dipp) via **route I**,[15] the 2,2-difluoroimidazoline $IPrF_2$ (**1a**, PhenoFluor™) represents a suitable starting material.[25] The corresponding difluoride $IMesF_2$ (**1b**) required for the synthesis of **2b** and **3b** (R = Mes) was prepared in 80 % yield by treatment of the 2-chloroimidazolium chloride [(IMes)Cl]Cl with ten equivalents of CsF in boiling toluene. The ^1H NMR spectrum in C_6D_6 shows a triplet at 5.45 ppm ($^4J_{(H,F)}$ = 1.54 Hz) for the imidazole hydrogen atoms, indicating covalent binding of the two fluorine atoms. The ^{19}F NMR spectrum for **1b** exhibits a sharp singlet at –34.8 ppm, which perfectly matches the chemical shift reported for **1a** (δ = –34.0 ppm) in the same solvent. Reaction of **1a** and **1b** with $As(SiMe_3)_3$[22] afforded the carbene-$AsSiMe_3$ adducts **2a** and **2b** as yellow powders in 52 % and 56 % yield, respectively (Scheme 1). The ^1H NMR spectra (in C_6D_6) show the expected signals for the Dipp and Mes substituents together with singlets at 6.31 and 5.89 ppm for the two imidazole CH and at 0.11 and 0.15 ppm for the nine Me_3Si hydrogen atoms, respectively. The ^{13}C NMR signals for the carbene carbon atoms in **2a** (δ = 176.8 ppm) and **2b** (δ = 173.6 ppm) are observed as relatively sharp singlets in the same range as reported for the arsinidene adducts **C** (Figure 1; (IMes)AsPh, δ = 174.3 ppm and (IMes)AsC_6F_5, δ = 172.2 ppm).[12]

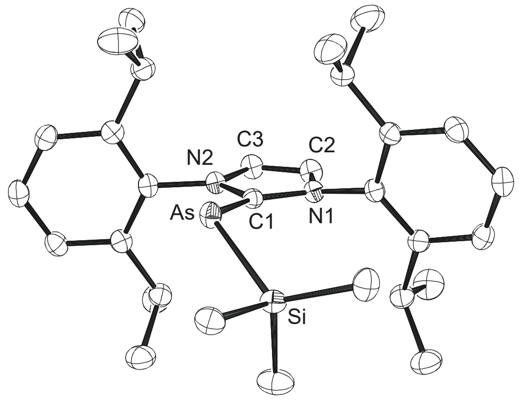


Figure 2: ORTEP diagram of one of the two independent molecules **2a** with thermal displacement parameters drawn at 50% probability level.

The molecular structures of **2a** and **2b** were determined by X-ray diffraction analysis and are presented in Figure 2 (for **2a**) and in Figure S33 (for **2b**, SI). Pertinent structural data are summarized in Table 1. The As–C bond lengths of 1.9130(15)/ 1.9125(15) Å and 1.906(2)/1.899(2) Å in **2a** and **2b** fall in the range reported for related N-heterocyclic carbene-arsinidene adducts such as **C**, *viz.* 1.899(3) Å in (IMes)AsPh and 1.902(7) Å in (IMes)AsC_6F_5,[12] whereas a shorter As–C bond length of 1.881(2) Å was reported for $(IPr)_2As_2$ (**E**). Arsaalkenes of the general formulae RR'C=AsR'' exhibit usually somewhat shorter arsenic-carbon bonds,[26] and for instance, identical As–C bond lengths of 1.807(3) Å were reported for two polarized fluorenylidene-arsinidene adducts.[27] The presence of the sterically more demanding Dipp substituents in **2a** in comparison with the Mes groups in **2b** leads to a pronounced deviation from the expected coplanar arrangement of the As–Si axis, and the TMS group is oriented with its silicon atom outside the plane of the imidazole ring, by 1.14/0.98 Å in the two independent molecules. In contrast, the silicon atom in **2b** is displaced by only 0.04/0.24 Å.

Completing the synthesis of the parent carbene-arsinidene adducts **3a** and **3b** via **route I** requires desilylation of **2a** and **2b**, which was successfully performed by stirring them in dry methanol for several hours to afford yellow solids in 58 % (**3a**) and 64 % (**3b**) yield. An alternative synthesis of these parent compounds should be possible using the 2-arsaethynolate salt [Na(18-crown-6)][AsCO], which has recently become available,[23],[24] however, all attempts to generate parent carbene-arsinidene adducts with this compound failed. Hence, crown ether-free [Na(dioxane)$_x$][AsCO] (x = 3.31) had to be prepared to access **3a** and **3b** directly via **route II** from the imidazolium chlorides **4a** (R = Dipp) and **4b** (R = Mes) by the reaction in THF at room temperature (Scheme 1). In addition, the imidazolium salt **4c** with the larger 2,6-bis(diphenylmethyl)-4-methylphenyl (Ar*) substituents was also employed. The reactions were terminated by filtration through Celite, and crystallization from concentrated THF solutions furnished **3a**–**3c** as microcrystalline yellow solids in comparatively low yield, *i.e.* 13 % (**3a**), 15 % (**3b**) and 9 % (**3c**). This is due to the high light sensitivity and instability of the products in solution at ambient temperature. As decomposition products, the free carbenes were identified indicating the easy removal of the parent arsinidene moiety. Their similar solubility decreases dramatically the isolated yields of the analytically pure products **3a**–**3c**.

The ^{1}H NMR spectra (in C_6D_6) of **3a**–**3c** display signals at 1.43, 1.47 and 2.26 ppm, which can be assigned to the hydrogen atom of the AsH moiety. The shift to lower field of the latter resonance can be ascribed to interaction with the Ar* substituents. In the spectrum of **3b**, this signal appears as a triplet with a $^{5}J_{(H,H)}$ coupling of 0.45 Hz together with a doublet at 6.00 ppm for the imidazole hydrogen atoms. For the latter, a variable-temperature ^{1}H NMR study of **3b** in toluene-d_8 afforded two resolved signals below a coalescence temperature of T_C = 195 K, which allowed to establish a barrier of rotation around the As—C bond of $\Delta G^{\#}$ = 9.66 ± 0.2 kcal mol^{-1} (SI, Figure S31). The ^{13}C NMR spectra reveal relatively sharp signals for the carbene-carbon atoms at 184.5 ppm (**3a**), 179.4 ppm (**3b**) and 180.9 ppm (**3c**), which is at lower field in comparison with the $AsSiMe_3$ adducts **3a** and **3b**. The IR spectra (Nujol) of **3a**–**3c** exhibit bands at 2080, 2059 and 2090 cm^{-1}, which can be assigned to respective As–H stretching frequencies. It should be noted that a significantly lower stretching frequency was reported for the uranium arsinidene complex **1** (1857 cm^{-1}),[7] whereas similar values were found for instance in metal arsenido complexes.[28]

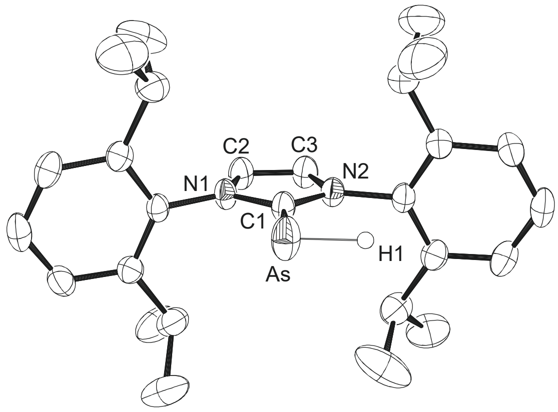


Figure 3: ORTEP diagram of the **3a** in the solid state with thermal displacement parameters drawn at 50% probability level.

The X-ray crystal structures of the three AsH adducts **3a**–**3c** could be established; the molecular structures are presented in Figure 3 (for **3a**) and in Figures S35 and S36 (for **3b** and **3c**, SI). Pertinent structural parameters are summarized in Table 1. The As–C bond lengths of 1.883(2) Å (**3a**), 1.896(2) Å (**3b**) and 1.886(4) Å (**3c**) are slightly shorter than those in the silylated derivatives **2a** and **2b** and those in the arsinidene adducts **C** (Figure 1).[12] The C–As–H angles are close to 90°, reflecting the high degree of p-character for the heavier main group element–element covalent bonds.

Table 1: Comparison of selected bond lengths (Å) and angles (°) of the carbene-pnictinidene adducts (X = H or $SiMe_3$).

Compound	C1-As	As-X	C1-As-X	N1-C1-N2
2a (X = $SiMe_3$)^a	1.9130(15)	2.3110(5)	108.68(5)	104.32(13)
	1.9125(15)	2.3142(5)	104.10(5)	104.34(12)
2b (X = $SiMe_3$)^a	1.906(2)	2.3234(6)	112.11(7)	104.56(18)
	1.899(2)	2.3243(6)	112.89(6)	103.84(17)
(IMes)AsPh[12]	1.899(3)	1.845(2)	97.3(1)	104.2(2)
(IMes)AsC_6F_5[12]	1.902(7)	1.976(7)	99.8(3)	104.6(6)
3a (X = H)	1.883(2)	1.47(5)	90.2(19)	104.58(18)
3b (X = H)	1.896(2)	1.42(4)	97.8(13)	105.2(2)
3c (X = H)	1.886(4)	–^{b}	–^{b}	104.5(3)

^{a} Values for two independent molecules; ^{b} The As–H bond length in **3c** was restrained, whereas the position of the hydrogen atom was freely refined in **3a** and **3b**.

To investigate the bonding situation in the N-heterocyclic carbene-arsinidene adducts **3a**–**3c**, various computations were carried out by using Gaussian09 at the PBE1PBE level of theory and the 6-31G(d,p) basis sets for all atoms. Besides the structural optimisation of the three compounds **3a**–**3c**, methylarsine (H_3CAsH_2) featuring a C–As single bond, as well as the arsaalkenes H_2CAsH and Ph_2CAsH as archetypical species exhibiting C=As double bonds were calculated for comparison. All computational data are assembled in Tables S3 and S4 (SI). While the computed As–H bond lengths vary only slightly (1.509–1.519 Å) the C–As–H angle is significantly closer to 90° for **3a**–**3c** (91.96°–92.95°) than for H_3CAsH_2 (95.22°), H_2CAsH (96.13°) or Ph_2CAsH (95.69°). This is due to weak C–H bonding contributions (e.g. in HOMO–1, HOMO–5, see SI, Figures S37). The computed C–As bond lengths of **3a**–**3c** (1.851–1.860 Å) are slightly shorter than the distances determined by X-ray diffraction (1.883–1.896), but are in between the values for a single bond (H_3CAsH_2: 1.961 Å) and a double bond (H_2CAsH: 1.766, Ph_2CAsH: 1.803 Å). Similarly, the Wiberg bond indices for the C–As bonds of **3a**–**3c** (1.26–1.27) were found to be between the values for single bond (H_3CAsH_2: 0.97) and double bond (H_2CAsH: 1.93, Ph_2CAsH: 1.62).

Natural Resonance Theory (NRT) shows three major resonance structures (see SI), weighing the one with the C=As double bond at 33% (Scheme 1, **I**) and the corresponding zwitterionic formulations (N^+, As^-) at 38% (Scheme 1, **II**). An ELF analysis (see SI) shows the typical dumbbell-shaped surface at an isovalue of 0.85 for H_2CAsH and similarly, but slightly less pronounced, for **3b**. Another tool to estimate the degree of multiple bonding is the ellipticity of the electron density perpendicular to the bonding path at the bonding critical point within QTAIM (SI). The ellipticity of the C–As bond in H_3CAsH_2 (0.05) is considerably smaller than for the arsaalkenes (0.28) or **3a**–**3c** (0.31–0.32), which also points to the presence of a C=As double bonds in **3a**–**3c**. The computed NBO charges *q*(H) are similar for all considered species (–0.033 to –0.070 *e*), but with dramatically differences for C and As: Whereas the C atoms in H_3CAsH_2 (–1.034 *e*), H_2CAsH (–0.866 *e*) or Ph_2CAsH (–0.371 *e*) bear a negative charge, in **3a**–**3c** the charge on the carbon amounts to +0.094, +0.091 and +0.094 *e*. On the other hand, the As atom is negatively polarised in **3a**–**3c** (–0.045, –0.058, –0.073, respectively) and bears positive charge in H_3CAsH_2 (+0.333 *e*), H_2CAsH (+0.436 *e*) or Ph_2CAsH (+0.399). Hence, it is similarly justified to rationalise the adducts of the parent arsinidene (AsH) and NHCs as inversely polarised arsaalkenes.

3.3. Conclusion

In summary, we have introduced two different synthetic protocols for the preparation of the first N-heterocyclic carbene adducts of the parent arsinidene (AsH). Three adducts of the type (NHC)AsH were fully characterised, including the determination of their molecular stuctures by X-ray diffraction analyses, which confirm the dicoordinate nature of the arsenic(I) atoms. These species are new members of the familiy of N-heterocyclic carbene adducts of parent pnictinidenes, which now comprises EH = NH, PH and AsH. An extension to the heavier antimony (SbH) and bismuth (BiH) analogues might also become possible by application of similar synthetic routes. These new (NHC)AsH species are ideally suited to serve as starting materials, e.g. for the preparation of unusual arsenic-containing main-group element compounds and as novel arsenic-donor ligands in transition metal chemistry.

3.4. References

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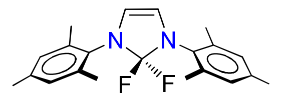
3.5. Supporting Information

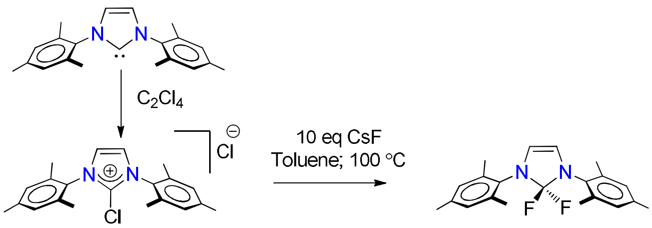
3.5.1. Experimental Section

General procedures: Due to the high sensitivity (to oxygen and moisture) of all the compounds reported in this study, all manipulations were performed under a strictly dry argon atmosphere using standard Schlenk line techniques and dry argon-filled glove boxes. All solvents were dried using an MBraun solvent purification system. Fluorobenzene was dried by passing through a column filled with well dried neutral Al_2O_3. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured on spectrometers (Bruker AV 300 (300 MHz), Bruker DRX 400 (400 MHz) devices). The chemical shifts are given in parts per million (δ; ppm) relative to residual solvent peaks (δ; 7.15 (C_6D_6), 1.96 (CD_3CN), 5.34 (CD_2Cl_2), 7.24 ($CDCl_3$), 3.58 (THF-d_8) ppm),[1] Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), m (multiplet), sept (septet) and br (broad). All the spectra were measured at room temperature unless otherwise stated. Mass spectra were recorded on Finnigan MAT 95 (EI) and Finnigan MAT 95 XL (ESI) systems. Elemental analyses were carried out on a Vario Micro Cube System. The starting materials Phenofluor27, $As(SiMe_3)_3$, [2] [IPrH]Cl[3], [IMesH]Cl[3], [IAr*H]Cl[3], [IMesCl]Cl (1,3-bis(2,4,6-trimethylphenyl)-2-chloroimidazolium chloride) [4] were prepared according to the literature procedures.

Synthesis of (1,3-Bis(2,4,6-trimethylphenyl)-2,2-difluoroimidazoline) (IMes)F_2 (1b):



(**1b**)



(**1b**)

Commercially available caesium fluoride (CsF) was dried at 170 °C for 15 h and was finely ground prior to use. [IMesCl]Cl was finely ground using a mortar and dried under vacuum at 70 °C for 5 h. To a Schlenk tube containing [IMesCl]Cl (4.46 g, 11.81 mmol) and CsF (17.94 g, 118.19 mmol) was added toluene (200 mL). The Schlenk tube was sonicated for 30 min, and then stirred vigorously at 100 °C for 4 days. Formation of a brown solution was observed during the reaction. The reaction mixture was brought to room temperature, filtered through a pad of Celite and the residue washed with toluene (10 mL × 5). The filtrate was concentrated and dried under vacuum, washed with cold n-hexane followed by CH_3CN (–10 °C) and dried under vacuum to afford 1b as a pale brown solid. Yield: 3.23 g (80 %).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ = 6.75–6.74 (m, 4H, *m*-Ar-H), 5.45 (t, 2H, $^3J_{(H,F)}$ = 1.54 Hz, NC*H*), 2.42 (s, 12H, *p*-CH_3), 2.08 (s, 6H, *o*-CH_3).

^{13}C NMR (C_6D_6, 75.5 MHz, 298 K); δ = 140.2 (N-*C*(Mes)), 138.6 (*o*-*C*(Mes)), 132.8 (*p*-*C*(Mes)), 129.9 (*m*-*C*(Mes)), 127.4 (t, $^1J_{(C,F)}$= 233.4 Hz, CF_2), 111.8 (N*C*H), 21.3 (*p*-*C*H_3), 18.9 (t, $J_{(C,F)}$ =2.9 Hz, *o*-*C*H_3).

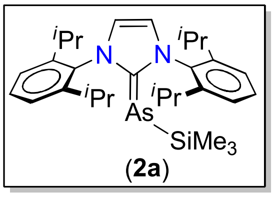
^{19}F NMR (C_6D_6, 282.5 Hz, 298 K): δ = –34.8.

Anal. Calcd (%) for $C_{21}H_{24}N_2F_2$ (342.425 g/mol): C 73.66, H 7.06, and N 8.18; Found: C 73.39, H 6.97 and N 8.39.

HRMS-ESI (*m/z*, CH_3OH) calcd for $C_{21}H_{24}N_2F$ $[M–F]^+$: 323.19180; Found: 323.19229.

EI-MS (m/z): 342.2 $[M]^{+\cdot}$ (calcd 342.190 g/mol) (60 %), 303.2 $[M–2F]^{+\cdot}$ (30 %).

Synthesis of [(IPr)AsSiMe$_3$] (2a):



To a Schlenk tube containing (IPr)F$_2$ (0.300 g, 0.704 mmol) in fluorobenzene (10 mL) was added As(SiMe$_3$)$_3$ (0.210 g, 0.713 mmol) in dropwise manner at room temperature. The resulting dark orange reaction mixture was stirred at room temperature for two days. The black precipitate formed was filtered off and the solvent removed under reduced pressure. The brown oily mass obtained was triturated with *n*-pentane until it became a yellow solid and then washed with cold (– 90 °C) *n*-pentane (1 mL × 3). This solid was then extracted with *n*-pentane and the solvent removed under reduced pressure affording 2a as yellow solid. Yield: 0.201 g (52 %).

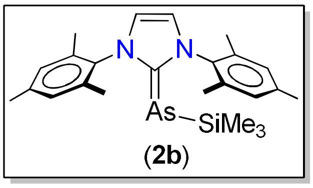
^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ = 7.29–7.15 (6H, Ar-*H*), 6.31 (s, 2H, NC*H*), 3.07 (sept, 4H, $^3J_{(H,H)}$ = 6.6 Hz, C*H*(CH$_3$)$_2$), 1.48 (d, $^3J_{(H,H)}$ = 6.8 Hz, CH(C*H$_3$*)$_2$), 1.09 (d, $^3J_{(H,H)}$ = 6.8 Hz, CH(C*H$_3$*)$_2$), 0.11 (s, 9H, As-SiMe$_3$).

^{13}C NMR (C_6D_6, 75.4 MHz, 298 K): δ = 176.8 (N*C*N), 147.1 (N*C*(Dipp)), 136.3 (*o*-*C*(Dipp)), 130.6 (*p*-*C*(Dipp)), 125.4 (*m*-*C*(Dipp)), 122.4 (N*C*H), 29.5 (*C*H(C*H$_3$*)$_2$), 25.3 (CH(C*H$_3$*)$_2$), 23.9 (CH(C*H$_3$*)$_2$), 5.42 (As-SiMe$_3$).

Anal. Calcd (%) for $C_{30}H_{45}AsN_2Si$ (536.257 g/mol): C 67.14, H 8.45 and N 5.22; Found: C 68.09, H 7.59 and N 5.41.

EI-MS (*m/z*): 536.2 (calcd 536.257 g/mol) [M]$^{+\cdot}$ (75 %), 521.2 [M–CH$_3$] (8 %), 493.2 [M–^{i}Pr] (100 %), 463.2 [M–SiMe$_3$] (25 %) and 387.3 [M–As(SiMe$_3$)] (40 %).

Synthesis of [(IMes)AsSiMe$_3$] (2b):



To a stirred solution of (IMes)F$_2$ (0.536 g, 1.566 mmol) in fluorobenzene (20 mL), was added As(SiMe$_3$)$_3$ (0.461 g, 1.566 mmol) in a drop wise manner. The resulting clear red reaction mixture was stirred for 3.5 h at room temperature. The black precipitate formed was filtered off, and volatiles were then removed *in vacuo*. The residue obtained was quickly washed with *n*-pentane (2 mL × 4) and dried under vacuum to obtain compound 2b as a pale yellow-brown solid. Yield; 0.401 g (56 % based on (IMes)F$_2$).

^{1}H NMR (C_6D_6, 300.13 MHz, 298 K): δ = 6.76 (br, 4H, *m*-Ar-H), 5.89 (s, 2H, NC*H*), 2.19 (s, 12H, *o*-C*H$_3$*), 2.09 (6H, *p*-CH$_3$), 0.15 (s, As-SiMe$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz, 298 K): δ = 173.6 (N*C*N), 140.3 (N-*C*(Mes)), 137.5 (*o*-*C*(Mes)), 136.8 (*p*-*C*(Mes)), 131.2 (*m*-*C*(Mes)), 121.5 (N*C*H), 22.4 (*p*-*C*H$_3$), 19.9 (*o*-*C*H$_3$), 6.3 (As-SiMe$_3$).

^{29}Si NMR (C_6D_6, 79.5 MHz, 298 K): δ= –5.25 (s).

Anal. Calcd (%) for $C_{24}H_{33}N_2AsSi$ (452.593 g/mol): C 63.70, H 7.35, and N 6.19; Found: C 64.95, H 7.29 and N 6.50.

EI-MS (*m/z*): 452.1 (calcd 452.162 g/mol) $[M]^{+\cdot}$ (10 %), 437.1 $[M–CH_3]^{+\cdot}$ (4 %), 379.1 $[M–SiMe_3]^{+\cdot}$ (5 %), 303.2 $[M–As(SiMe_3)]^{+\cdot}$(100 %).

Note: The reaction was performed under the exclusion of light and the solid obtained was stored at –30 °C. The solid can be stored at low-temperatures, but slowly decomposes even under inert conditions to a black solid when stored for hours at room temperature. Furthermore, over a period of time, NMR samples in C_6D_6 always showed the formation of a black insoluble solid.

Synthesis of [Na(dioxane)$_x$][AsCO][5]:

Sodium (6.900 g, 300 mmol; in small pieces), arsenic (7.500 g, 100 mmol; powder), and naphthalene (250 mg, 1.95 mmol) were combined in a Schlenk flask. Then, 200 ml of dimethoxyethane (DME) were added, immediately forming a green solution. The mixture was stirred with a glass-covered stirrer bar at 70 °C for three days, forming a dark greenish solution and black microcrystalline precipitate. To the suspension, *tert*-butanol (14.820 g, 200 mmol) was added via syringe. The suspension was stirred for six hours. When all solid had dissolved, the solution had turned greenish-yellow. Diethylcarbonate (11.810 g, 100 mmol) was added via syringe and the suspension was stirred overnight. The initially greenish-yellow suspension turned orange-yellow during this process. All volatiles were removed *in vacuo* at ambient temperature. To the pale yellowish residue 300 ml of THF were added, resulting in the formation of a dark yellow suspension. After vigorous stirring for 1 hour, the mixture was left to settle overnight. The mixture was filtered over a Celite-padded sinter, affording a clear yellow solution, which was then concentrated to approximately half of the original volume. Then an approximate four-fold amount of 1,4-dioxane was added to precipitate the crude product. The solution was filtered off and the yellow solid was redissolved in THF. After filtration, the solution was concentrated and an approximate four-fold amount of 1,4-dioxane was added to precipitate the product. Drying of the bulk sample at ambient temperature under vacuum for an hour afforded an off-white solid (3.31 molecules of dioxane per Na(AsCO) 23.520 g, 56.3 mmol, 56%). The dioxane content was determined via ^{1}H NMR of a sample dissolved in THF-d_8 vs cyclohexane as internal standard. The product, $[Na(dioxane)_{3.31}][AsCO]$, is not stable for prolonged storage at ambient temperature in a brown-glass bottle under an argon atmosphere, in coincidence with solvent loss. Also, thorough drying *in vacuo* causes off-white $[Na(dioxane)_{3.31}][AsCO]$ to decompose to a black solid. Thus, storage in a freezer is recommended.

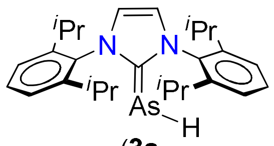
Anal. Calcd (%) for $C_{14.24}H_{26.48}O_{7.62}NaAs$: C 40.96, H 6.39, N 0.00; no satisfactory analysis could be obtained.

^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 3.56 (s, dioxane).

^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 298 K): δ = 67.63 (s, dioxane), 178.38 (s, As*C*O).

IR (nujol mull, cm^{-1}): 1748 (CO)).

Synthesis of (IPr)AsH (3a):



(**3a**

Route I: To a Schlenk tube containing (IPr)AsSiMe$_3$ (0.050 g, 0.093 mmol) in toluene (5 mL) was added CH_3OH (0.4 mL) at room temperature. The resulting reaction mixture was stirred for 1 h at the same temperature. All the volatiles were removed under reduced pressure, washed the residue with cold (–80° C) *n*-pentane (1 mL × 3) and dried under vacuum affording 3a as pale yellow solid. Yield: 0.025 g (58 %).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ = 7.27–7.19 (m, 4H, Ar-H), 7.13 (m, 2H, Ar-H), 6.31 (s, 2H, NC*H*), 3.01 (sept, 4H, $^3J_{(H,H)}$= 7.0 Hz, C*H*(CH$_3$)$_2$), 1.49 (d, 12H, $^3J_{(H,H)}$ = 6.8 Hz, CH(C*H$_3$*)$_2$), 1.43 (s, 1H, As-*H*), 1.14 (d, 12H, $^3J_{(H,H)}$ = 6.9 Hz, CH(C*H$_3$*)$_2$).

^{13}C NMR (C_6D_6, 75.5 MHz, 298 K): δ = 184.5 (N*C*N), 147.5 (N*C*(Dipp)), 135.5 (*o*-*C*(Dipp)), 130.6 (*p*-*C*(Dipp)), 125.3 (*m*-*C*(Dipp)), 121.1 (N*C*H), 29.4 (*C*H(C*H$_3$*)$_2$), 24.9 (CH(C*H$_3$*)$_2$), 24.3 (CH(C*H$_3$*)$_2$).

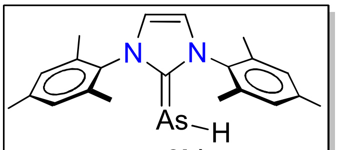
EI-MS (*m/z*): 464.2 (calcd 464.217 g/mol) $[M]^{+\cdot}$ (100 %), 421.1 [M–^{i}Pr] (55 %), 387.3 [M–AsH] (90 %).

Route II: The reaction procedure was carried out under rigorous exclusion of light: 0.110 g (0.24 mmol, 1 eq.) of [IPr-H][Cl] and 0.150 g (0.36 mmol, 1.5 eq.) of [Na(dioxane)$_{3.31}$][AsCO] were suspended in ca. 10 mL THF. The grey suspension was stirred at room temperature overnight. After removal of the solvent *in vacuo* the brownish solid was suspended in hexane and filtered over Celite. The volume of the obtained yellow solution was reduced to 3 mL and stored at –30 °C. After 2 days, the product was isolated as yellow crystalline solid. Yield: 14 mg (13 %). The ^{1}H and ^{13}C NMR spectra are similar to the reported for route I.

Anal. Calcd (%) for $C_{27}H_{37}N_2As$ (464.217 g/mol): C 69.81, H 8.03 and N 6.03; Found: C 68.49, H 7.73 and N 6.65.

IR (nujol mull, cm^{-1}): 2080 (As-H).

Synthesis of (IMes)AsH (3b):


(**3b**)

Route I: To a stirred solution of (IMes)AsSiMe$_3$ (0.230 g, 0.508 mmol) in toluene (15 mL), excess dry CH_3OH (0.652 mL, 20.349 mmol) was added at room temperature. The resulting solution was stirred for 5 h at 45 °C. All volatiles were then removed *in vacuo*, extracted with toluene and the solvent removed under vacuum. The residue obtained was quickly washed with *n*-pentane (1 mL × 7) and dried to afford compound 3b as a pale yellow to white solid. Yield; 0.123 g (64 %).

^{1}H NMR (C_6D_6, 300.1 MHz, 298 K): δ = 6.76–6.74 (m, 4H, *m*-Ar-*H*), 6.00 (d, 2H, $^5J_{(H,H)}$ = 0.45 Hz, NC*H*), 2.19 (s, 12H, *o*-C*H$_3$*), 2.07 (6H, *p*-C*H$_3$*), 1.47 (t, $^5J_{(H,H)}$ = 0.45 Hz, As-*H*).

^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz, 298 K): δ = 179.4 (N*C*N), 139.3 (N-*C*(Mes)), 136.5 (*o*-*C*(Mes)), 135.4 (*p*-*C*(Mes)), 130.1 (*m*-*C*(Mes)), 119.5 (N*C*H), 21.4 (*p*-*C*H$_3$), 18.6 (*o*-*C*H$_3$).

Anal. Calcd (%) for $C_{21}H_{25}N_2As$ (380.123 g/mol): C 66.31, H 6.62 and N 7.37; Found: C 66.86, H 6.57 and N 7.59.

EI-MS (*m/z*): 380.1 (calcd 380.1233) $[M]^{+\cdot}$ (60%), 365.1[M–CH_3] (8%), [M–AsH] (100 %).

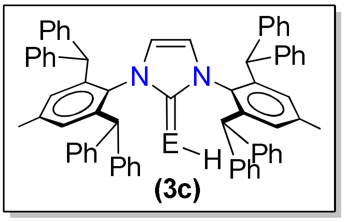
Note: The reaction was performed under the exclusion of light and the solid obtained was stored at –30 °C. Over a period of time, NMR samples in C_6D_6 always showed the formation of a black insoluble solid at room temperature.

Route II: A grey suspension of 0.200 g (0.59 mmol, 1 eq.) [(IMes)H][Cl] and 0.290 g (0.70 mmol, 1.2 eq.) [Na(dioxane)$_{3.31}$][AsCO] in 10 mL THF was stirred at room temperature for 2 h. After removal of the solvent *in vacuo*, the brownish solid was suspended in toluene and filtrated over Celite. The resulting yellow solution was concentrated to a volume of 5 mL and stored at –30 °C. After 2 days the yellow blocks formed were filtered and dried under vacuum to obtain 3b. Yield: 30 mg (15%). The ^{1}H and ^{13}C NMR spectra are similar to the reported for route I.

Anal. Calcd (%) for $C_{21}H_{25}N_2As$ (380.358 g/mol): C 66.31, H 6.62 and N 7.37; found: C 66.89, H 6.70 and N 7.38.

IR (nujol mull, cm^{-1}): 2059 (As-H).

Synthesis of [(IAr*)AsH] (3c):



Route II: The reaction procedure was carried out under rigorous exclusion of light. A light brown suspension of 0.200 g (0.21 mmol, 1 eq.) [(IAr*)H]Cl and 0.110 g (0.27 mmol, 1.3 eq.) [Na(dioxane)$_{3.31}$][AsCO] in ca. 10 mL THF was stirred at room temperature overnight. After the removal of the solvent under vacuum, the brown solid was suspended in toluene and filtered over Celite. The volume of the brownish solution was reduced to 3 mL and stored at –30 °C. After 5 days, the product was obtained as light yellow crystalline solid. Yield: 18 mg (9 %).

^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 7.85 (d, $^3J_{(H,H)}$ = 7.6 Hz, 8 H, *o*-CH_{Ph}), 7.20 (t, $^3J_{(H,H)}$ = 7.6 Hz, 8 H, *m*-CH_{Ph}),7.10 (s, 4 H, *p*-CH_{Ph}), 6.96 (s, 20 H, CH_{Ph}), 5.96 (s, 4 H, *m*-C*H*), 5.19 (s, 2 H, NC*H*), 2.26 (s, 1 H, As*H*), 1.72 (s, 6 H, CH_3).

^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K); δ = 180.9 (N*C*N), 143.6 (s, *C*), 144.4 (s, *C*), 143.0 (s, *C*), 140.2 (s, *C*), 134.7 (s, *C*), 131.1 (s, *C*H), 130.8 (s, *C*H), 130.0 (s, *C*H), 128.7 (s, *C*H), 128.4 (s, *C*H), 127.0 (s, *C*H), 126.5 (s, *C*H), 120.9 (s, *C*H), 52.3 (s, Ph$_2$*C*H), 21.4 (s, *C*H_3).

Anal. Calcd (%) for $C_{69}H_{57}N_2As$ (988.373 g/mol): C 83.78, H 5.81 and N 2.83; Found: C 83.44, H 5.82 and N 2.89.

IR (nujol mull, cm^{-1}): 2090 (As–H).

Note: The low yields for 3a, 3b and 3c by route-II are due to the fractional crystallization in order to obtain product free of carbene as the crude extract always contained 20-30 % of the respective free carbene.

3.5.2. NMR data and other spectra

[(IMes)Cl]Cl:

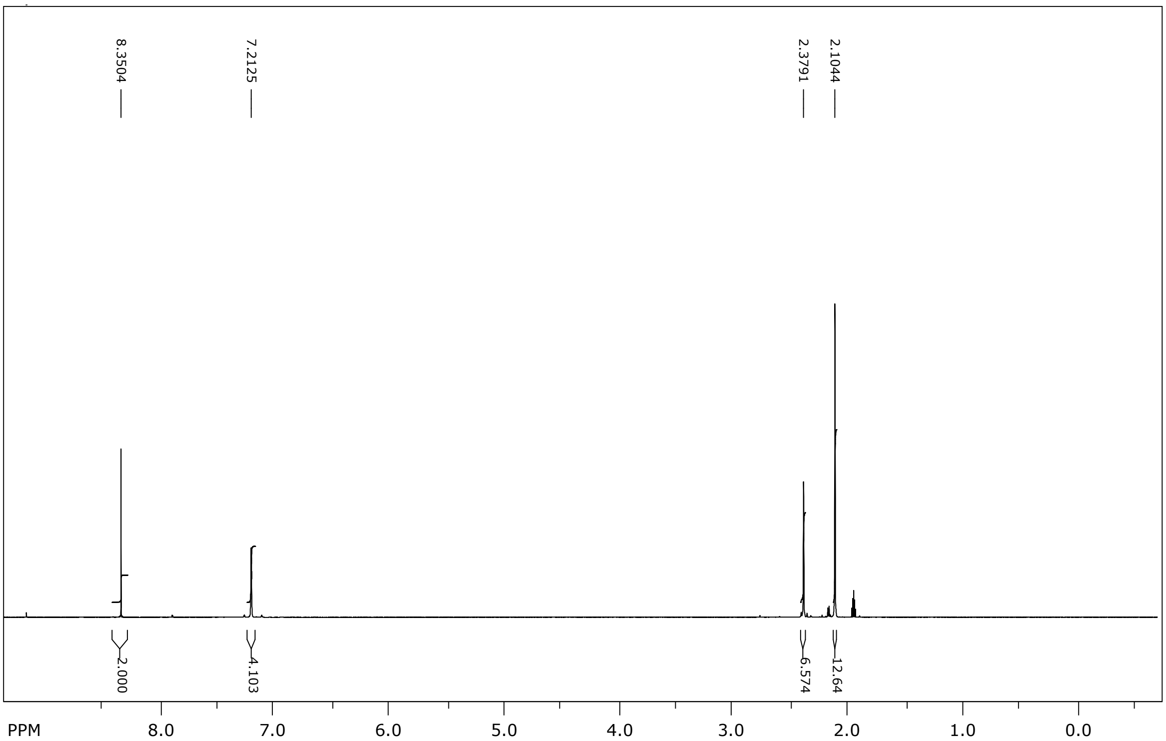


Figure S1: ^{1}H NMR spectrum of chloro-imidazolium chloride [(IMes)Cl]Cl in CD_3CN at room temperature.

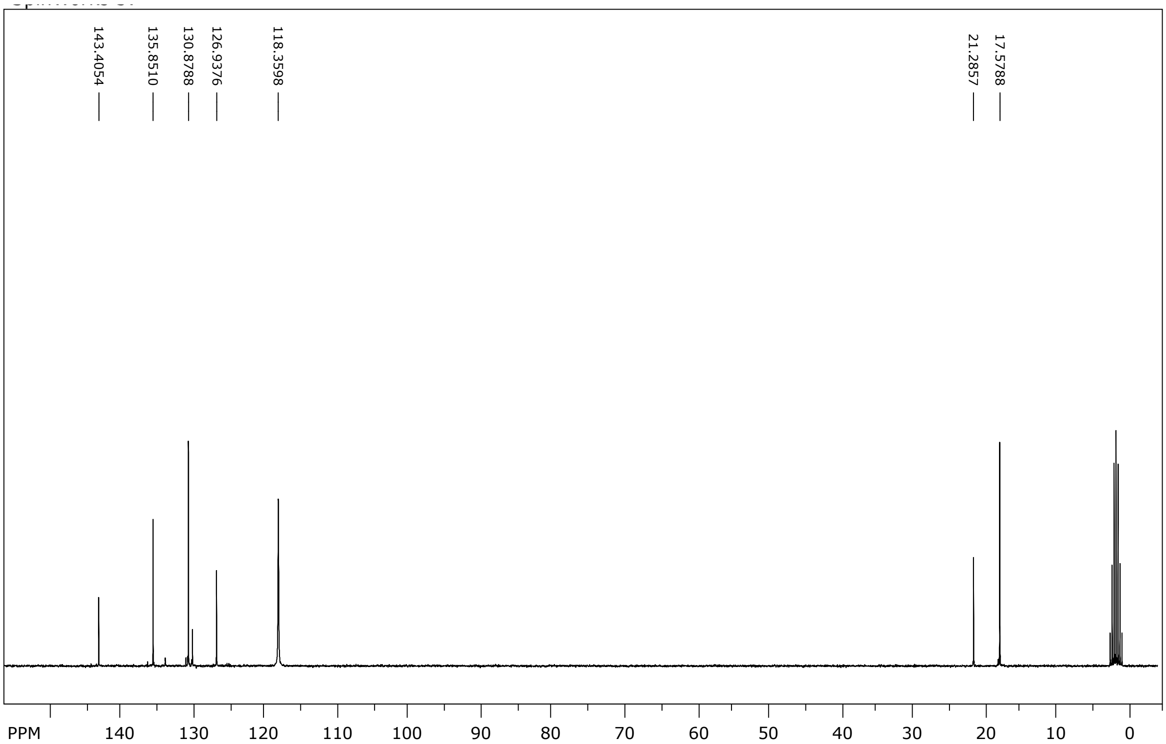


Figure S2: ^{13}C NMR spectrum of [(IMes)Cl]Cl in CD_3CN at room temperature.

[(IMes)F₂:

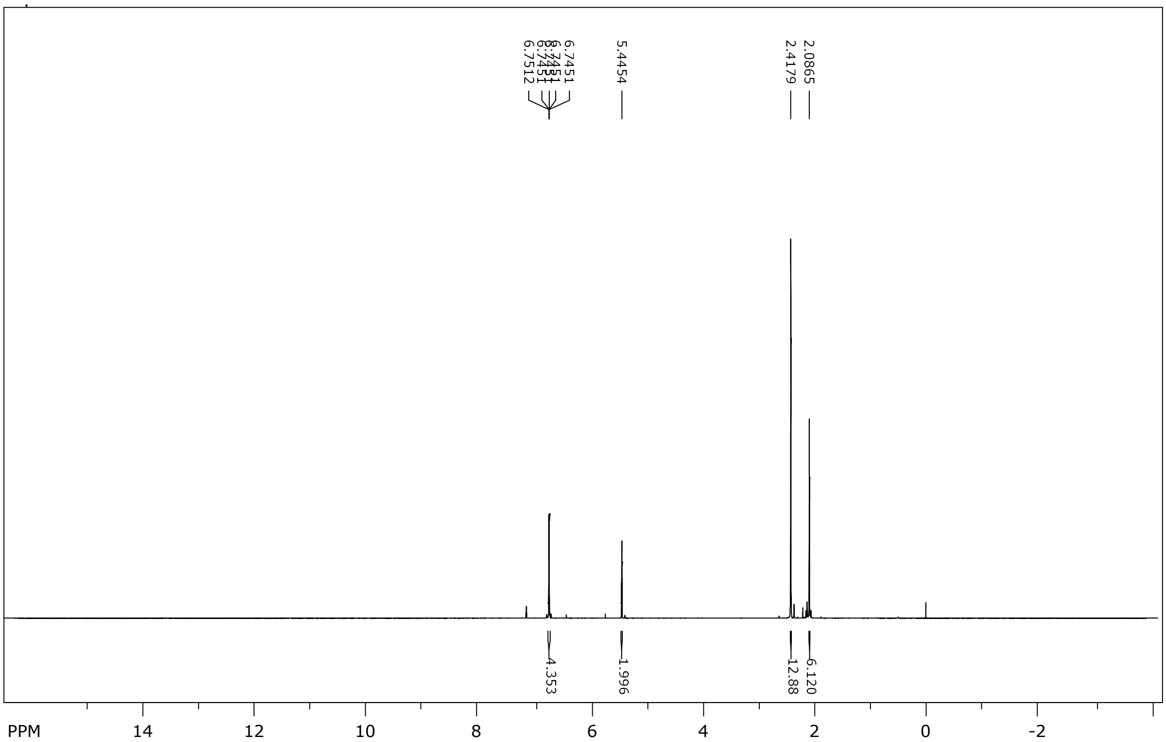


Figure S3: [1]H NMR spectrum of (IMes)F_2 (**1b**) in C_6D_6 at room temperature.

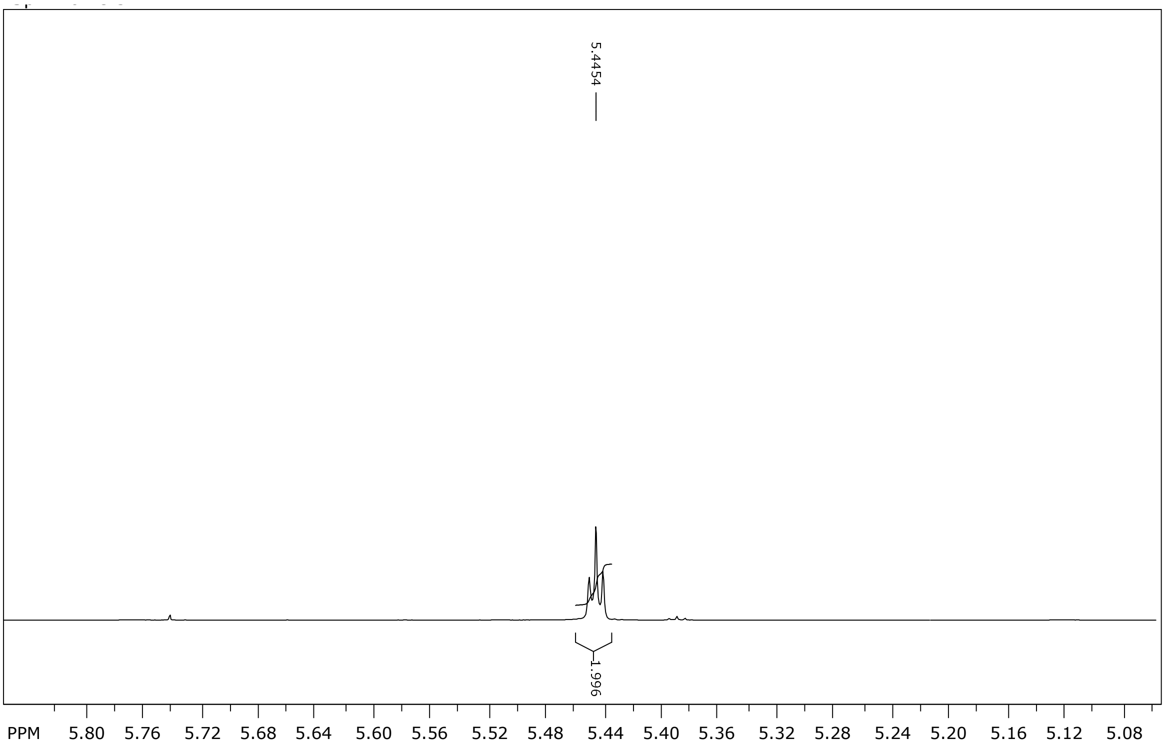


Figure S4: [1]H NMR spectrum (expanded) of (IMes)F_2 (**1a**) in C_6D_6 at room temperature.

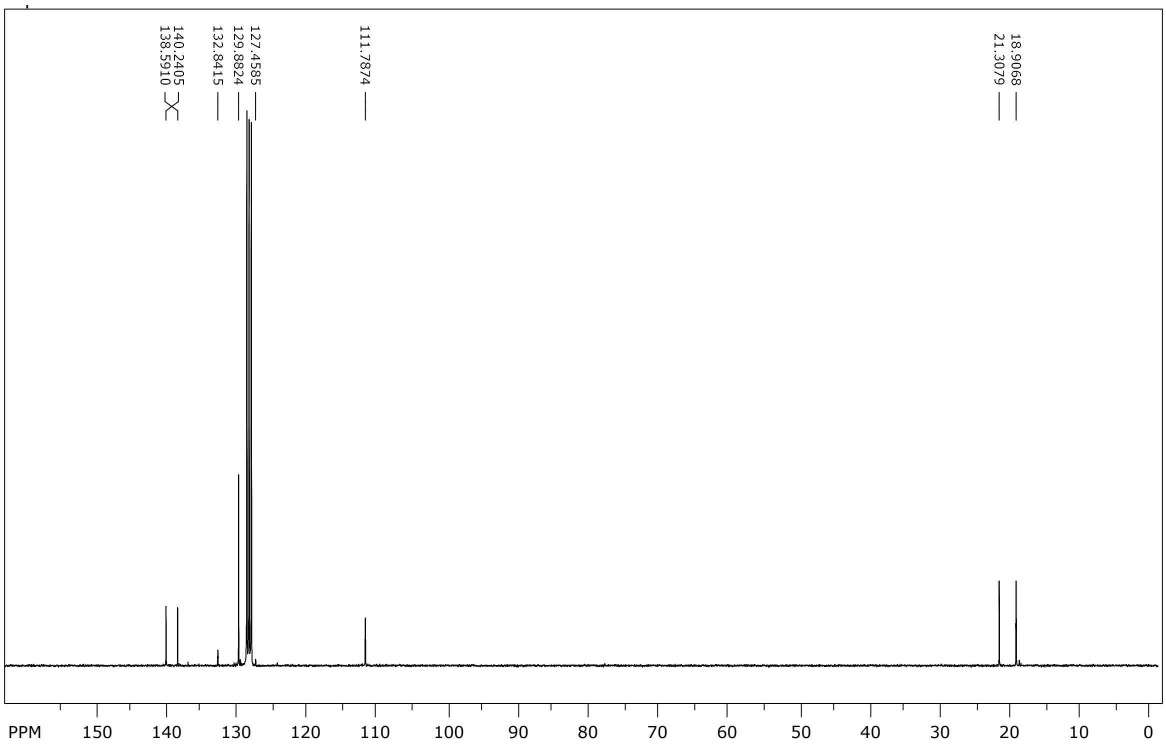


Figure S5: ^{13}C NMR spectrum of (IMes)F_2 (**1b**) at room temperature.

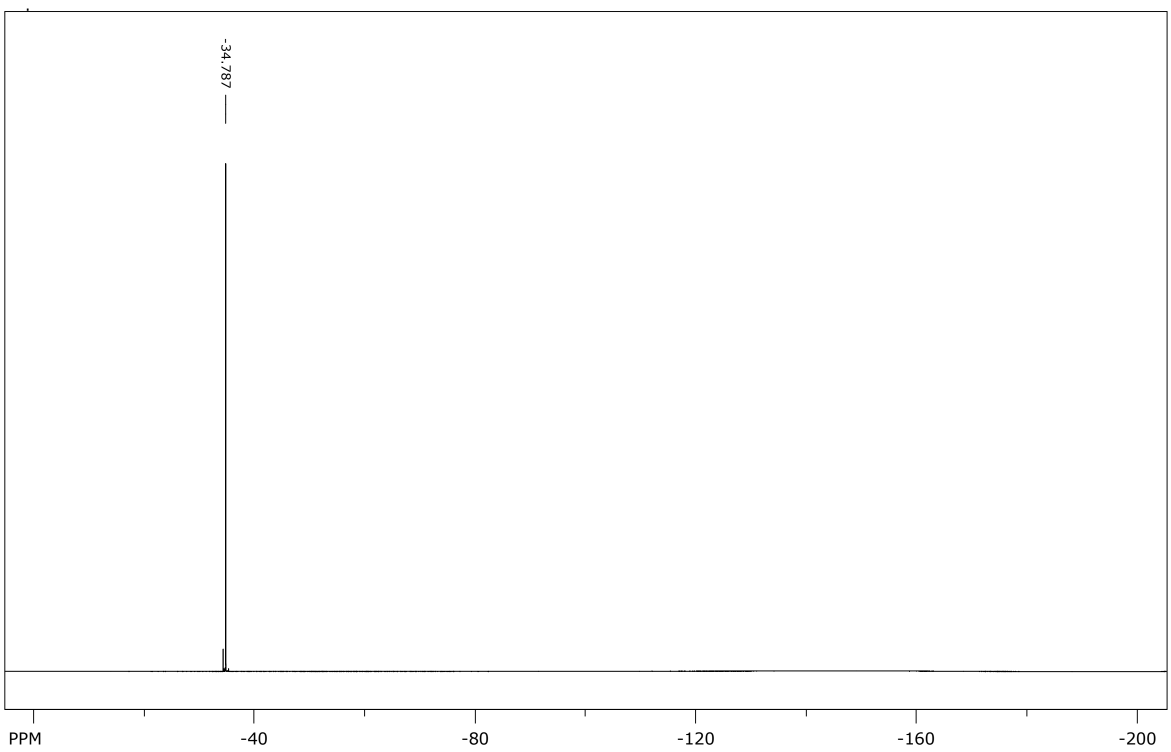


Figure S6: ^{19}F NMR spectrum of **(**IMes)F_2 (**1b**) at room temperature.

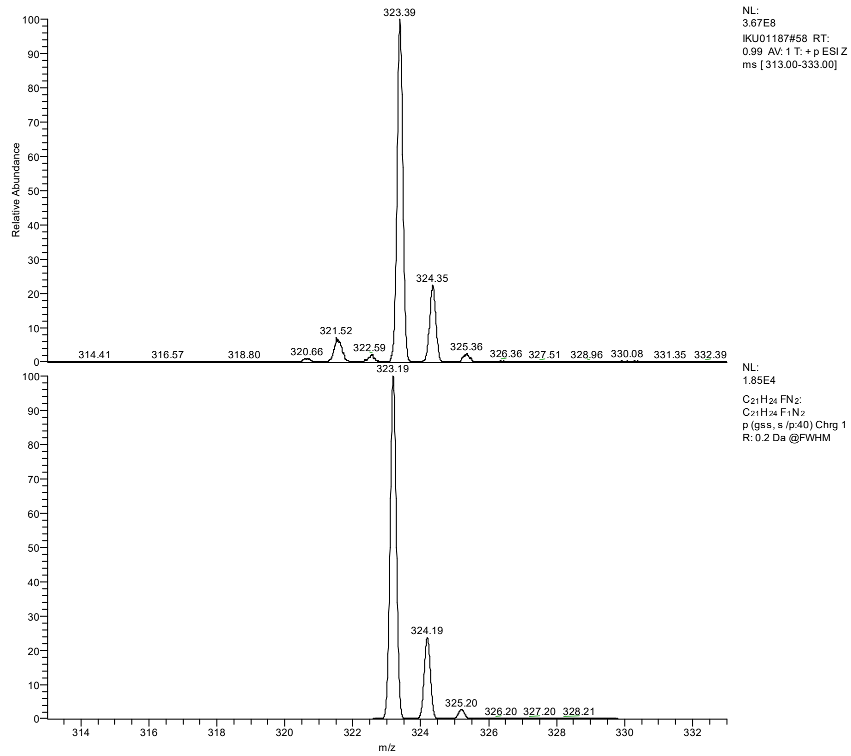


Figure S7: ESI-MS of (IMes)F_2 (in acetonitrile) (**1b**). Isotopic pattern of the experimental sample (top) and calculated (bottom).

[(IPr)AsSi(CH_3)$_3$]

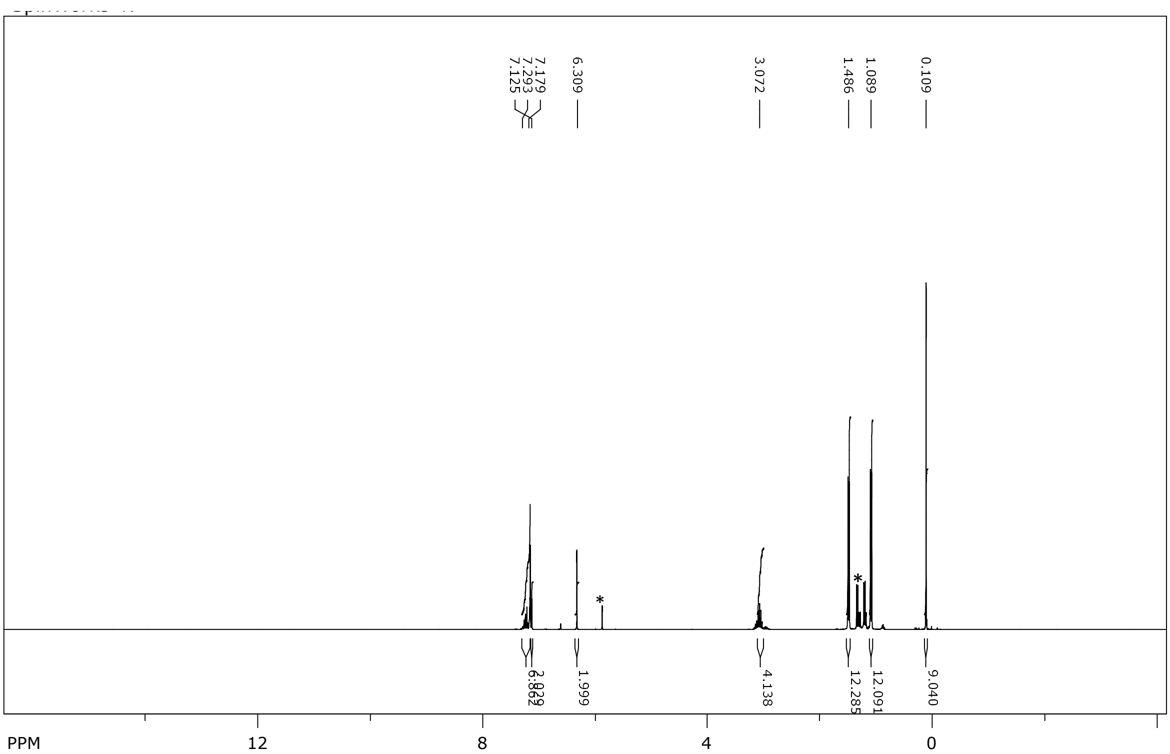


Figure S8: [1]H NMR spectrum of [(IPr)AsSi(CH_3)$_3$] (**2a**) in C_6D_6 (* Despite many attempts, other impurities could not be removed).

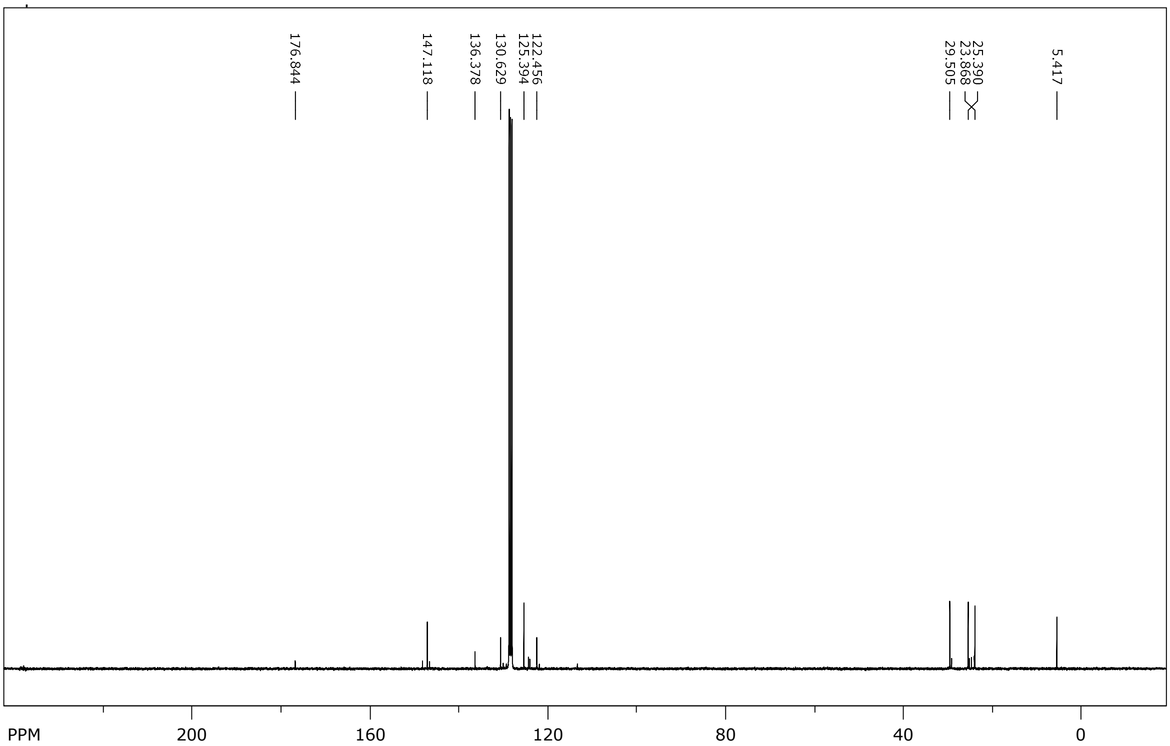


Figure S9: ^{13}C NMR spectrum of [(IPr)AsSi(CH_3)$_3$] (**2a**) in C_6D_6.

[(IMes)AsSi(CH_3)$_3$]

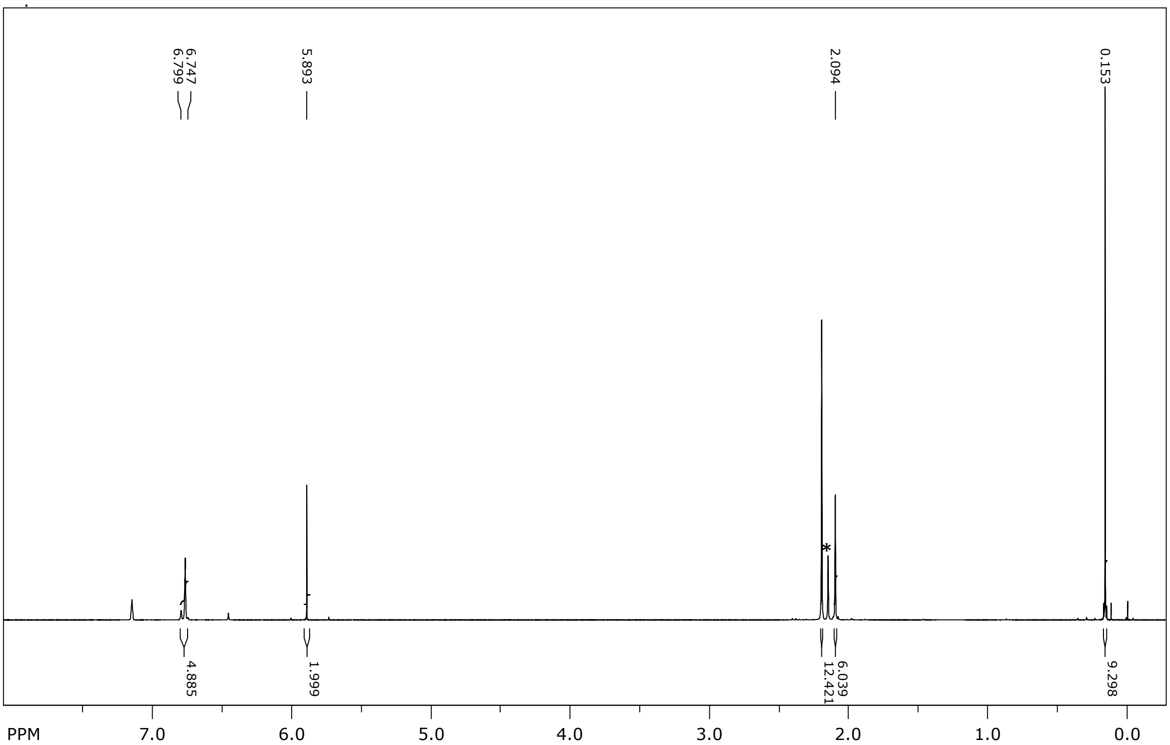


Figure S10: ^{1}H NMR spectrum of [(IMes)AsSi(CH_3)$_3$] (**2b**) in C_6D_6 at room temperature (*impurity).

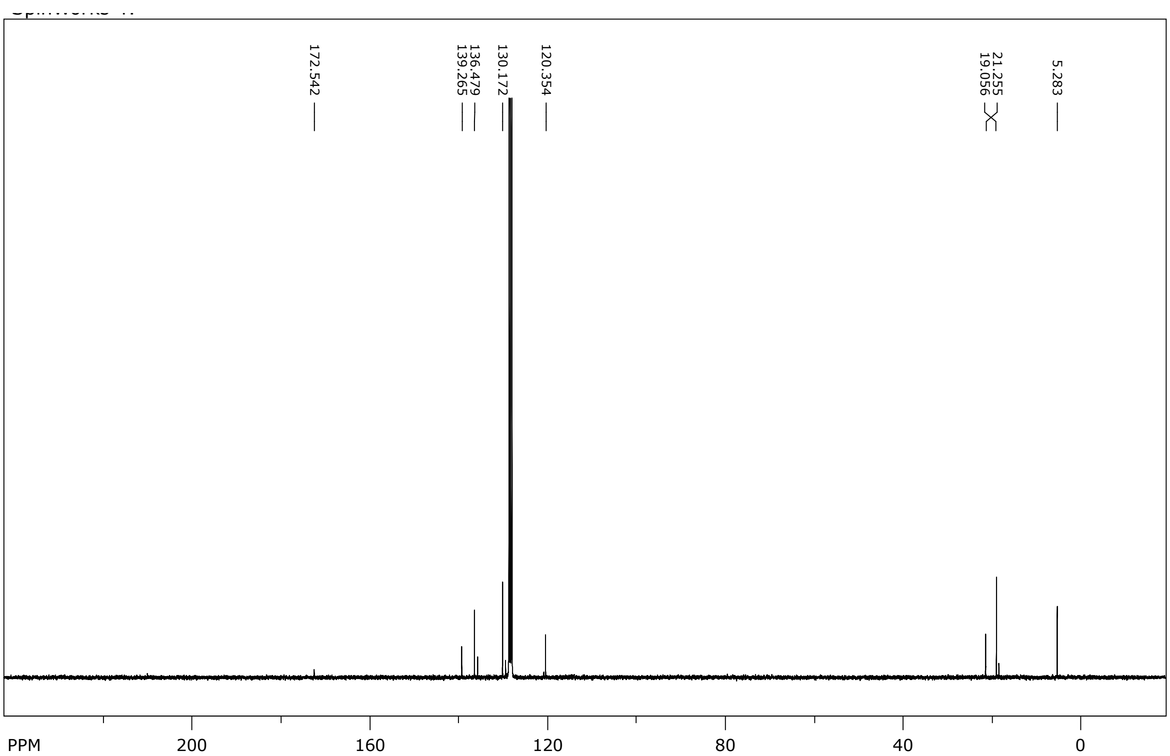


Figure S11: ^{13}C NMR spectrum of [(IMes)AsSi(CH$_3$)$_3$] (**2b**) in C_6D_6 at room temperature.

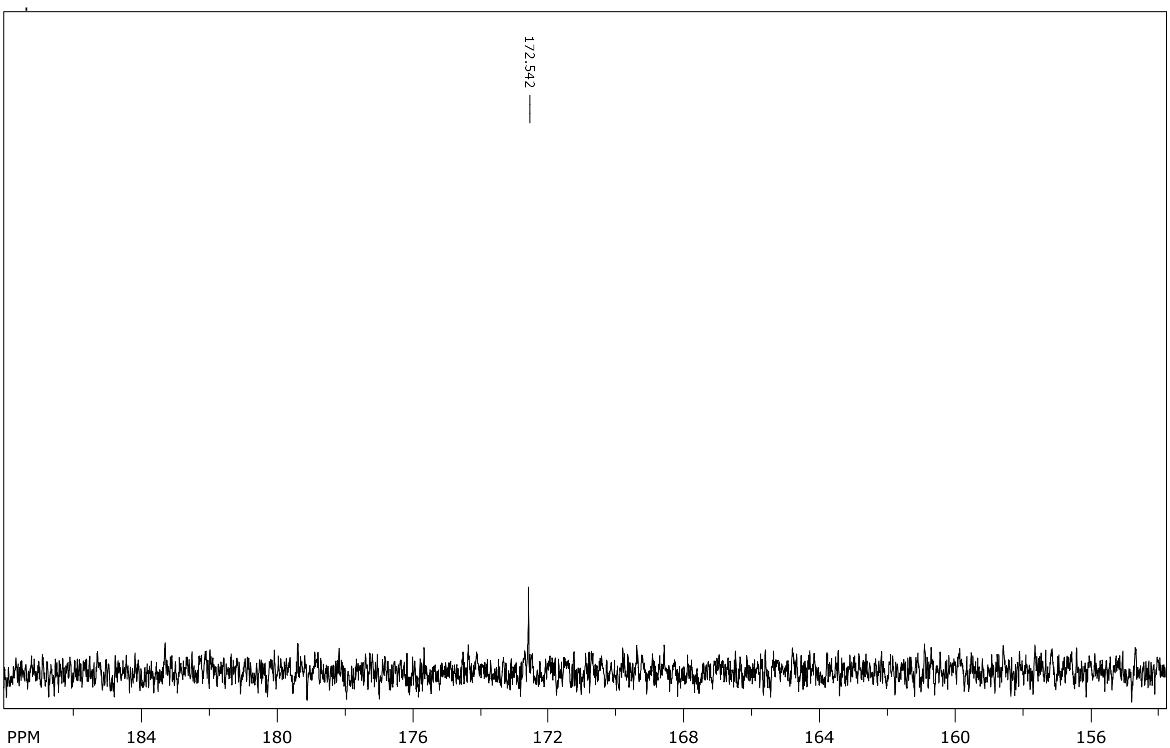


Figure S12: ^{13}C NMR spectrum of [(IMes)AsSi(CH$_3$)$_3$] (**2b**) in C_6D_6 (expanded).

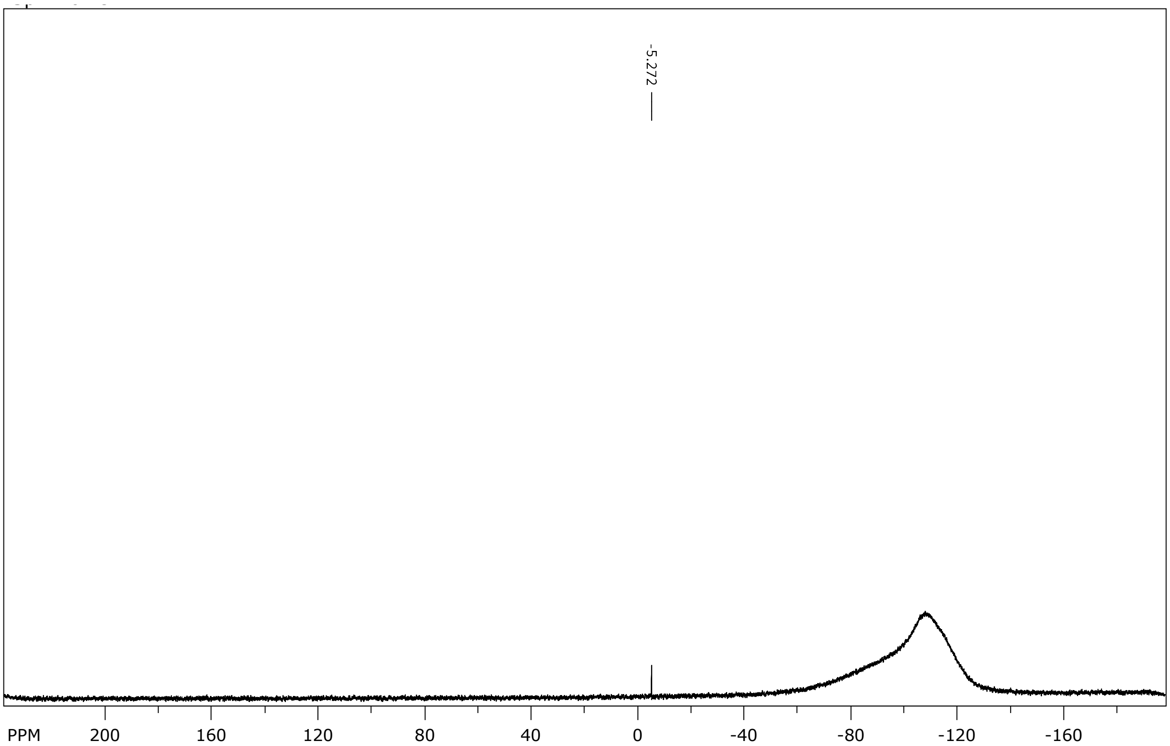


Figure S13: ^{29}Si NMR spectrum of [(IMes)AsSi(CH_3)$_3$] (**2b**) in C_6D_6 at room temperature.

[(IPr)AsH]:

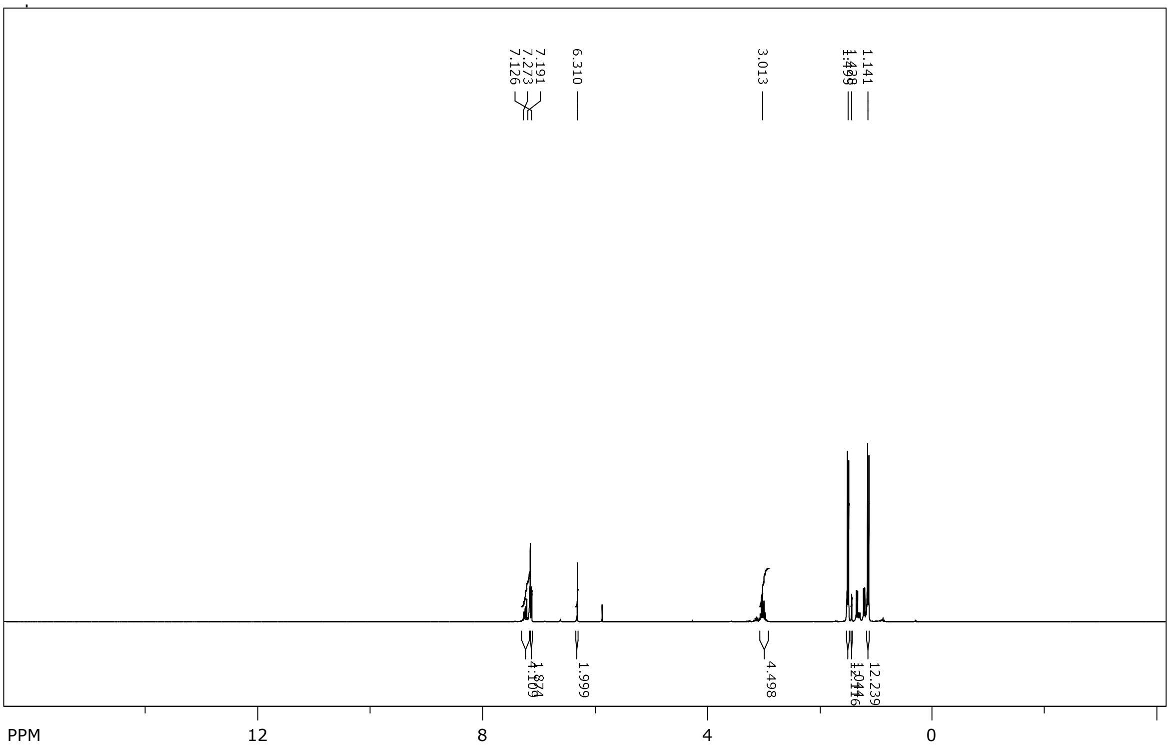


Figure S14: ^{1}H NMR spectrum of [(IPr)AsH] (**3a**) in C_6D_6 at 298 K (route-I).

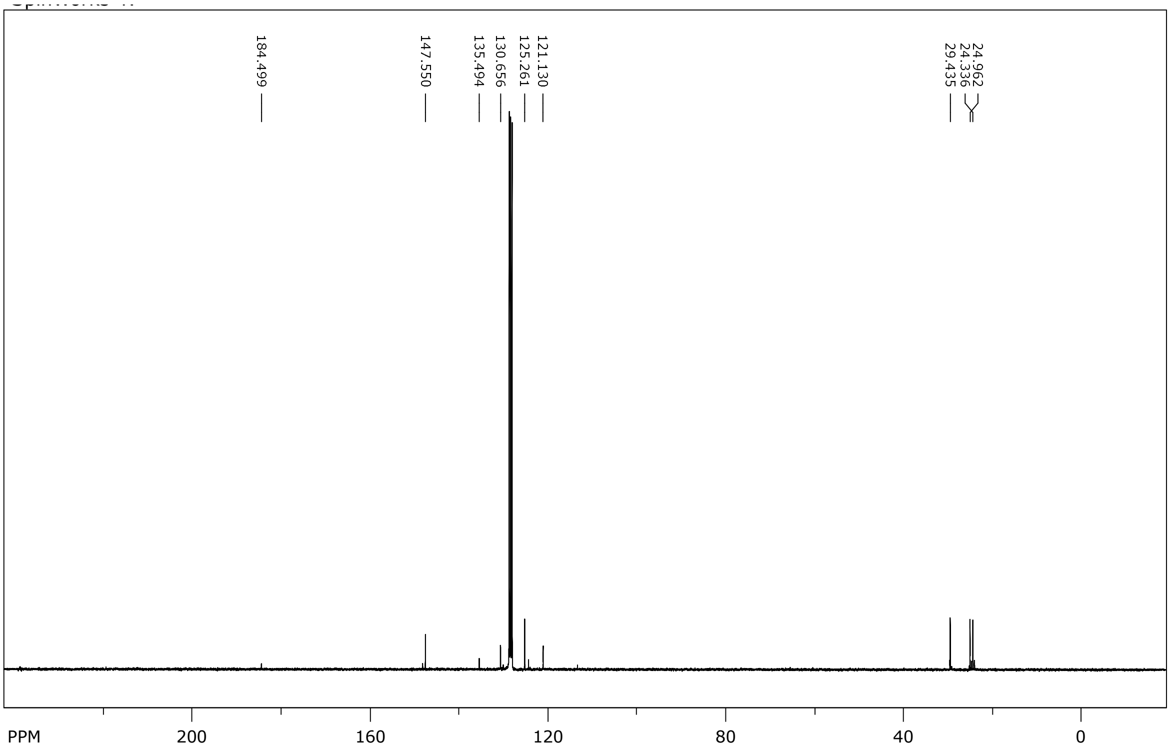


Figure S15: ^{13}C NMR spectrum of [(IPr)AsH] (**3a**) in C_6D_6 at 298 K (route-I).

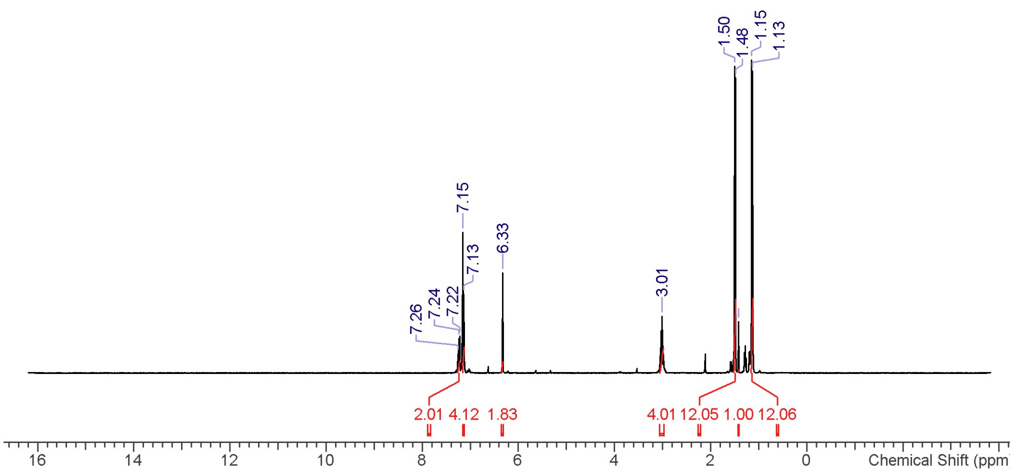


Figure S16: ^{1}H NMR spectrum of [(IPr)AsH] (**3a**) (route-II).

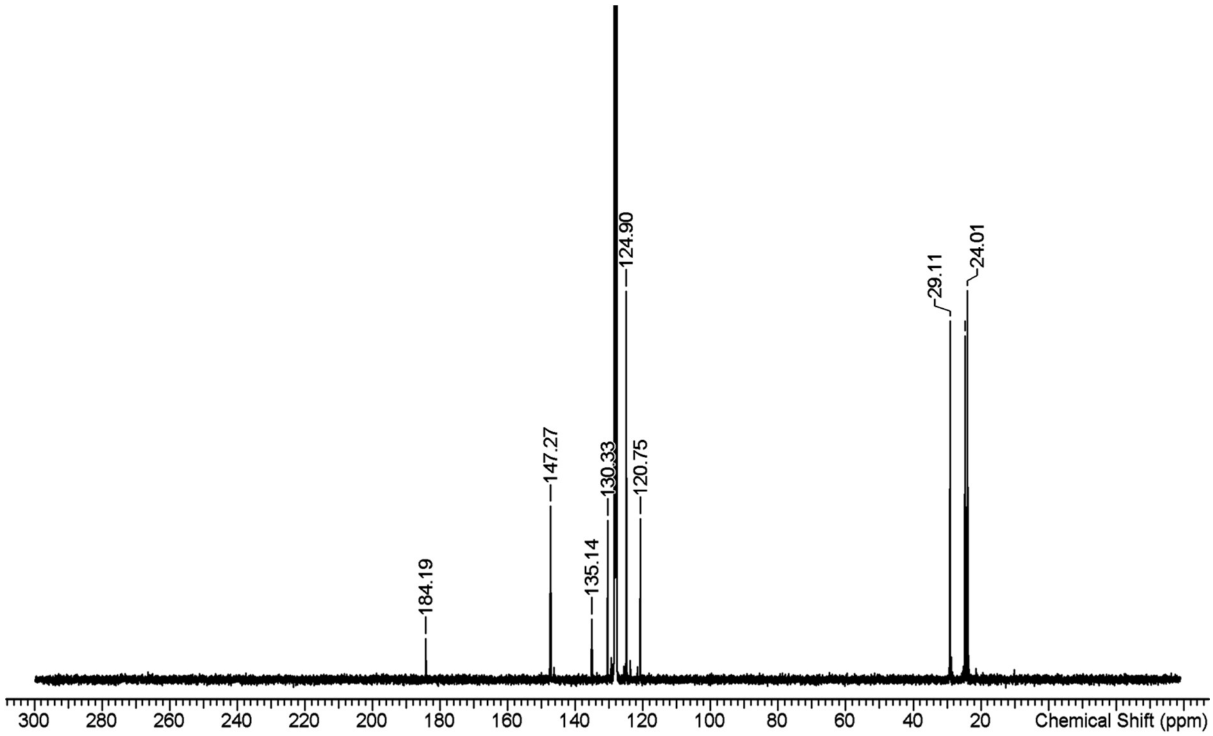


Figure S17: $^{13}C\{^1H\}$ NMR spectrum of [(IPr)AsH] (**3a**) (route-II).

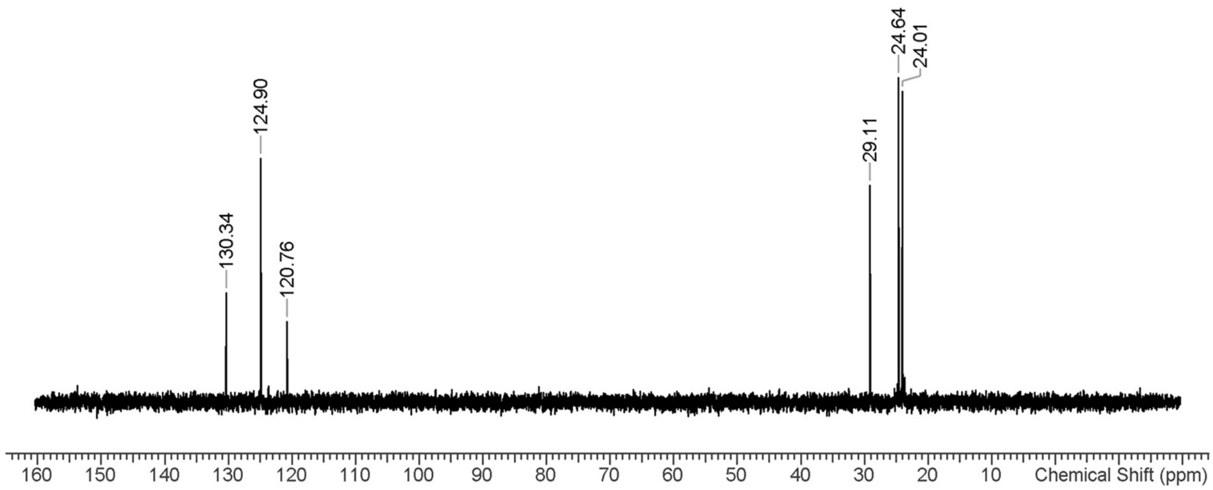


Figure S18: ^{13}C DEPT NMR spectrum of [(IPr)AsH] (**3a**) (route-II).

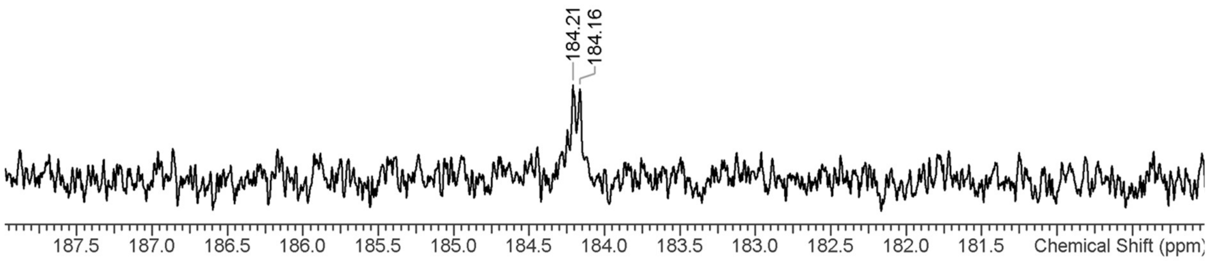


Figure S19: ^{13}C NMR spectrum of [(IPr)AsH] (**3a**) (route-II).

[(IMes)AsH]:

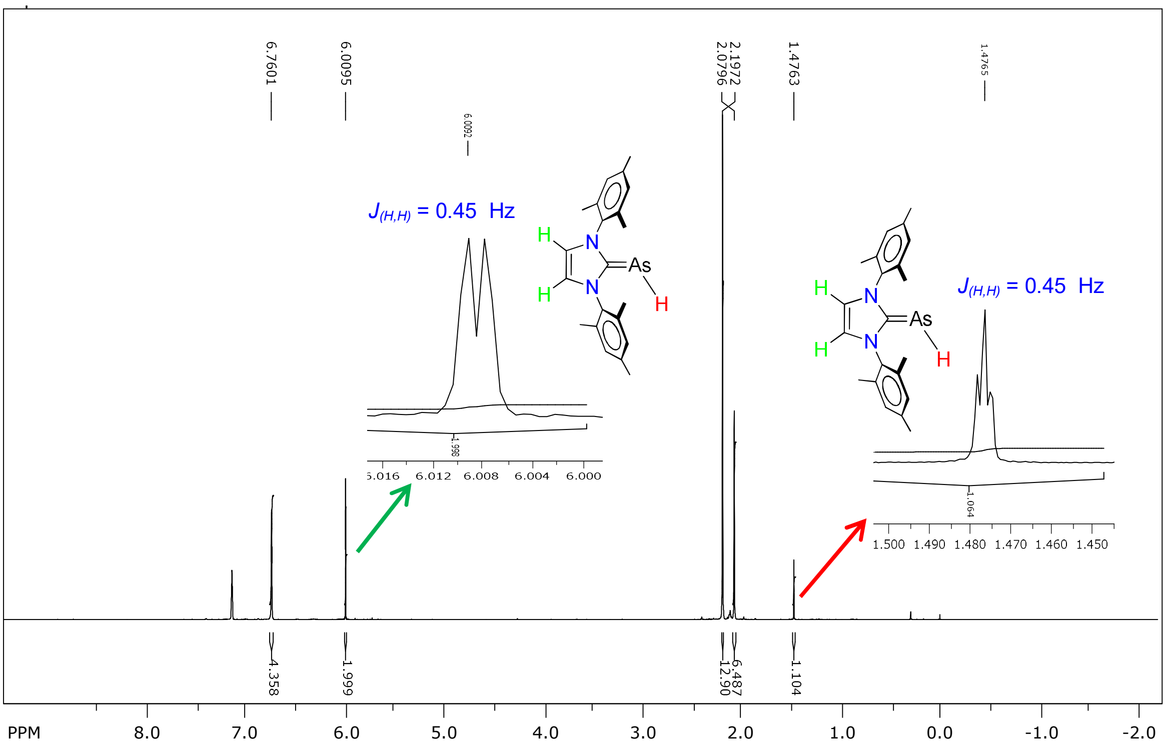


Figure S20: ^{1}H NMR spectrum of [(IMes)AsH] (**3b**) in C_6D_6 at RT (route-1).

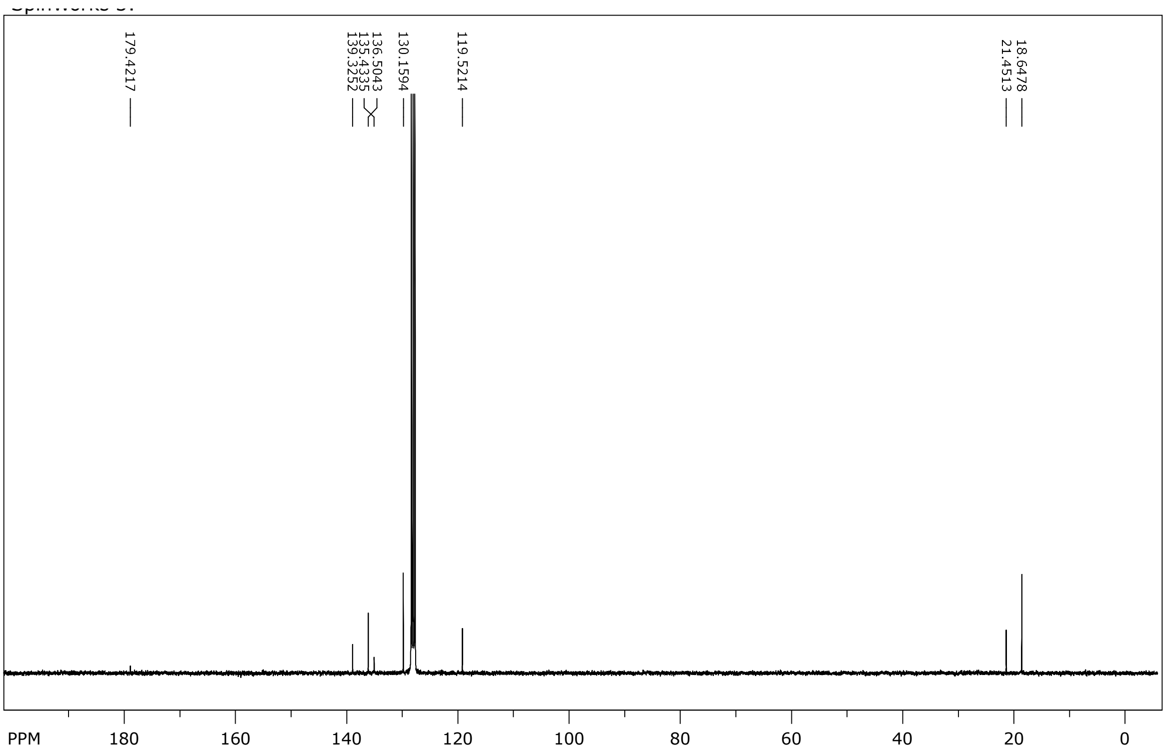


Figure S21: ^{13}C NMR spectrum of [(IMes)AsH] (**3b**) in C_6D_6 at RT (route-1).

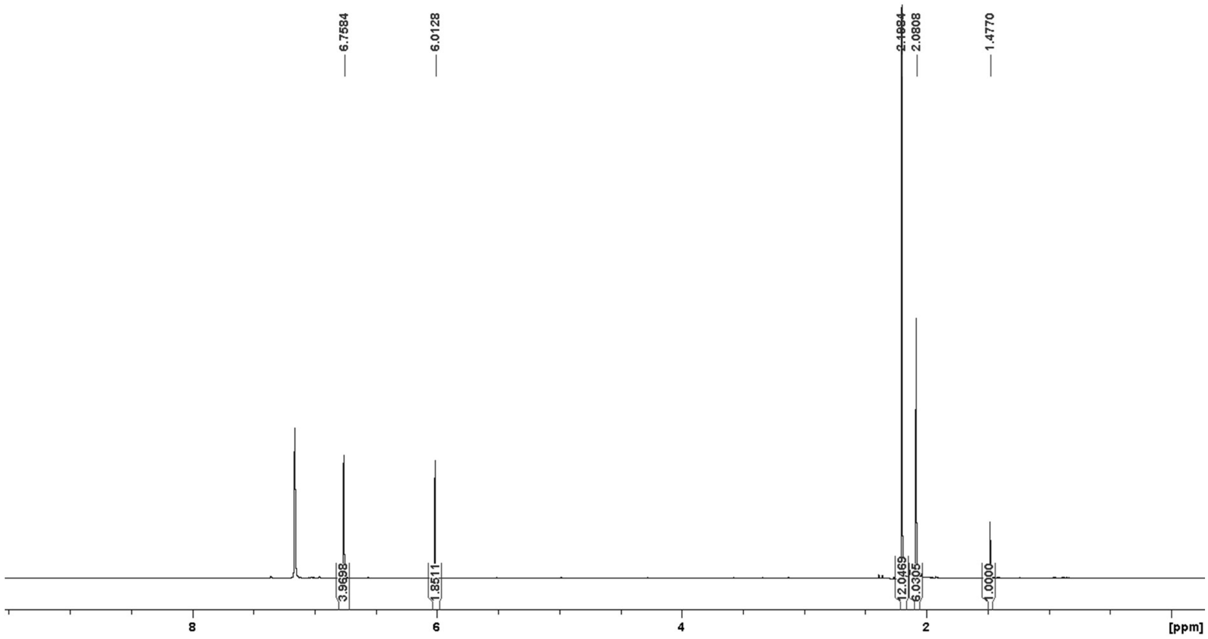


Figure S22: ^{1}H NMR spectrum of [(IMes)AsH] (**3b**) by route-II**.**

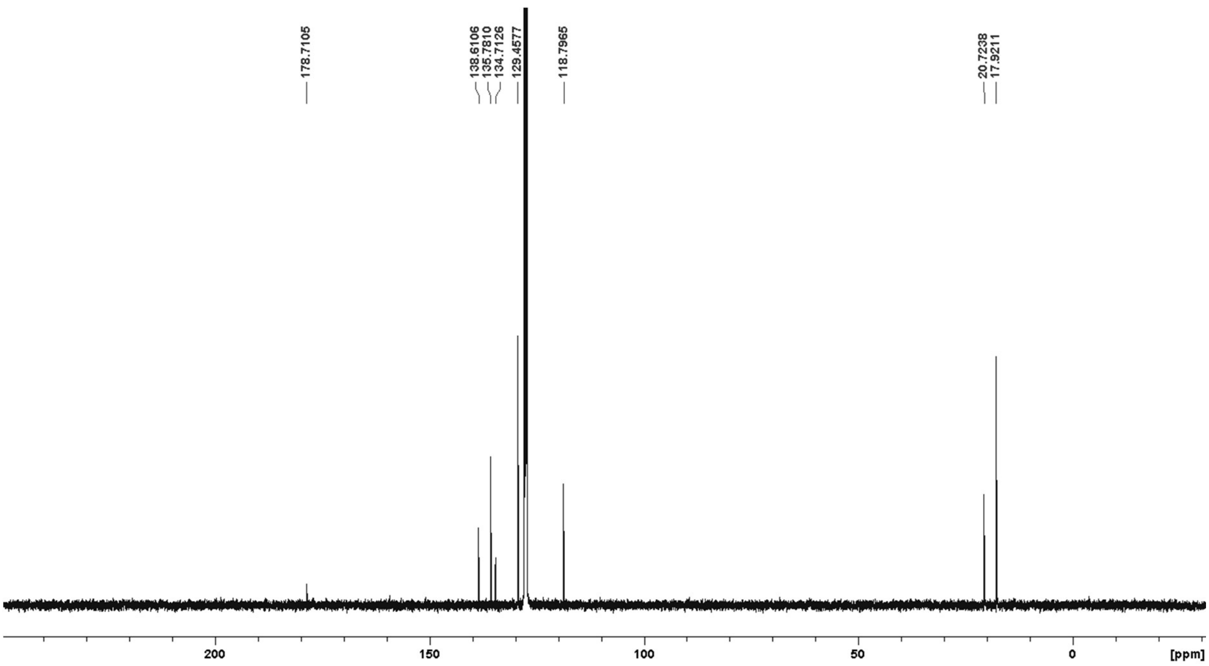


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of [(IMes)AsH] (**3b**) by route-II**.**

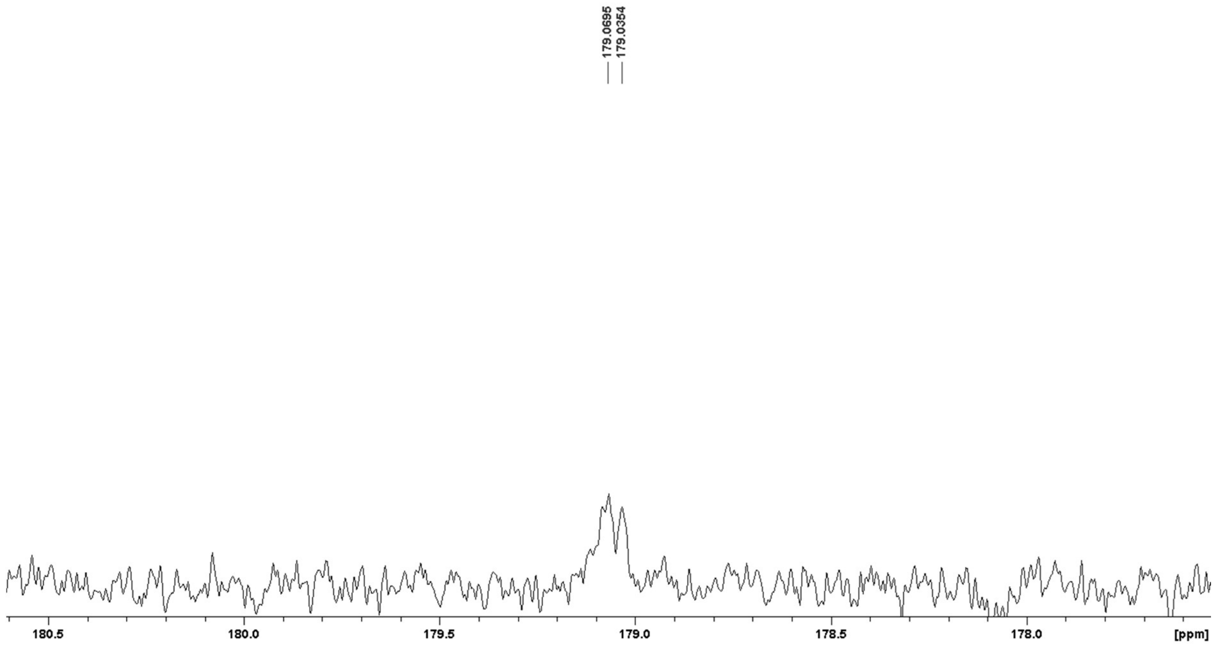


Figure S24: ^{13}C NMR spectrum of [(IMes)AsH] (**3b**) by route-II.

[(IAr*)AsH]:

MW083.001.001.1r.esp

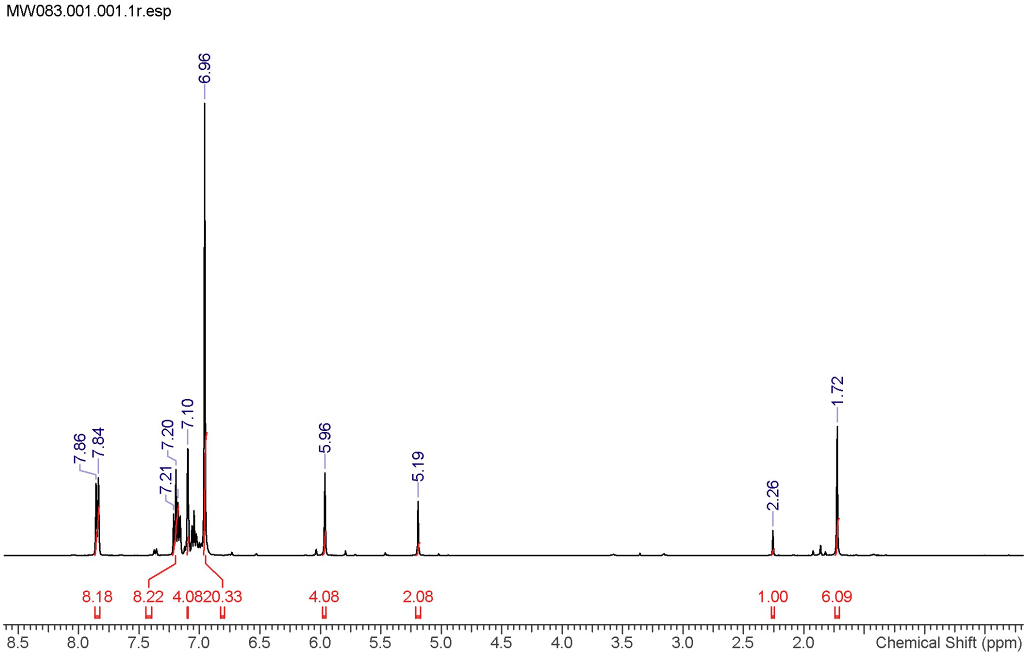


Figure S25: ^{1}H NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6.

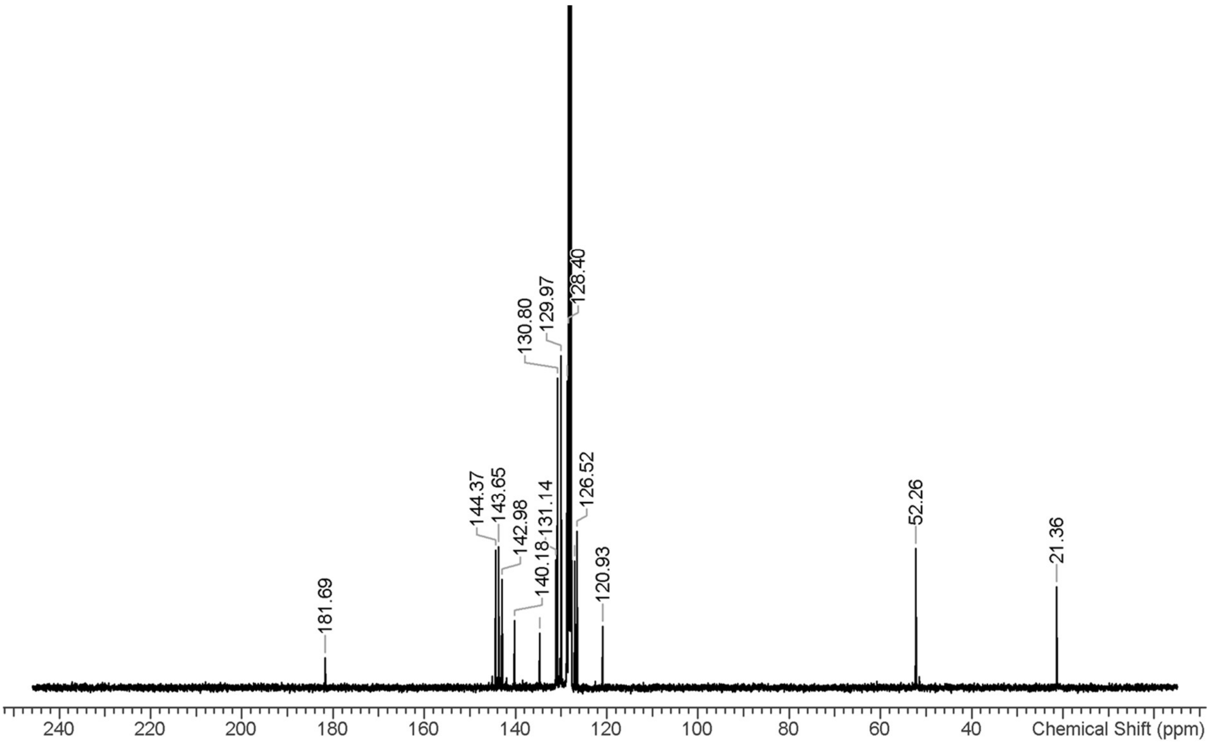


Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6 .

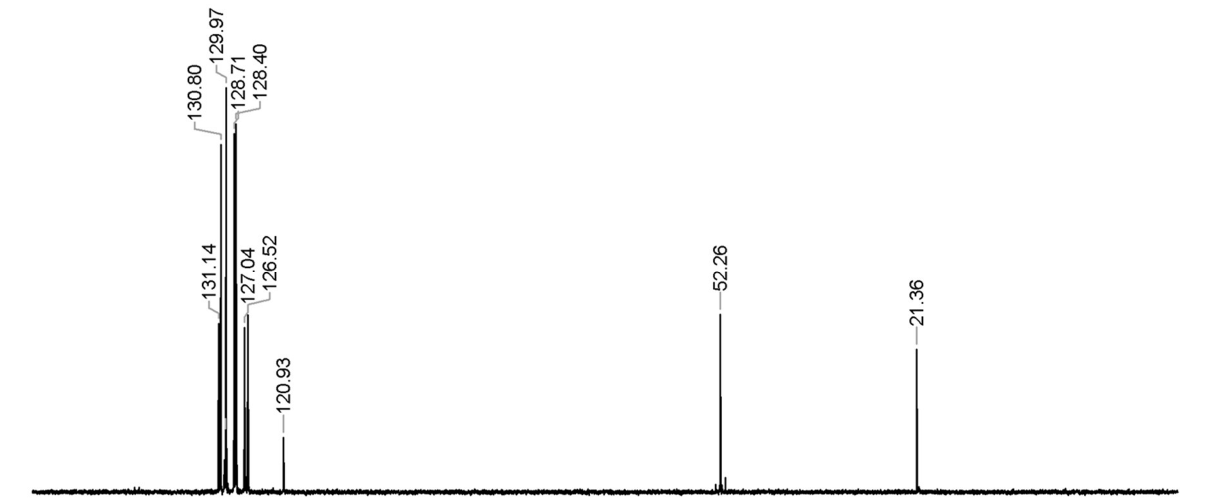


Figure S27: ^{13}C DEPT NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6.

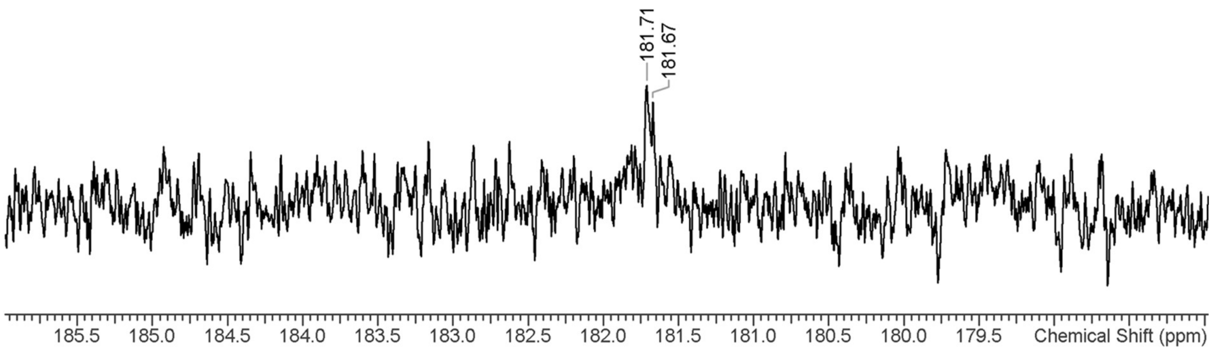


Figure S28: ^{13}C NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6.

[Na(dioxane)$_x$][AsCO]:

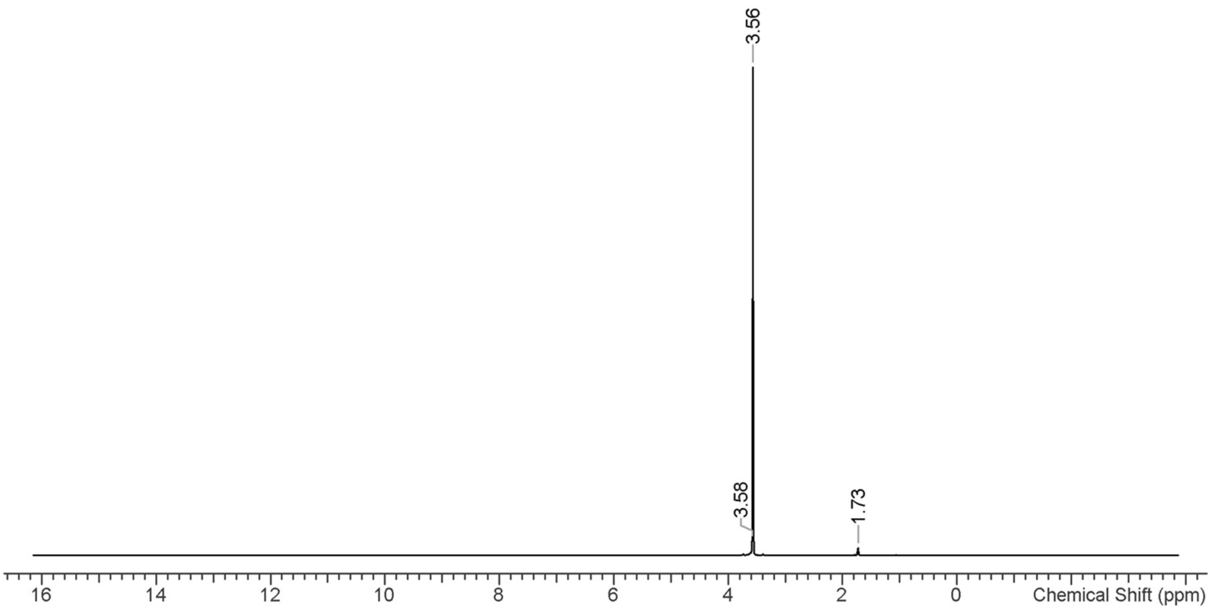


Figure S29: ^{1}H NMR spectrum of [Na(dioxane)$_x$][AsCO] in [D$_8$]-THF.

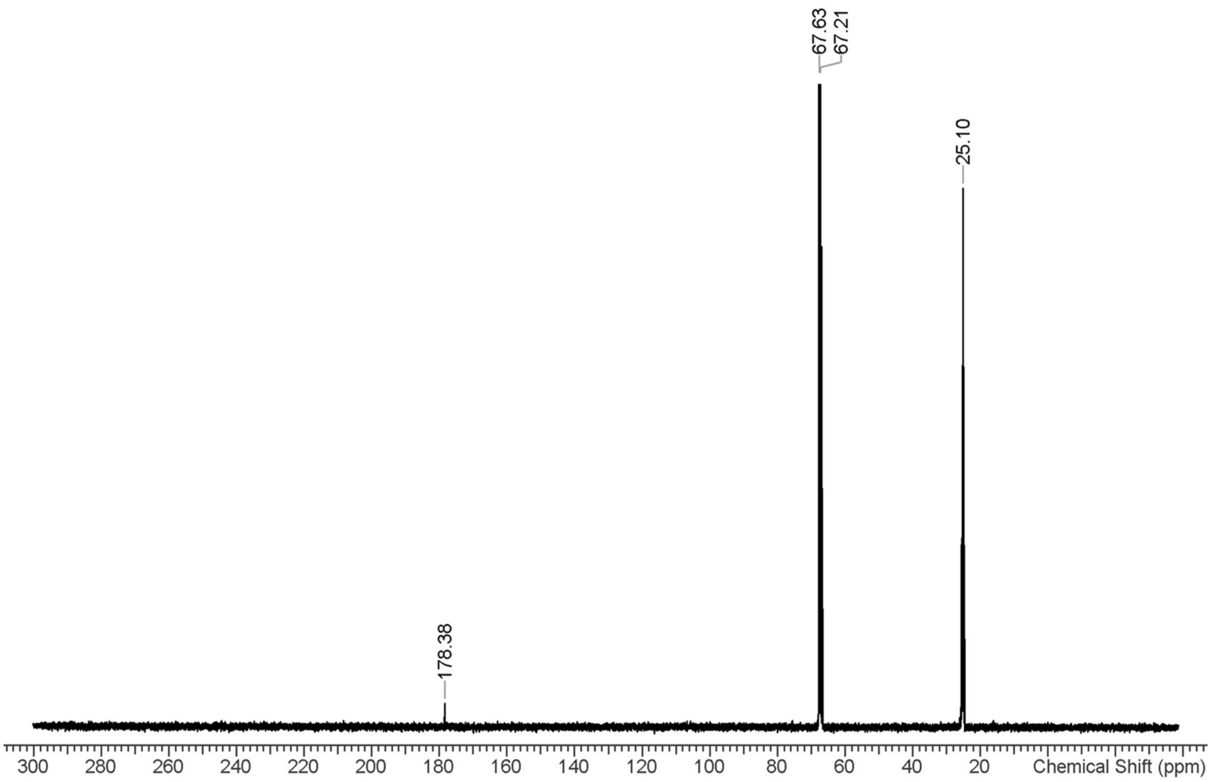


Figure S30: ^{13}C {^{1}H} NMR spectrum of [Na(dioxane)$_x$][AsCO] in [D$_8$]-THF.

VT NMR Studies (Variable temperature NMR spectra) of the NHC-parent arsinidene adduct [(IMes)AsH] (3b)

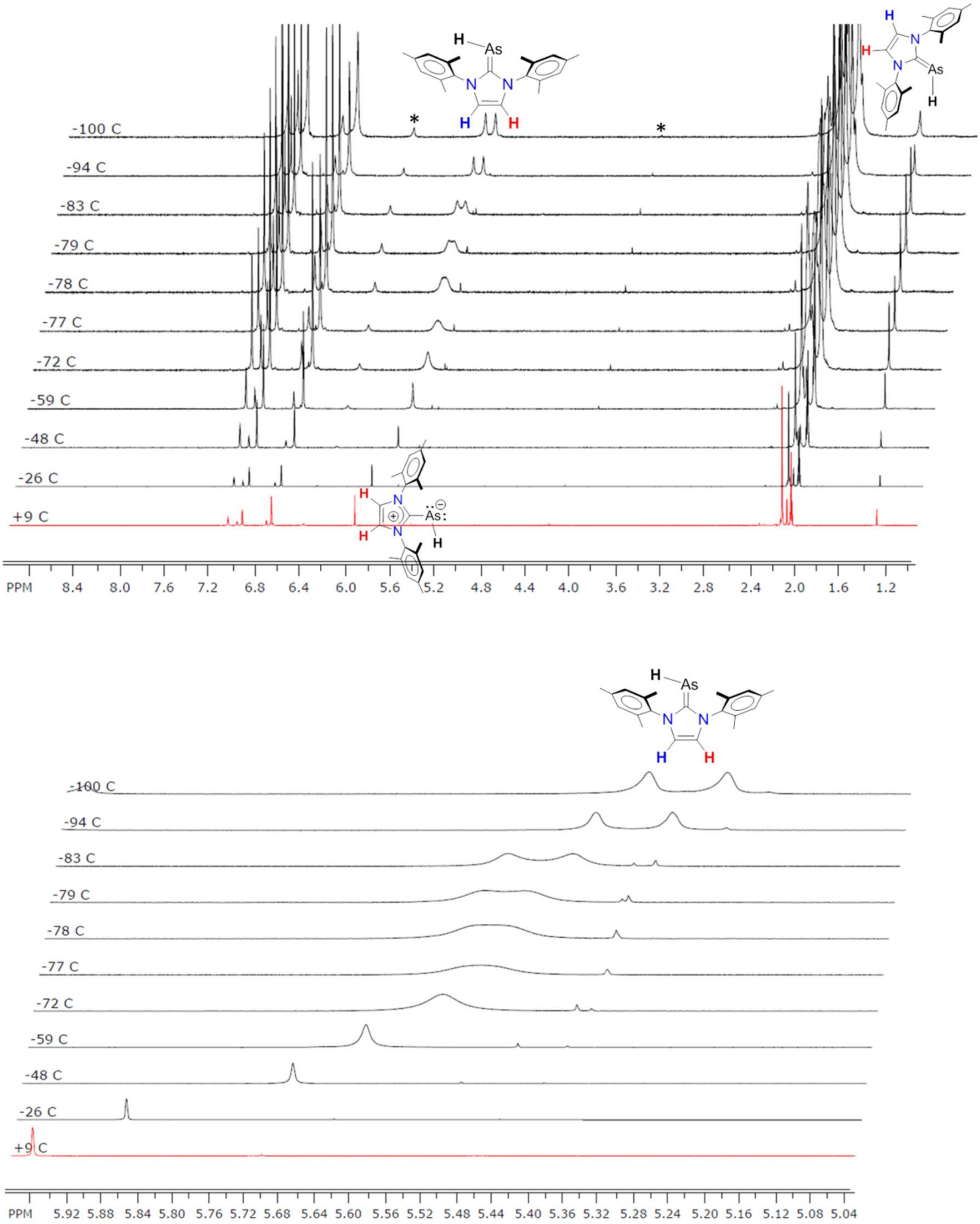


Figure S31: ^{1}H NMR of the carbene-parent arsinidene adduct [(IMes)AsH] (**3a**) at different temperatures in tol-d[8] (* = impurities).

Estimation of barrier rotation of NHC-parent arsinidene adduct (3b) by NMR spectroscopy

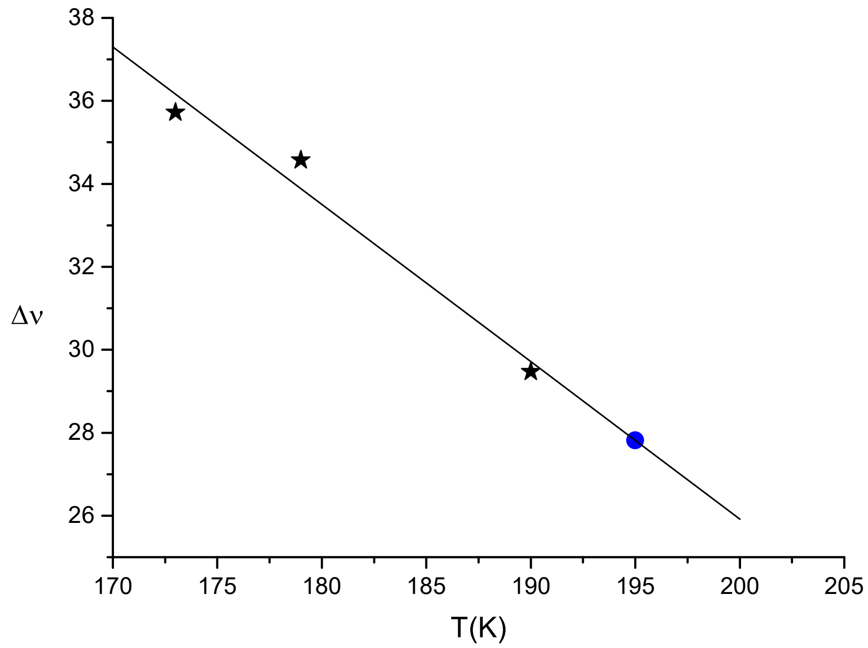


Figure S32: A linear fit of the data points obtained by variable temperature NMR studies. Separation in Hz between the two signals (Δ*v* = 27.81 Hz) at the coalescence temperature (*Tc* = 195 K)).

Rate constant at the coalescence temperature, $k_{\mathrm{C}} = \frac{\pi \Delta v}{\sqrt{2}}$

The following approximate equation was used to calculate the barrier of rotation around the As–C bond.[6]

$$\Delta G_C^{\#} = 4.58\, T_C \left[10.32 + log\left(\frac{T_C}{k_C}\right)\right] cal/mol$$

3.5.3. Crystallographic data

Single crystal X-ray structure determination: Single-crystal X-ray diffraction data were collected using Oxford Diffraction diffractometers equipped with a 135 mm Atlas or 165 mm Titan S2 CCD area detector. Crystals were selected under inert oil and mounted on micromount loops (**2b**·0.5(C_6H_{12}), **3a-c**) glass needles (**2a**) or a human hair (**2b**) and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data were collected using mirror monochromated Cu K_α radiation (λ = 1.5418 Å). Data collected on the Oxford Diffraction Supernova (**3a**, **3c**), Nova (**2a**, **2b**) and Agilent GV1000 (**2b**·0.5(C_6H_{12}), **3b**) diffractometers were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro.[7a] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Absorption correction based on face indexation was applied to the datasets for **2b, 2b**·0.5(C_6H_{12}), **3a** and **3b**. Structures were subsequently solved using direct methods and refined on F^2 using ShelXL.[7b] Hydrogen atoms were included by using a riding model or rigid methyl groups. The position of hydrogen H1 in **3a** and **3b** was refined freely, whereas the P-H distance in **3c** was restrained. The crystallographic data are listed in Tables S1 to S2.

Table S1. Crystallographic data for compounds **2a**, **2b** and **2b**·0.5(C_6H_{12}).

Compound	**2a**	**2b**	**2b·0.5(C_6H_{12})**
Formula	$C_{30}H_{45}AsN_2Si$	$C_{24}H_{33}AsN_2Si$	$C_{25.5}H_{36}AsN_2Si$
$D_{calc.}$ / g · cm^{-3}	1.170	1.212	1.145
μ/mm^{-1}	2.012	2.384	2.173
Formula Weight	536.69	452.53	473.57
Colour	yellow	yellow	yellow
Shape	prism	irregular	block
Size/mm^3	0.19×0.17×0.02	0.22×0.15×0.10	0.106×0.67×0.048
T/K	100(2)	100(2)	123(1)
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	*C2/c*
a/Å	20.0991(4)	19.0082(3)	15.8764(6)
b/Å	14.6635(2)	9.1958(2)	9.1798(3)
c/Å	21.6679(4)	28.5266(5)	38.5234(13)
α/°	90	90	90
β/°	107.342(2)	95.759(2)	101.949(4)
γ/°	90	90	90
V/Å^3	6095.7(2)	4961.16(16)	5492.8(3)
Z	8	8	8
Z'	2	2	2
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	Cu K_α
Θ_{min}/°	3.579	3.114	2.345
Θ_{max}/°	76.276	76.128	74.642
Measured Refl.	86050	51994	29510
Independent Refl.	12722	10317	5569
R_{int}	0.0584	0.0368	0.0683
Parameters	635	523	289
Restraints	0	0	0
Largest Peak	0.303	0.484	0.941
Deepest Hole	-0.701	-0.700	-0.994
GooF	1.016	1.024	1.044
wR_2 (all data)	0.0837	0.0956	0.1853
wR_2	0.0801	0.0917	0.1731
R_1 (all data)	0.0371	0.0409	0.0662
R_1	0.0321	0.0359	0.0568

Table S2. Crystallographic data for compounds **3a**, **3b** and **3c**.

Compound	3a	3b	3c
Formula	$C_{27}H_{37}AsN_2$	$C_{21}H_{25}AsN_2$	$C_{76}H_{65}AsN_2$
$D_{calc.}$ / g · cm^{-3}	1.164	1.302	1.236
μ/mm^{-1}	1.824	2.380	1.136
Formula Weight	464.51	380.35	1081.22
Colour	yellow	colorless	colorless
Shape	block	block	block
Size/mm^3	0.30×0.16×0.10	0.182×0.081×0.055	0.23×0.14×0.08
T/K	150.01(10)	123(1)	150(2)
Crystal System	monoclinic	monoclinic	orthorhombic
Space Group	*C2/c*	$P2_1/c$	$Pna2_1$
a/Å	20.0571(5)	8.2857(2)	19.3683(2)
b/Å	7.0854(2)	14.8334(2)	14.8549(2)
c/Å	39.0742(10)	16.1781(4)	20.2018(3)
α/°	90	90	90
β/°	107.303(3)	102.690(2)	90
γ/°	90	90	90
V/Å^3	5301.6(3)	1939.80(7)	5812.34(13)
Z	8	4	4
Z'	2	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	Cu K_α
Θ_{min}/°	4.618	4.090	3.693
Θ_{max}/°	76.340	73.896	74.113
Measured Refl.	15093	11051	21416
Independent Refl.	5484	3778	9425
R_{int}	0.0267	0.0216	0.0306
Parameters	283	226	719
Restraints	0	0	38
Largest Peak	0.715	0.699	0.325
Deepest Hole	-0.587	-1.152	-0.854
GooF	1.042	1.063	1.065
wR_2 (all data)	0.1472	0.1304	0.1530
wR_2	0.1425	0.1269	0.1267
R_1 (all data)	0.0541	0.0484	0.0527
R_1	0.0502	0.0448	0.0453

Molecular structures of compounds 2b and 2b·0.5(C_6H_{12})

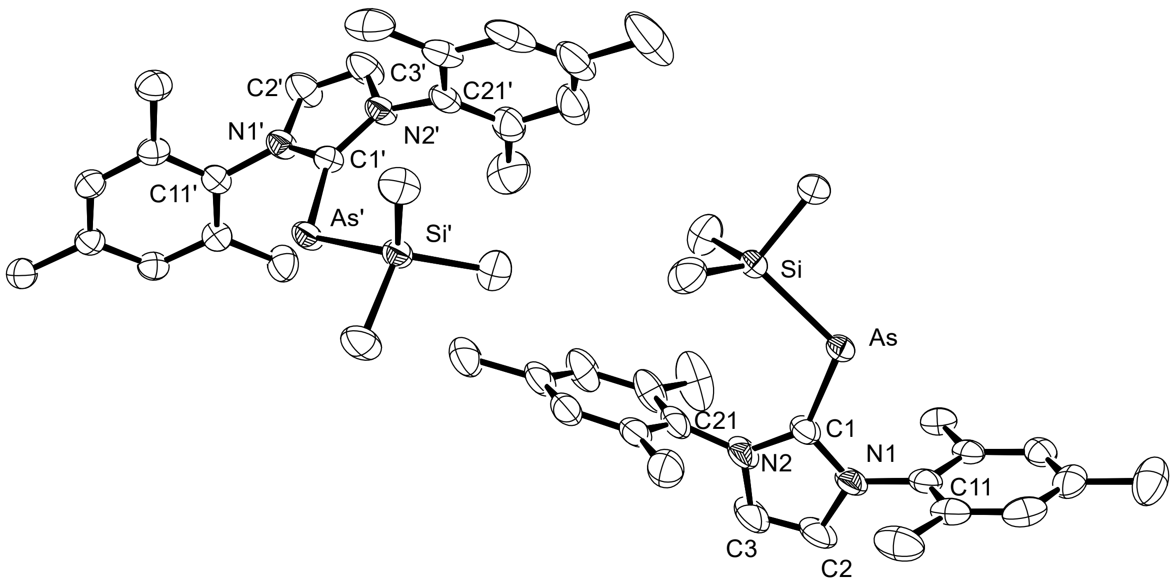


Figure S33: ORTEP diagram of **2b** with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [º] of molecule 1/molecule 2: As–Si 2.3234(6)/2.3243(6), C1–As 1.906(2)/1.899(2), C1–N1 1.369(3)/1.373(3), C1–N2 1.371(3), C2–C3 1.336(4)/1.343(3), N1–C1–N2 104.56(18)/103.84(17), C1–As–Si 112.73(7)/112.89(6).

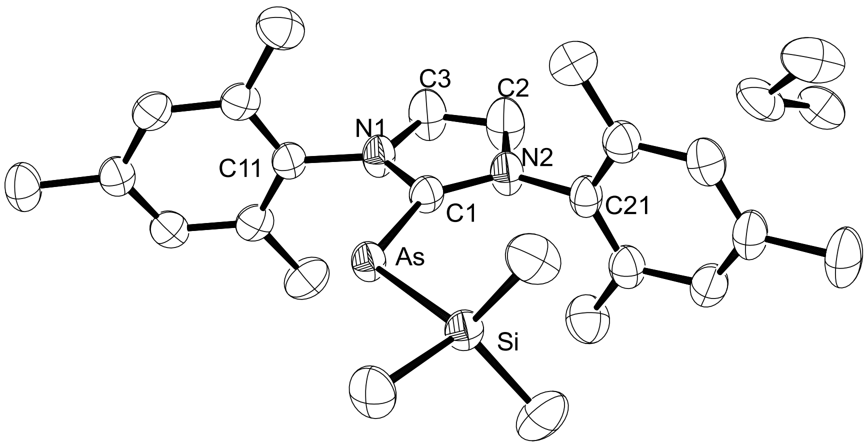


Figure S34: ORTEP diagram of **2b**·0.5(C_6H_{12}) with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [º]: As–Si 2.3209(8), C1–As 1.907(3), C1–N1 1.368(4), C1–N2 1.356(4), C2–C3 1.328(6), N1–C1–N2 104.4(3), C1–As–Si 114.03(9).

Molecular structures of compound 3b and 3c

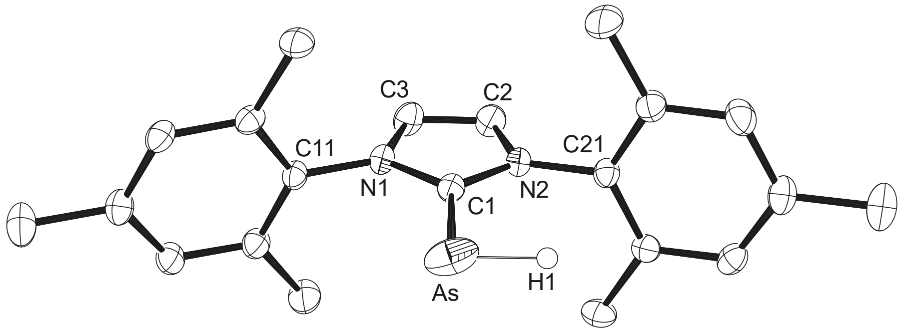


Figure S35: ORTEP diagram of the **3b** with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [°]: C1–As 1.896(2), C1–N1 1.367(3), C1–N2 1.363(3), C2–C3 1.347(3), N1–C1–N2 105.2(2), N2–C1–As1 128.05(16), N1–C1–As1 126.72(16), C1–N1–C11 124.78(19), C1–N2–C21 124.75(19), C1–As–H1 97.75.

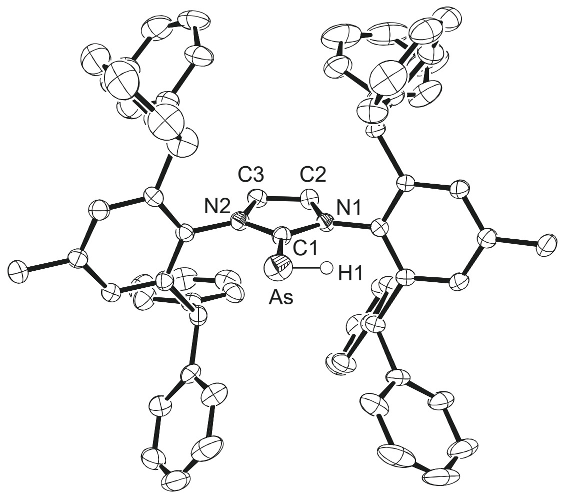


Figure S36: ORTEP diagram of the **3c** in the solid state with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [°]: C1–As 1.886(4), C1–N1 1.366(5), C1–N2 1.383(5), C2–C3 1.346(5), N1–C1–N2 104.5(3), N2–C1–As1 129.2(3), N1–C1–As1 126.3(3), C1–As–H1 89.79.

3.5.4. Computational data

Computational details. All computations were performed using Gaussian09[8] utilizing the PBE1PBE level of theory and 6-31G(d,p) basis sets. No solvent corrections were applied. Natural Bond Orbital and Natural Resonance Theory were applied to study the electronic states.[9−11]

Table S3. Summary of computational data (part 1, d in Å, angle in °, q in e, δ in ppm, ν in cm^{-1}, E in a.u.).

property	H_2CAsH	Ph_2CAsH	$^{Me2}NHCAsH$	$^{Mes}NHCAsH$
C–As	1.766	1.803	1.860	1.851
C–As (X-ray)				1.879(3)
As–H	1.519	1.515	1.509	1.515
C–As–H	96.13	95.69	93.11	91.96
q C	-0.866	-0.371	+0.079	+0.091
q As	+0.436	+0.399	-0.066	-0.058
q H	-0.070	-0.064	-0.059	-0.046
WBI CAs	1.9345	1.6206	1.2748	1.2704
WBI AsH	0.9727	0.9687	0.9658	0.9620
ellipticity CAs	0.285	0.277	0.320	0.310
ellipticity AsH	0.010	0.014	0.106	0.106
δ(^{13}C)	199.66	230.46	178.13	175.75
δ(^{1}H)	6.68	6.05	2.09	1.69
ν(AsH)	2156	2157	2180	2159
total energy	-2273.2450	-2734.8402	-2538.5168	-3157.1927

Table S4. Summary of computational data (part 2, d in Å, angle in °, q in e, δ in ppm, ν in cm^{-1}, E in a.u.).

property	$^{Dipp}NHCAsH$	$^{Ar*}NHCAsH$	H_3CAsH_2
C–As	11.853	1.855	1.961
C–As (X-ray)	1.885(2)	1.884(4)	
As–H	1.515	1.514	1.516
C–As–H	92.84	92.95	95.22
q C	+0.094	+0.094	-1.034
q As	-0.045	-0.073	+0.333
q H	-0.039	-0.033	-0.042
WBI CAs	1.2556	1.2191	0.9662
WBI AsH	0.9608	0.9599	0.9813
ellipticity CAs	0.315	0.296	0.048
ellipticity AsH	0.108	0.107	0.011
δ(^{13}C)	183.65	177.46	0.28
δ(^{1}H)	1.80	2.78	2.70
ν(AsH)	2167	2170	2153, 2167
total energy	-3392.7928	-5003.4800	-2274.4903

Optimised geometries

MesNHCAsH:

0 1

As	0.15743000	-0.00267400	-1.70489900
H	-1.34531000	-0.00008600	-1.89419100
N	-1.11020700	0.00060700	0.95369900
N	1.06060700	0.00089200	0.99003400
C	-0.01113200	-0.00021600	0.13863500
C	-0.71823300	0.00230300	2.28822700
H	-1.44292200	0.00316200	3.08652300
C	0.63135000	0.00235800	2.30934300
H	1.33063200	0.00330600	3.12998700
C	-2.46604800	0.00048100	0.51036600
C	-3.10279100	-1.22449000	0.28514000
C	-4.44158100	-1.19969300	-0.10057500
H	-4.95278500	-2.14249400	-0.28277100
C	-5.13242800	0.00041000	-0.27765500
C	-4.44298300	1.20023800	-0.09687200
H	-4.95520900	2.14304700	-0.27582400
C	-3.10365000	1.22512100	0.28849400
C	-2.32228700	-2.50311900	0.36578500
H	-1.51150500	-2.46896300	-0.37343400
H	-2.95644600	-3.36671800	0.15337300
H	-1.86232500	-2.64509700	1.34939400
C	-6.58661000	-0.00105200	-0.65706000
H	-6.83467800	-0.86088400	-1.28578600
H	-6.85913800	0.90783200	-1.20038900
H	-7.22418100	-0.05386300	0.23354900
C	-2.32426800	2.50428900	0.37188900
H	-1.51289900	2.47198000	-0.36671600
H	-1.86521800	2.64527500	1.35606500
H	-2.95893800	3.36769400	0.16022300
C	2.42025600	0.00046100	0.55463000
C	3.05698500	1.22598300	0.32575900
C	4.39153500	1.19959800	-0.07326500
H	4.90258600	2.14241400	-0.25560100
C	5.07953000	-0.00026300	-0.26016700
C	4.39348700	-1.19923000	-0.06591100
H	4.90597500	-2.14237000	-0.24194100
C	3.05811300	-1.22498100	0.33281700
C	2.29495400	2.51333800	0.43859700
H	1.81350200	2.62327000	1.41581800
H	1.50458800	2.52705600	-0.32261500
H	2.95026500	3.37244400	0.27842700
C	6.52903000	0.00162500	-0.65693300
H	7.17690200	0.08721900	0.22365900
H	6.76167900	0.84412500	-1.31445200
H	6.80257800	-0.92080900	-1.17617600
C	2.29785400	-2.51280800	0.45224100
H	2.95406600	-3.37179400	0.29517300
H	1.50676400	-2.53096100	-0.30808200
H	1.81751700	-2.61915200	1.43040600

DippNHCAsH:

0 1

As	0.14866200	0.07417300	-1.85069200
H	-1.35127700	0.09089500	-2.06374300
N	1.06119600	-0.05486900	0.83246800
C	0.64686400	-0.11824400	2.15452700
H	1.35608300	-0.13514400	2.96635700
N	-1.11020900	-0.10330600	0.82014800
C	2.42098300	0.03432600	0.39864600
C	-0.70178600	-0.15157000	2.14869500
H	-1.41676200	-0.20603600	2.95371600
C	2.93803400	1.29749300	0.06763300

C	4.27996700	1.36390200	-0.31151500
H	4.71185800	2.32731800	-0.56680700
C	5.06805000	0.22257200	-0.36181200
H	6.11065000	0.29679700	-0.65806400
C	4.52692100	-1.01616000	-0.04173900
H	5.15055700	-1.90299400	-0.09799600
C	3.19156100	-1.14016200	0.34344300
C	2.10450300	2.56249400	0.14013700
H	1.06656600	2.27025700	0.32327500
C	2.56264100	3.44578200	1.30426700
H	1.93155100	4.33774900	1.37915100
H	3.59685700	3.77971300	1.16588200
H	2.51038500	2.91163700	2.25857600
C	2.11792300	3.32392200	-1.18629100
H	1.73375800	2.67904800	-1.98151100
H	3.12324500	3.66621700	-1.45475500
H	1.47403600	4.20720300	-1.11911400
C	2.58252700	-2.50473900	0.60580700
H	1.67890900	-2.35807800	1.20808000
C	3.50349700	-3.43930600	1.38935900
H	3.84725200	-2.98299800	2.32308600
H	4.38683700	-3.72545700	0.80885300
H	2.97197100	-4.36339500	1.63783300
C	2.14824300	-3.12699200	-0.72680400
H	1.61575500	-4.07007400	-0.56136700
H	3.02045400	-3.33385800	-1.35724700
H	1.49338500	-2.43635100	-1.26775200
C	-2.47308400	-0.08961300	0.39278200
C	-3.09487900	-1.31063500	0.08507700
C	-4.42108100	-1.26583200	-0.34897100
H	-4.92847400	-2.19055100	-0.60783400
C	-5.09832800	-0.05879700	-0.45643700
H	-6.12932500	-0.04570500	-0.79877700
C	-4.46557300	1.13236600	-0.12383700
H	-5.00970500	2.06809600	-0.20636100
C	-3.13990600	1.14559000	0.31225600
C	-2.35856700	-2.63443000	0.17581600
H	-1.43859300	-2.46391800	0.74585700
C	-3.16663400	-3.69848800	0.92057600
H	-4.06752900	-3.98700300	0.36884300
H	-3.47694300	-3.35171600	1.91131000
H	-2.56409500	-4.60337600	1.04932100
C	-1.94584700	-3.11450300	-1.21970100
H	-2.82419400	-3.28145800	-1.85344700
H	-1.39002900	-4.05609300	-1.15387000
H	-1.30593300	-2.36407400	-1.69338700
C	-3.33117600	3.41501300	1.43245500
H	-4.16719300	3.78873800	0.83195200
H	-2.74838100	4.28677000	1.74640600
H	-3.74514200	2.94131800	2.32816000
C	-2.44318100	2.45433300	0.64058100
H	-1.57812900	2.21919000	1.27172700
C	-1.90913400	3.11478700	-0.63622600
H	-2.73072300	3.36620100	-1.31662400
H	-1.22188900	2.44077600	-1.15845600
H	-1.37563700	4.04070200	-0.39363500
C	-0.02135600	-0.04325200	-0.00924500

^{Ar*}NHCAsH

0 1

As	0.05493700	-0.06246800	-2.19782400
H	-0.19261800	1.42120100	-2.36874100
N	0.03404800	-1.05519200	0.46620500
N	-0.04531700	1.11833400	0.49706800
C	0.00299200	0.04482000	-0.34660300
C	0.00456300	-0.66463800	1.79965000
H	0.03247000	-1.38668100	2.59903700

C	-0.05168800	0.68311100	1.82002700
H	-0.10497300	1.38029900	2.64004700
C	0.25788700	-2.37758000	-0.03308500
C	-0.80524000	-3.09258600	-0.61463000
C	-0.53526900	-4.35813100	-1.12424000
H	-1.34530400	-4.91716500	-1.58395000
C	0.74673500	-4.91364700	-1.08839100
C	1.77312700	-4.17576300	-0.50908300
H	2.78543600	-4.57263200	-0.50664000
C	1.54926400	-2.91095100	0.04062800
C	-2.20667600	-2.50027900	-0.65851800
H	-2.07251200	-1.43861500	-0.90674300
C	-2.92845400	-2.56720900	0.67921100
C	-4.07052700	-1.77731400	0.86093500
H	-4.39886500	-1.12379800	0.05575200
C	-4.79383300	-1.83194700	2.04717800
H	-5.67985100	-1.21384700	2.16422500
C	-4.38301800	-2.67217300	3.08156900
H	-4.94691700	-2.71540500	4.00901400
C	-3.24897000	-3.45828400	2.91257600
H	-2.92091400	-4.12001500	3.70956900
C	-2.52942700	-3.40889600	1.71871400
H	-1.64939000	-4.03358500	1.59418300
C	-3.04627500	-3.08172900	-1.78988100
C	-3.95551100	-4.12154500	-1.58428200
H	-4.10003100	-4.51680000	-0.58253200
C	-4.68743800	-4.64447100	-2.64824100
H	-5.39219500	-5.45216600	-2.47045600
C	-4.52391800	-4.13035300	-3.93065000
H	-5.09942500	-4.53376500	-4.75906500
C	-3.62032800	-3.09149800	-4.14346500
H	-3.48726800	-2.68111000	-5.14083100
C	-2.88517400	-2.57340100	-3.08280800
H	-2.17345200	-1.76557500	-3.24272500
C	1.00607900	-6.26356800	-1.69479900
H	0.26093600	-6.99591500	-1.36849800
H	1.99604300	-6.64055100	-1.42622400
H	0.95296000	-6.21495900	-2.78819500
C	2.68592300	-2.13845700	0.68726300
H	2.37401300	-1.08962200	0.73786700
C	3.92190800	-2.14131500	-0.20580600
C	3.80128200	-1.55053100	-1.47049200
H	2.83369500	-1.14707500	-1.77053000
C	4.89433800	-1.48852900	-2.32462500
H	4.78823200	-1.01721500	-3.29765600
C	6.12172200	-2.02402900	-1.93301300
H	6.97692500	-1.97472800	-2.60098700
C	6.24379800	-2.61869600	-0.68270600
H	7.19603700	-3.03847900	-0.37005000
C	5.14909400	-2.67518800	0.18094200
H	5.25406400	-3.12896500	1.16212200
C	2.94510200	-2.56096400	2.12791200
C	2.85016200	-3.88578300	2.56255600
H	2.54815900	-4.66244800	1.86688900
C	3.12186300	-4.22381100	3.88631100
H	3.04041200	-5.26017500	4.20229200
C	3.48870800	-3.24243000	4.80172900
H	3.69665300	-3.50674300	5.83460500
C	3.57926400	-1.91785600	4.38257800
H	3.85688000	-1.13870600	5.08713700
C	3.30865800	-1.58248700	3.05986100
H	3.37821700	-0.54531400	2.74237000
C	-0.24883600	2.46267200	0.05859000
C	0.82524500	3.18352100	-0.49350300
C	0.57541900	4.47378100	-0.94828400
H	1.39104700	5.03723000	-1.39248100
C	-0.70023300	5.04384500	-0.89465800
C	-1.74393300	4.28778900	-0.37155600

H	-2.75485500	4.68833600	-0.38200500
C	-1.53918700	2.99857400	0.12667400
C	2.19833000	2.53713200	-0.61426000
H	2.00596700	1.49811900	-0.91618400
C	2.96985200	2.50276700	0.69537900
C	4.06794900	1.64035700	0.80073600
H	4.32826500	1.00273300	-0.04102500
C	4.83638500	1.60353500	1.95859400
H	5.68430100	0.92673000	2.01693000
C	4.51616400	2.42425200	3.03986500
H	5.11647800	2.39661800	3.94482800
C	3.42434000	3.28027700	2.94767300
H	3.16609600	3.92614200	3.78249800
C	2.65815600	3.32031100	1.78299800
H	1.81016500	3.99660700	1.71881900
C	3.03052000	3.12955600	-1.74370300
C	3.90685000	4.19813900	-1.53958300
H	4.02997300	4.60544300	-0.53942400
C	4.63356900	4.73094200	-2.60130400
H	5.31216700	5.56130800	-2.42633400
C	4.50012000	4.19622400	-3.87952000
H	5.07219600	4.60759200	-4.70634400
C	3.63579400	3.12453600	-4.08925000
H	3.53175600	2.69417400	-5.08152300
C	2.90532800	2.59632700	-3.02985600
H	2.23151700	1.75559300	-3.18333300
C	-0.93181600	6.43772800	-1.40571200
H	-1.99739500	6.64446100	-1.53339600
H	-0.43618700	6.59411200	-2.36857700
H	-0.52896900	7.18343700	-0.71044200
C	-2.69629300	2.18624800	0.68124900
H	-2.35411200	1.14856100	0.74512700
C	-3.85954200	2.15334800	-0.30539900
C	-3.66666800	1.47809500	-1.51864600
H	-2.69426300	1.03572300	-1.73954100
C	-4.69807400	1.39288500	-2.44541700
H	-4.53815600	0.85457700	-3.37537000
C	-5.93247800	1.98587500	-2.18116900
H	-6.73836600	1.91587800	-2.90612200
C	-6.12518900	2.66365400	-0.98310300
H	-7.08370800	3.12805300	-0.76789900
C	-5.09481300	2.74387000	-0.04619100
H	-5.25752800	3.25794800	0.89681000
C	-3.08435500	2.57237500	2.10324600
C	-2.99077400	3.87400300	2.60192200
H	-2.59416600	4.66604100	1.97475800
C	-3.38425600	4.16884900	3.90586500
H	-3.30153200	5.18828400	4.27253900
C	-3.87246000	3.16638200	4.73711800
H	-4.17499600	3.39680300	5.75460800
C	-3.96059900	1.86289300	4.25469100
H	-4.32931600	1.06614600	4.89489300
C	-3.56899700	1.57130400	2.95296400
H	-3.63529400	0.54972200	2.58754900

H_2CAsH

0 1

As	0.35828400	-0.04902200	-0.00002000
H	0.58120300	1.45349500	0.00028900
C	-1.40656200	0.02213400	0.00024200
H	-1.99134700	0.93634300	-0.00078800
H	-1.97385500	-0.90493200	-0.00027800

^{Me2}NHCAsH

0 1

As	-1.68834200	-0.10063100	-0.00003400

H	-1.70779400	-1.60961400	0.00101000
N	1.13363100	-0.99226000	0.00008600
N	0.85677700	1.15753400	0.00000100
C	0.16970400	-0.02376500	0.00003700
C	2.39238000	-0.41421700	0.00001300
H	3.29252100	-1.00776600	0.00002100
C	2.21864500	0.92545200	-0.00002700
H	2.93641700	1.72998800	-0.00004700
C	0.18727400	2.43054500	0.00002000
H	-0.45210800	2.51422500	-0.88672300
H	-0.45287800	2.51367200	0.88626200
H	0.92734700	3.23154400	0.00057900
C	0.85026200	-2.40278900	-0.00007300
H	0.26944000	-2.67288600	0.88784200
H	0.26838400	-2.67234100	-0.88746100
H	1.79150600	-2.95425500	-0.00078800

Ph_2CAsH

0 1

As	0.14193300	0.18971500	0.34471500
C	-1.64584300	0.13508400	0.11658900
C	-2.51824200	1.31781900	0.15744300
C	-2.33538800	2.33154500	1.11068400
C	-3.56449600	1.46039100	-0.76985100
C	-3.15005400	3.45661100	1.12121500
H	-1.55929600	2.20934700	1.86064200
C	-4.36932400	2.59248600	-0.76635100
H	-3.72461500	0.68286400	-1.51088400
C	-4.16630400	3.59514800	0.17913500
H	-2.99715400	4.22362800	1.87491400
H	-5.15981600	2.69193000	-1.50470200
H	-4.80279000	4.47514600	0.18744400
C	-2.27339200	-1.17961500	-0.08946200
C	-3.52671600	-1.47002400	0.47824800
C	-1.63123000	-2.19013700	-0.82516700
C	-4.09678500	-2.72848700	0.34097500
H	-4.03863500	-0.70271500	1.05077900
C	-2.20389700	-3.44826300	-0.96101000
H	-0.68805100	-1.96377800	-1.31519000
C	-3.43744100	-3.72406800	-0.37685600
H	-5.05981300	-2.93477300	0.79914700
H	-1.69245700	-4.21156900	-1.54014700
H	-3.88813200	-4.70579300	-0.48958000
H	0.25136200	1.70074000	0.31231000

H_3CAsH_2

0 1

As	-0.41739000	0.00000100	-0.06499600
H	-0.60200900	-1.07936000	0.98317100
C	1.54215500	-0.00002200	0.02200100
H	1.90961100	-0.88401200	-0.50245200
H	1.90942400	0.88545600	-0.50007300
H	-0.60182600	1.07935000	0.98321800
H	1.90573300	-0.00135000	1.04900300

Analyses of the electronic structure

The electronic structure was analysed with the program MULTIWFN 3.3.9,[12] thereby CDA,[13] ELF,[14] and bond ellipticities/AIM[15] were studied.

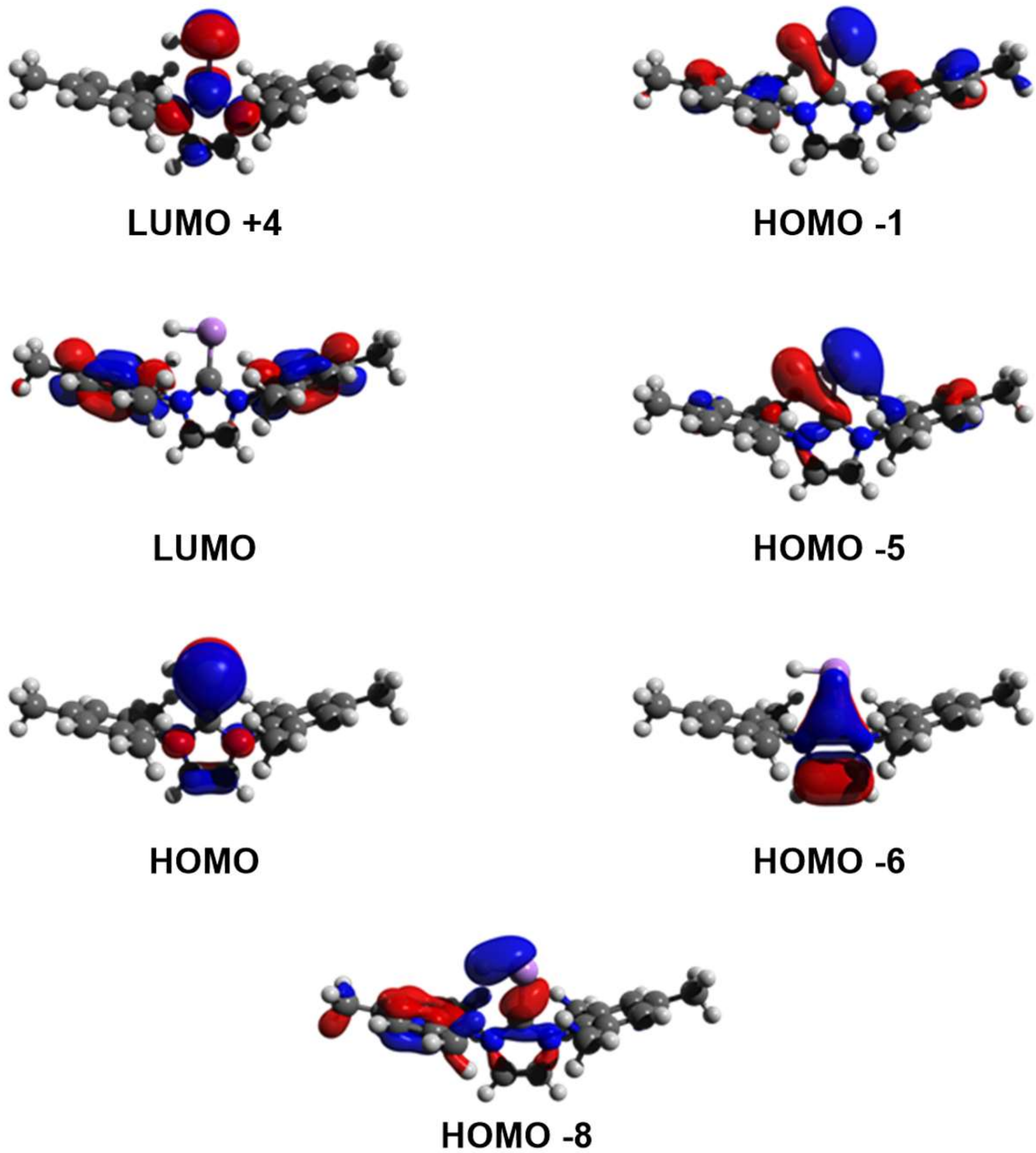


Figure S37: Molecular orbitals of [(IMes)AsH]

Selected NBO data

H_2CAsH:

```
 1. (1.98361) BD ( 1)As   1 - H   2
          ( 46.28%)   0.6803*As   1 s( 11.80%)p 7.42( 87.59%)d 0.05(  0.61%)
                                   0.0000  0.0000  0.0001  0.3408 -0.0428
                                   0.0090  0.0000  0.0000  0.0000  0.0000
                                  -0.1741 -0.0350  0.0000 -0.0002  0.9183
                                   0.0337  0.0000  0.0000 -0.0001  0.0000
                                  -0.0007 -0.0144  0.0000  0.0000  0.0000
                                   0.0000  0.0000 -0.0656  0.0000 -0.0396
          ( 53.72%)   0.7329* H   2 s( 99.91%)p 0.00(  0.09%)
                                   0.9996  0.0017  0.0031 -0.0296  0.0000
 2. (1.99969) BD ( 1)As   1 - C   3
          ( 47.19%)   0.6869*As   1 s(  0.00%)p 1.00( 99.42%)d 0.01(  0.58%)
                                   0.0000  0.0000  0.0000 -0.0004  0.0001
                                   0.0000  0.0000  0.0000  0.0000  0.0000
                                  -0.0010 -0.0001  0.0000  0.0000  0.0001
                                   0.0000  0.0000  0.0000  0.9962 -0.0407
                                   0.0000  0.0000  0.0000  0.0727  0.0000
                                   0.0234  0.0000 -0.0001  0.0000  0.0000
          ( 52.81%)   0.7267* C   3 s(  0.00%)p 1.00( 99.94%)d 0.00(  0.06%)
                                   0.0000 -0.0011  0.0000  0.0000  0.0006
                                   0.0000 -0.0002  0.0000  0.9988 -0.0418
                                   0.0000 -0.0247 -0.0013  0.0000  0.0000
 3. (1.99727) BD ( 2)As   1 - C   3
          ( 35.46%)   0.5954*As   1 s( 18.32%)p 4.44( 81.30%)d 0.02(  0.39%)
                                   0.0000  0.0001  0.0000  0.4174 -0.0944
                                  -0.0062 -0.0001  0.0000  0.0000  0.0000
                                   0.8993  0.0591  0.0000  0.0001  0.0175
                                  -0.0220  0.0000  0.0000  0.0011 -0.0001
                                   0.0000  0.0202  0.0000  0.0001  0.0000
                                   0.0000  0.0000  0.0542  0.0000 -0.0228
          ( 64.54%)   0.8034* C   3 s( 36.54%)p 1.74( 63.42%)d 0.00(  0.04%)
                                   0.0001  0.6045  0.0069 -0.0007 -0.7963
                                  -0.0030 -0.0078 -0.0009  0.0012 -0.0001
                                   0.0011  0.0000  0.0000  0.0167 -0.0106
```

^{Ar*}NHCAsH:

```
 2. (1.97326) BD ( 1)As   1 - C   5
          ( 30.42%)   0.5516*As   1 s( 14.00%)p 6.11( 85.57%)d 0.03(  0.43%)
                                   0.0000 -0.0002  0.0004 -0.3690  0.0617
                                  -0.0032 -0.0014  0.0000  0.0000  0.0000
                                   0.0252 -0.0010  0.0000 -0.0001 -0.0204
                                   0.0130  0.0000 -0.0005 -0.9225 -0.0588
                                   0.0000 -0.0020  0.0000  0.0053 -0.0001
                                  -0.0185  0.0000 -0.0058 -0.0002 -0.0628
          ( 69.58%)   0.8341* C   5 s( 42.60%)p 1.35( 57.39%)d 0.00(  0.01%)
                                   0.0003 -0.6520 -0.0310  0.0004 -0.0092
                                   0.0016  0.0030 -0.0027  0.7554 -0.0566
                                   0.0005  0.0007 -0.0024  0.0011 -0.0089
256. (1.96567) LP ( 1)As   1           s( 73.45%)p 0.36( 26.53%)d 0.00(  0.02%)
                                   0.0000 -0.0001 -0.0001  0.8569  0.0151
                                   0.0002  0.0002  0.0000  0.0000  0.0000
                                   0.0528  0.0017  0.0000  0.0001 -0.3906
                                   0.0059 -0.0001 -0.0005 -0.3314  0.0047
                                   0.0000  0.0026 -0.0001  0.0016  0.0006
                                  -0.0099  0.0001  0.0068 -0.0001 -0.0042
257. (1.55393) LP ( 2)As   1           s(  0.03%)p99.99( 99.80%)d 4.78(  0.17%)
                                   0.0000  0.0000 -0.0001  0.0186 -0.0005
                                  -0.0008  0.0001  0.0000  0.0003  0.0018
                                   0.9849 -0.0441  0.0001  0.0003  0.1600
                                  -0.0106  0.0000  0.0000  0.0159 -0.0012
                                   0.0000  0.0210 -0.0034  0.0336 -0.0003
```

```
                              0.0025  0.0001 -0.0082 -0.0001  0.0015

258. LP (   1) N   3            /260. LP*(   1) C   5            126.80    0.13    0.134
259. LP (   1) N   4            /260. LP*(   1) C   5            126.92
```

^{Mes}NHCAsH

```
  1. (1.96837) BD ( 1)As   1 - H   2
           ( 47.10%)   0.6863*As   1 s( 12.82%)p 6.76( 86.69%)d 0.04(  0.49%)
                                0.0000  0.0000  0.0003  0.3559 -0.0390
                               -0.0049 -0.0006 -0.0001  0.0000  0.0002
                               -0.9103 -0.0535  0.0000  0.0000  0.0015
                                0.0001  0.0000  0.0001 -0.1853 -0.0310
                                0.0000 -0.0002  0.0012  0.0070  0.0000
                                0.0000  0.0001  0.0614  0.0000 -0.0332
           ( 52.90%)   0.7273* H   2 s( 99.92%)p 0.00(  0.08%)
                                0.9996  0.0006  0.0287 -0.0001  0.0035
  2. (1.97472) BD ( 1)As   1 - C   5
           ( 30.14%)   0.5490*As   1 s( 13.97%)p 6.12( 85.56%)d 0.03(  0.47%)
                                0.0000 -0.0001  0.0004 -0.3663  0.0744
                               -0.0048 -0.0006 -0.0001  0.0000  0.0001
                                0.0468 -0.0103  0.0000  0.0000 -0.0012
                                0.0000  0.0001 -0.0005 -0.9217 -0.0607
                                0.0000  0.0000  0.0001  0.0232  0.0000
                               -0.0002  0.0001  0.0058 -0.0002 -0.0641
           ( 69.86%)   0.8358* C   5 s( 42.78%)p 1.34( 57.21%)d 0.00(  0.01%)
                                0.0003 -0.6534 -0.0309  0.0005 -0.0276
                                0.0053  0.0009 -0.0001  0.7538 -0.0559
                                0.0000  0.0030  0.0000 -0.0014 -0.0090
 96. (1.97197) LP ( 1)As   1           s( 73.78%)p 0.36( 26.20%)d 0.00(  0.02%)
                                0.0000 -0.0001  0.0001  0.8588  0.0191
                                0.0004  0.0001  0.0000  0.0000 -0.0001
                                0.3999 -0.0079  0.0000  0.0000 -0.0008
                                0.0000  0.0000 -0.0005 -0.3193  0.0070
                                0.0000  0.0000 -0.0006  0.0110  0.0000
                                0.0000 -0.0001 -0.0068 -0.0002 -0.0034
 97. (1.55176) LP ( 2)As   1           s(  0.00%)p 1.00( 99.79%)d 0.00(  0.21%)
                                0.0000  0.0000  0.0000  0.0003  0.0000
                                0.0000  0.0000  0.0000  0.0000  0.0000
                               -0.0018  0.0001 -0.0002 -0.0019 -0.9979
                                0.0449  0.0000  0.0000  0.0011  0.0000
                               -0.0002  0.0268  0.0000  0.0000  0.0037
                               -0.0377  0.0000  0.0001  0.0000  0.0001
```

^{Me2}NHCAsH

```
  2. (1.98423) BD ( 1)As   1 - C   5
           ( 69.76%)   0.8352*As   1 s(  0.00%)p 1.00( 99.73%)d 0.00(  0.27%)
                                0.0000  0.0000  0.0000  0.0001  0.0000
                                0.0000  0.0000  0.0000  0.0000  0.0000
                               -0.0002  0.0000  0.0000  0.0000 -0.0006
                                0.0000  0.0000  0.0001  0.9980 -0.0374
                                0.0000  0.0000  0.0000 -0.0479  0.0000
                               -0.0196  0.0000  0.0000  0.0000  0.0000
           ( 30.24%)   0.5499* C   5 s(  0.00%)p 1.00( 99.94%)d 0.00(  0.06%)
                                0.0000  0.0001  0.0000  0.0000  0.0001
                                0.0000 -0.0002  0.0001  0.9983 -0.0535
                                0.0000  0.0242 -0.0001  0.0000  0.0000
  3. (1.97588) BD ( 2)As   1 - C   5
           ( 30.55%)   0.5527*As   1 s( 13.92%)p 6.15( 85.60%)d 0.03(  0.48%)
                                0.0000  0.0001 -0.0004  0.3642 -0.0809
                                0.0055 -0.0001  0.0000  0.0001 -0.0004
                               -0.9205 -0.0612  0.0000  0.0000  0.0679
                                0.0171  0.0000  0.0000 -0.0002  0.0000
                                0.0001  0.0083  0.0000  0.0000  0.0000
                                0.0000  0.0002  0.0623  0.0000 -0.0290
           ( 69.45%)   0.8334* C   5 s( 42.07%)p 1.38( 57.92%)d 0.00(  0.01%)
```

```
                                         -0.0003  0.6478  0.0322 -0.0005  0.7543
                                         -0.0623 -0.0799  0.0021 -0.0001  0.0000
                                          0.0012  0.0000  0.0000  0.0075 -0.0065
   41. (1.97346) LP ( 1)As   1           s( 73.55%)p 0.36( 26.43%)d 0.00(  0.02%)
                                          0.0000 -0.0001  0.0002  0.8573  0.0217
                                          0.0004  0.0000  0.0000  0.0000  0.0004
                                          0.3639 -0.0079  0.0000 -0.0002  0.3629
                                         -0.0093  0.0000  0.0000  0.0002  0.0000
                                          0.0006 -0.0113  0.0000  0.0000  0.0000
                                          0.0000  0.0001 -0.0028  0.0002  0.0054

42. LP (   1) N   3             /163. BD*(   1)As   1 - C   5          71.59
42. LP (   1) N   3             /173. BD*(   2) C   6 - C   8          35.48
43. LP (   1) N   4             /163. BD*(   1)As   1 - C   5          70.81    0.22    0.116
43. LP (   1) N   4             /173. BD*(   2) C   6 - C   8          36.16
```

NRT analysis

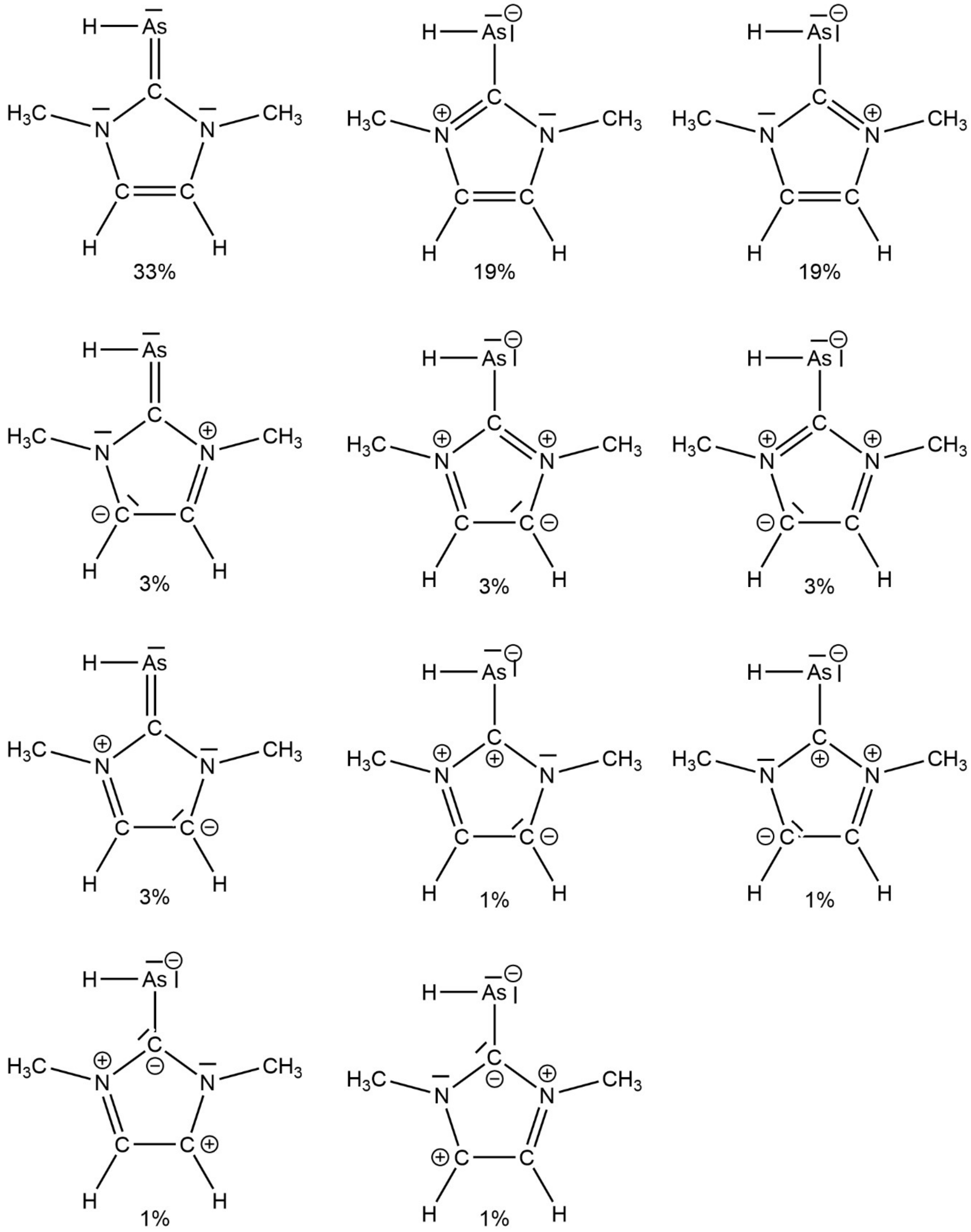


Figure S38: NRT weighting scheme for ^{Me2}NHCAsH.

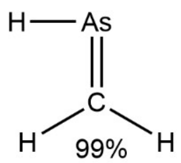


Figure S39: NRT weighting scheme for H_2CAsH.

ELF calculations

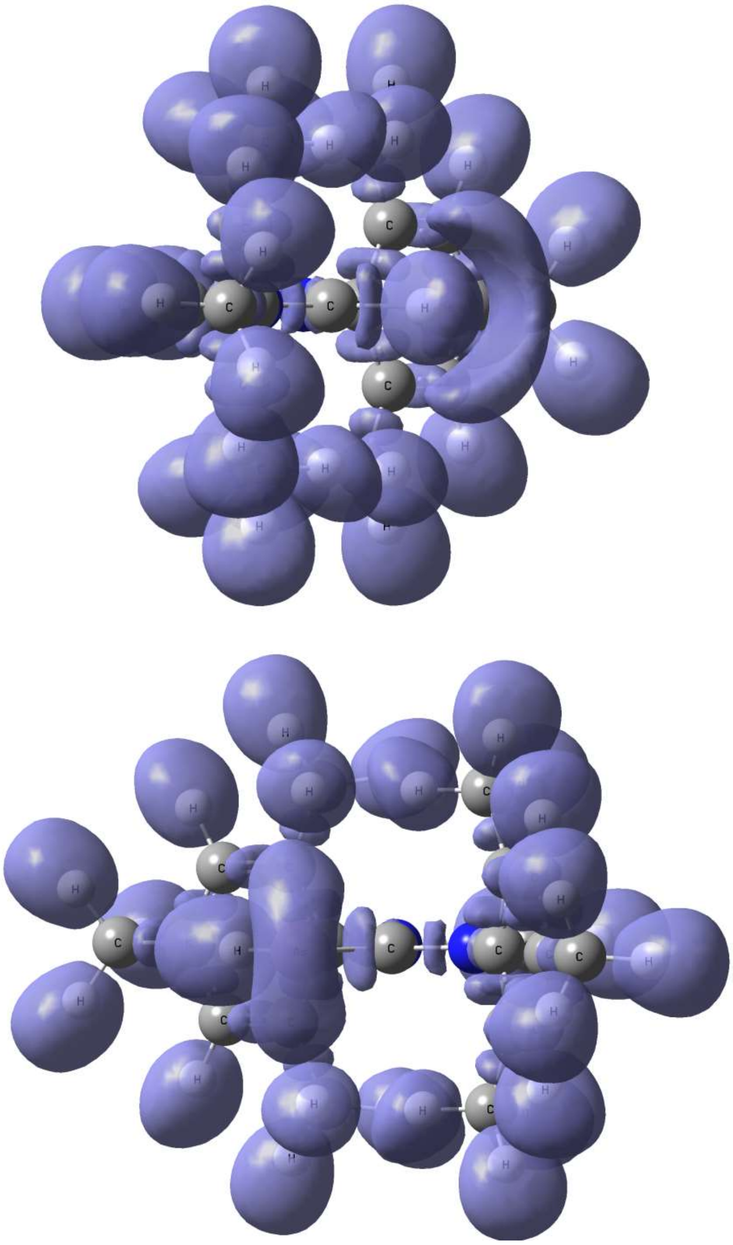


Figure S40: Depiction of the ELF of ^{Mes}NHCAsH at isovalue of 0.85.

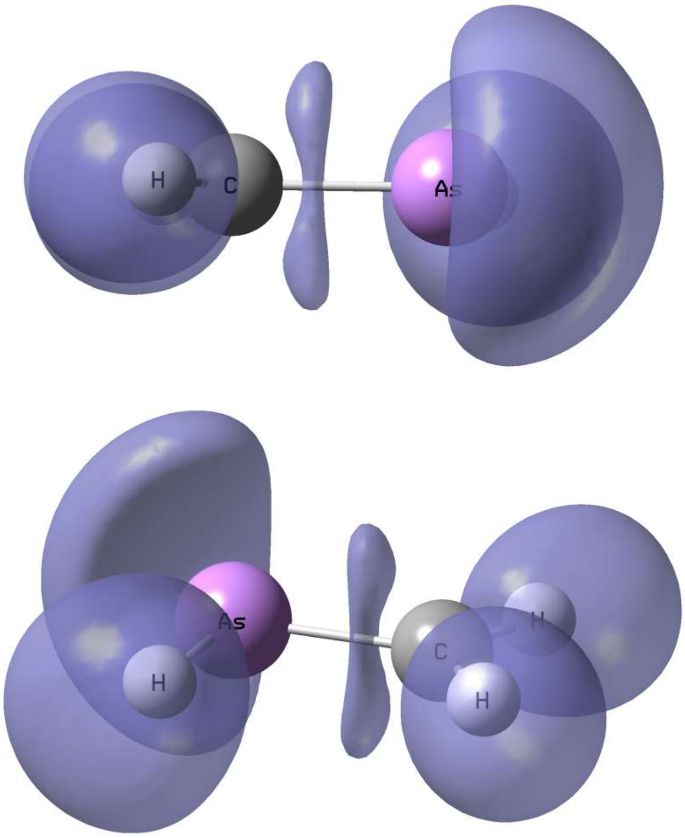


Figure S41: Depiction of the ELF of H_2CAsH at isovalue of 0.85.

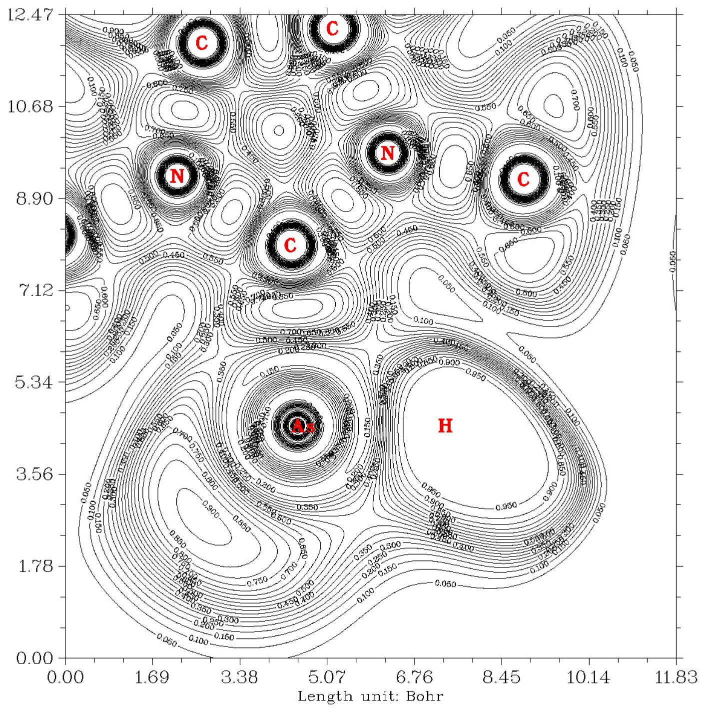


Figure S42: Contour plot of the ELF of ^{Mes}NHCAsH in the CAsH plane.

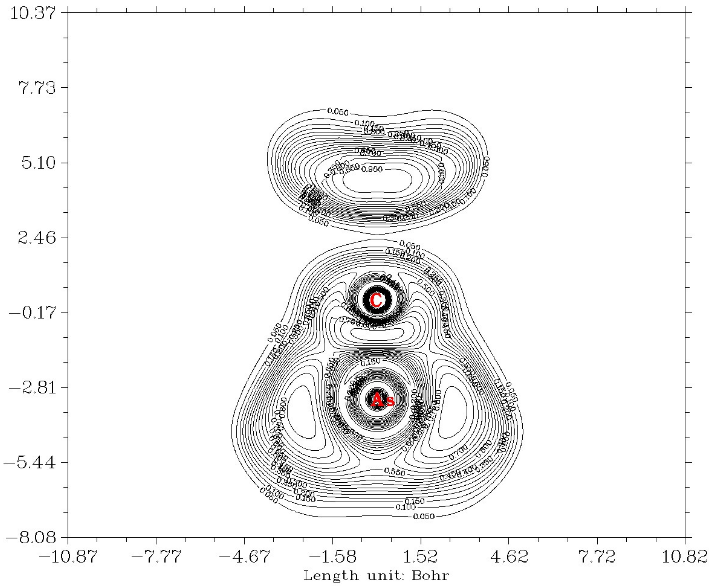


Figure S43: Contour plot of the ELF of ^{Mes}NHCAsH perpendicular to the CAsH plane.

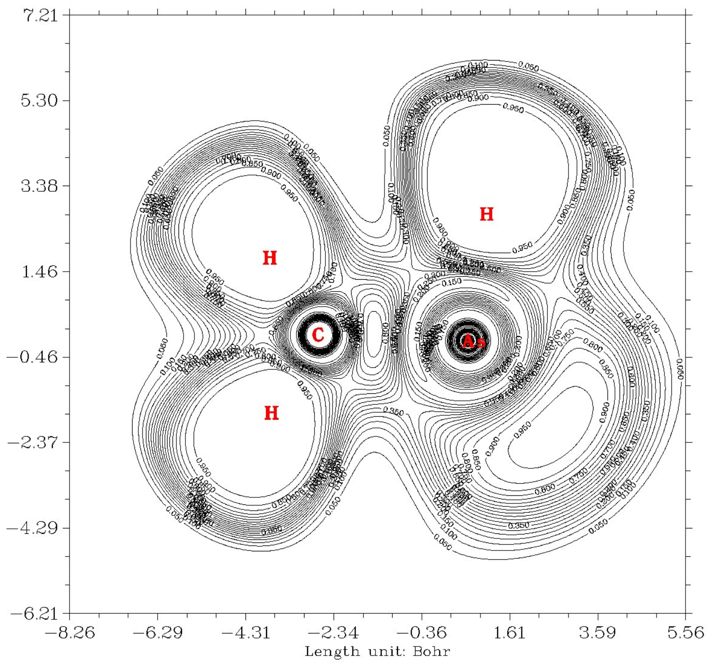


Figure S44: Contour plot of the ELF of H_2CAsH in the CAsH plane.

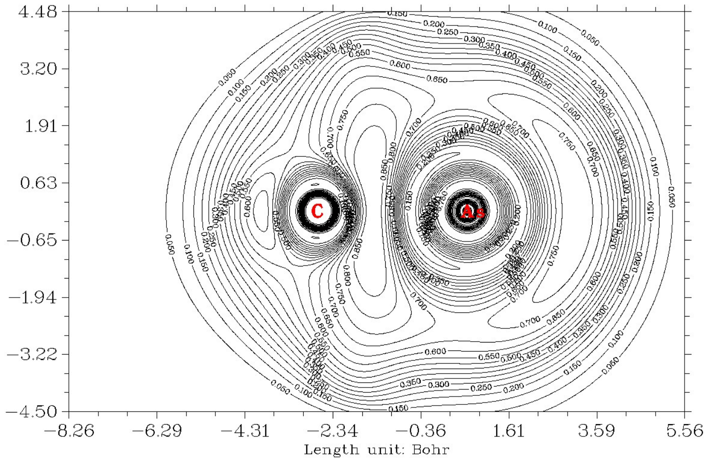


Figure S45: Contour plot of the ELF of H_2CAsH perpendicular to the CAsH plane.

Bond ellipticities at BCP

The ellipticity of 0 means rotational symmetry around the bonding path, while values >0 imply anisotropic distribution of the electron density as it would be expected for a π bond.

Table S5. As–H and C–As bond values, C–As values in bold.

Index	x/y/z Coordinate (Bohr)			Distance	Values
^{Mes}NHCAsH					
63	**0.15894152**	**-0.00295246**	**-1.61704218**	**1.8600**	**0.30972862E+00**
56	-1.38096693	-0.00224921	-3.45184338	1.6500	0.10579991E+00
H_2CAsH					
52	**-0.88865861**	**-0.02823631**	**0.00010787**	**1.5300**	**0.28525157E+00**
38	0.94637638	1.58247993	0.00026892	1.1100	0.99418700E–02
H_3CAsH_2					
38	**-1.00552385**	**-1.22008465**	**1.03104700**	**1.1100**	**0.48347821E–01**
24	3.34260348	1.04948698	-0.57722675	0.6900	0.10842457E–01
^{Dipp}NHCAsH					
63	**0.13818626**	**0.03964248**	**-1.89421777**	**1.8600**	**0.31453519E+00**
56	-1.39434289	0.15929085	-3.75290267	1.6500	0.10817843E+00
^{Me2}NHCAsH					
63	**-1.57384251**	**-0.11738765**	**-0.00000729**	**1.8600**	**0.32010277E+00**
56	-3.22849610	-1.87694305	0.00108695	1.6500	0.10608733E+00
$^{Ar^*}$NHCAsH					
63	**0.06139118**	**-0.03079967**	**-2.54206971**	**1.8600**	**0.29559946E+00**
38	-0.16748481	1.54092343	-4.36062104	1.1100	0.10719466E+00
Ph_2CAsH					
53	**-1.31182345**	**0.31320053**	**0.45143586**	**1.5600**	**0.27723919E+00**
38	0.40716312	2.04680570	0.62034951	1.1100	0.13706356E–01

Laplacian of electron density

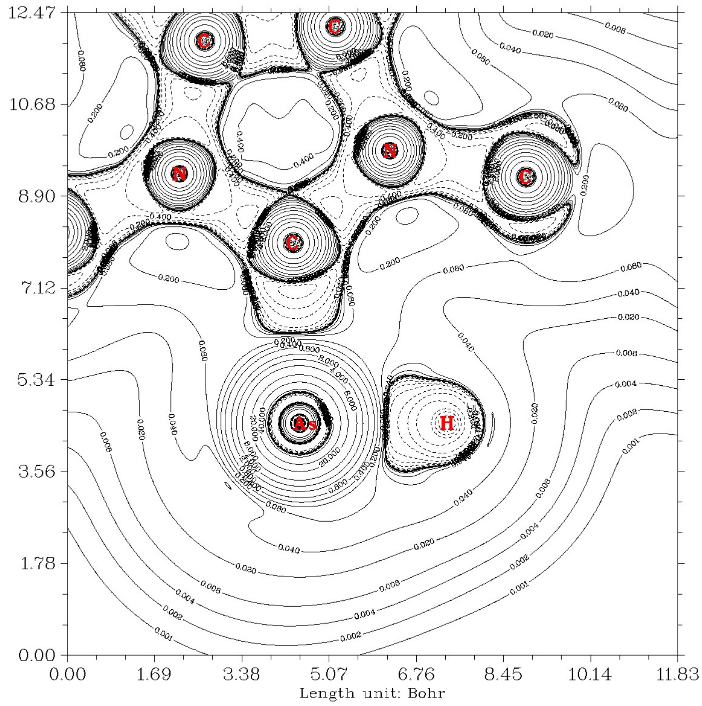


Figure S46: Contour plot of the Laplacian of the electron density of ^{Mes}NHCAsH in the CAsH plane.

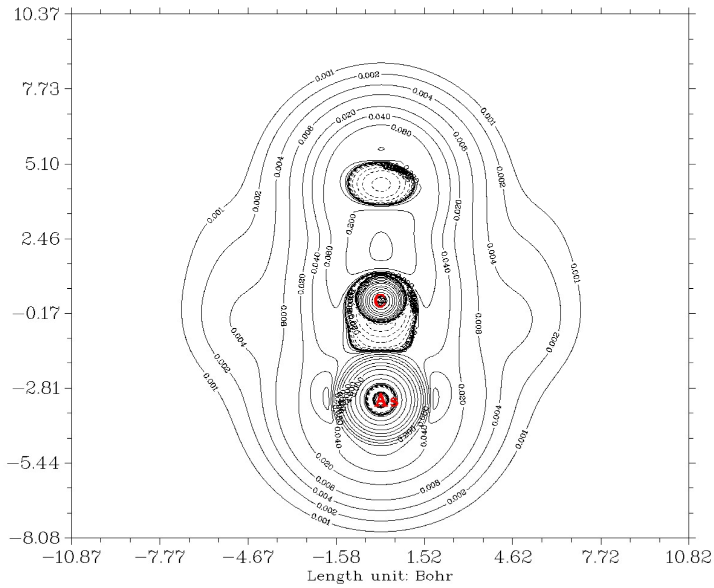


Figure S47: Contour plot of the Laplacian of the electron density of ^{Mes}NHCAsH perpendicular to the CAsH plane.

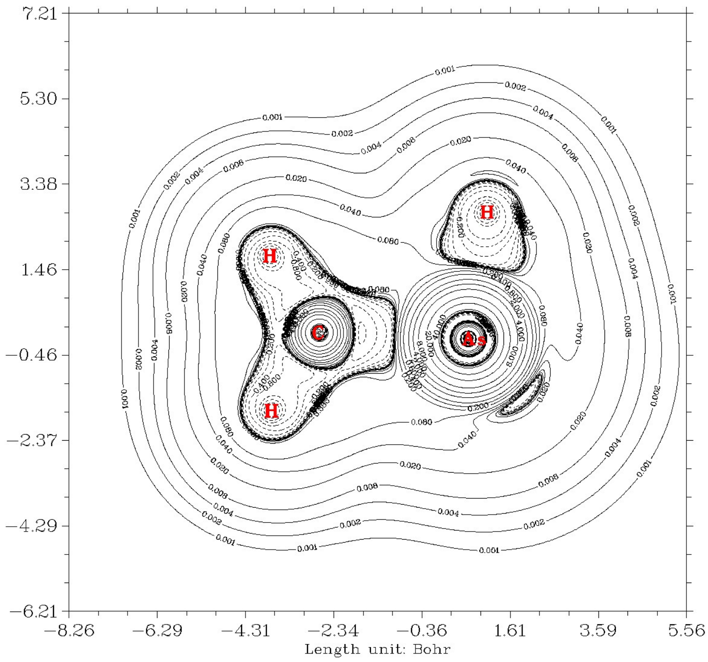


Figure S48: Contour plot of the Laplacian of the electron density of H_2CAsH in the CAsH plane.

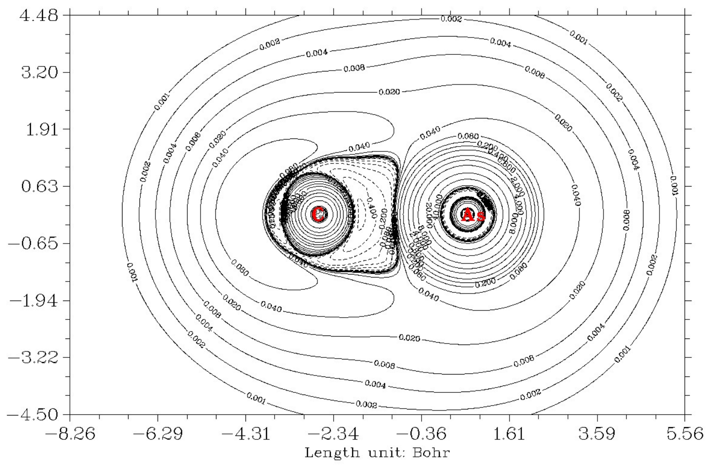


Figure S49: Contour plot of the Laplacian of the electron density of H_2CAsH perpendicular to the CAsH plane.

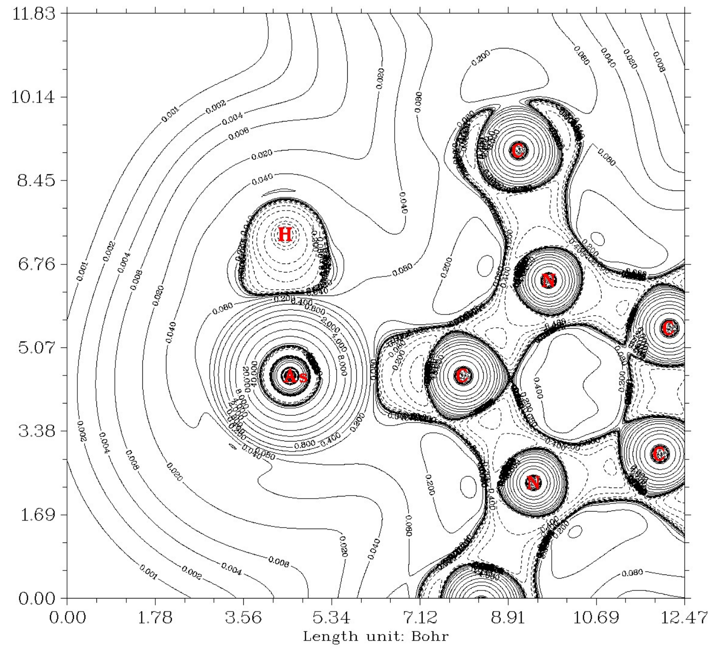


Figure S50: Contour plot of the Laplacian of the electron density of ^{Mes}NHCAsH in the CAsH plane.

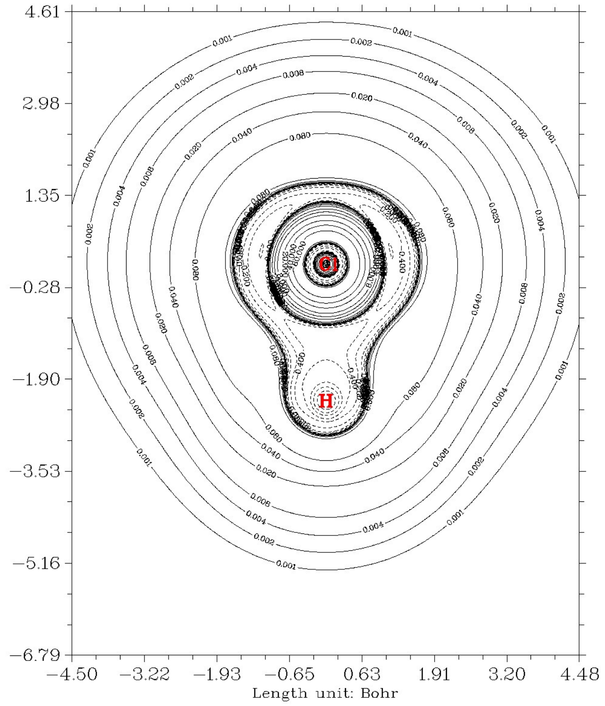


Figure S51: Contour plot of the Laplacian of the electron density of HCl.

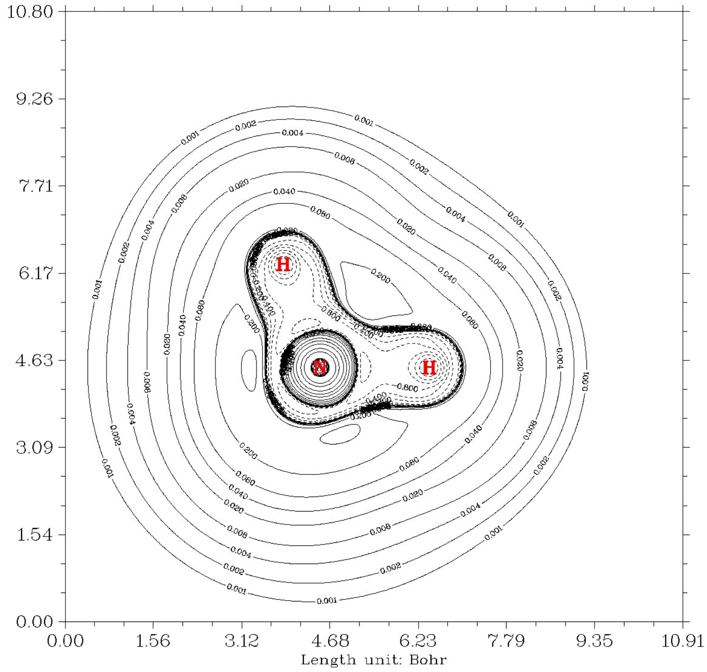


Figure S52: Contour plot of the Laplacian of the electron density of NH_4^+.

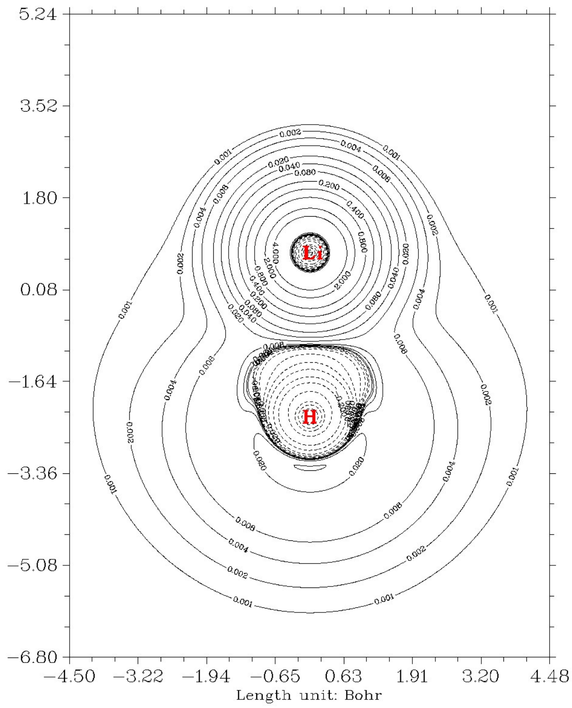


Figure S53: Contour plot of the Laplacian of the electron density of LiH.

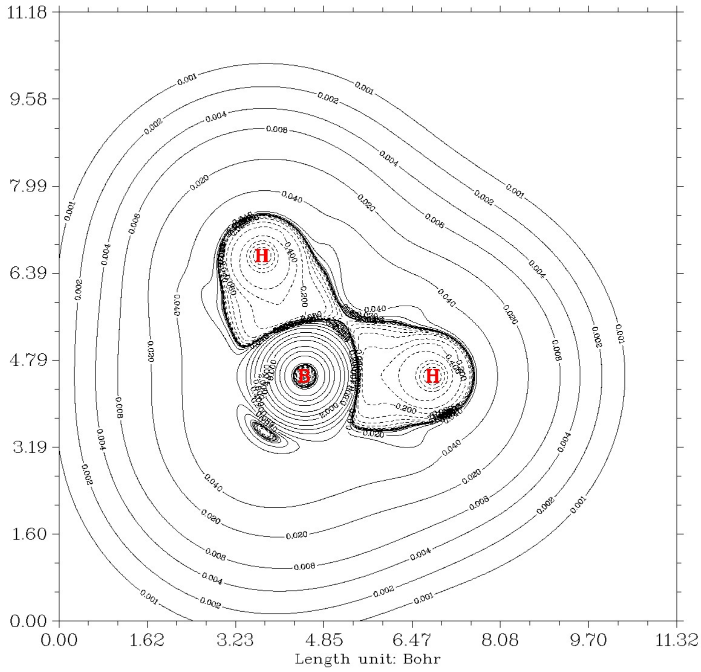


Figure S54: Contour plot of the Laplacian of the electron density of BH_4^-.

Table S6. E–H bond character, ρ and $\nabla^2\rho$ at the BCP.

molecule	**ρ(r$_c$)**	**∇^2ρ(r$_c$)**
GaH_3	0.1103893575	0.1361723698
GeH_4	0.1290480255	0.07569410550
^{Mes}NHCAsH	**0.1417169466**	**-0.02743252112**
AsH_3	0.1450980079	-0.05453278431
AsH_4^+	0.1640913825	-0.1638143282
SeH_2	0.1731443529	-0.1877223664
BrH	0.1989594987	-0.3326934586
LiH	0.03479502518	0.1539985370
BH_4^-	0.1444078202	-0.01014669296
NH_4^+	0.3328411735	-1.1864811273

Electron density

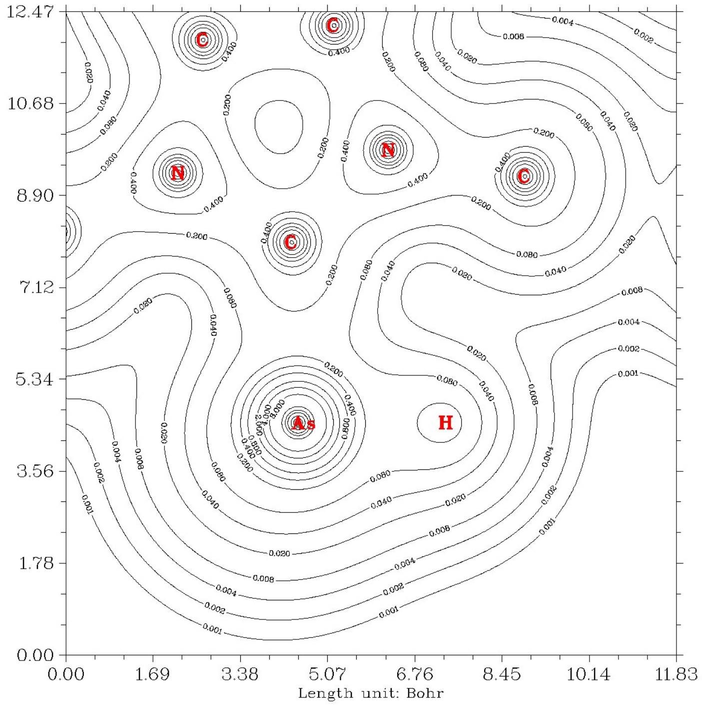


Figure S55: Contour plot of the electron density of ^{Mes}NHCAsH in the CAsH plane.

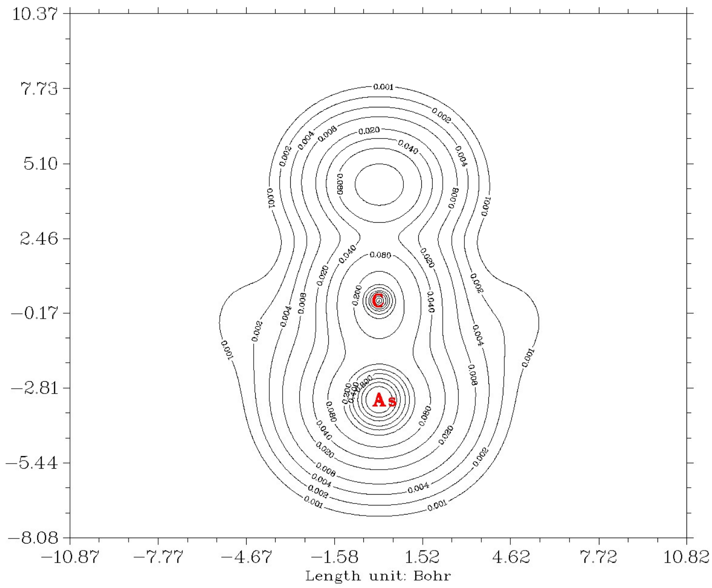


Figure S56: Contour plot of the electron density of ^{Mes}NHCAsH perpendicular to the CAsH plane.

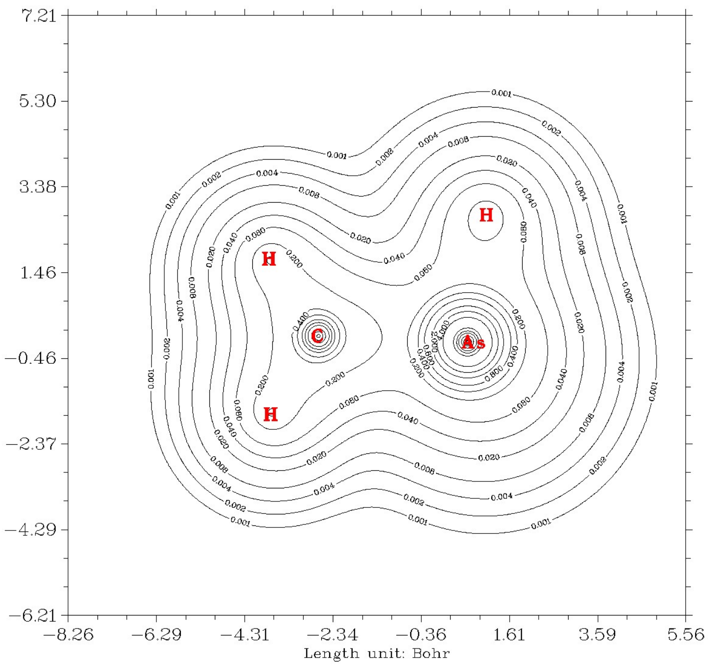


Figure S57: Contour plot of the electron density of H_2CAsH in the CAsH plane.

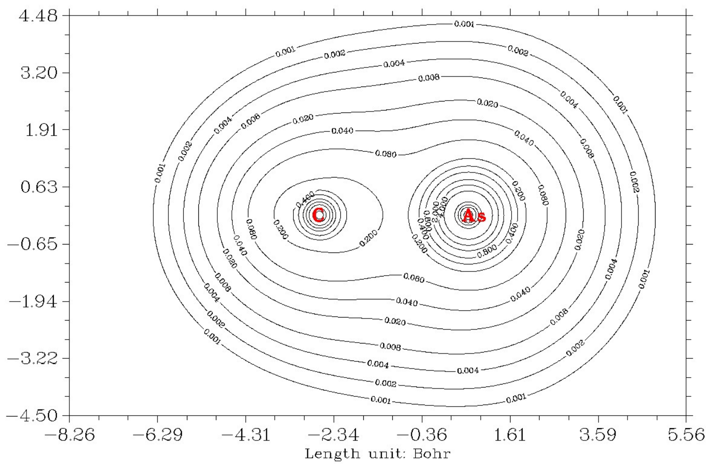


Figure S58: Contour plot of the electron density of H_2CAsH perpendicular to the CAsH plane.

Charge decomposition analysis

^{Mes}NHCAsH

Singlet state of fragments:

d	+0.185
b	+0.325
d–b	-0.140
r	-0.315
total	-0.354 e As→C

HOMO main As→C donor.

HOMO-1, HOMO-2 main C→As back donors.

Triplet state of fragments:

	a	b	total
d	-0.016	-0.214	-0.231
b	-0.220	-0.007	-0.227
d–b	+0.204	-0.207	-0.004
r	+0.106	+0.139	+0.245
total	+1.177	-0.823	+0.354

H_2CAsH

Singlet state of fragments:

d	+0.196
b	+0.316
d–b	-0.120
r	-0.176
total	+0.04 e As→C

HOMO main As→C donor.

HOMO-1, HOMO-2 main C→As back donors.

Triplet state of fragments:

	a	b	total
d	+0.230	-0.006	+0.223
b	+0.009	+0.274	+0.283
d–b	+0.221	-0.280	-0.060
r	-0.099	-0.089	-0.188
total	+1.020	-0.980	-+0.040

Transition states for rotation around the C–As bond

	^{Mes}NHC	^{Dipp}NHC
E [a.u.]	-3157.19274463	-3392.79279759
E# [a.u.]	-3157.16837886	-3392.76412058
ΔE [a.u.]	0.02436577	0.02867701
ΔE [kJ mol^{-1}]	64.0	75.3

^{Dipp}NHCAsH:

```
0 1
 As        0.00000400  -0.32170100  -1.91963800
 H        -0.00018100  -1.82595300  -1.71202300
 N        -1.07587500   0.02609900   0.80140400
 C        -0.67781000   0.19280500   2.11233200
 H        -1.39015600   0.29728100   2.91511500
 N         1.07578500   0.02639800   0.80139600
 C        -2.46033000   0.04450800   0.40558500
 C         0.67768900   0.19302200   2.11232200
 H         1.39001100   0.29771100   2.91509700
 C        -3.15124500  -1.16722800   0.27926400
 C        -4.52596700  -1.10091700   0.04404300
 H        -5.08977900  -2.02351300  -0.05921600
 C        -5.17762400   0.11865300  -0.07054100
 H        -6.24847200   0.14718100  -0.25068700
 C        -4.45850800   1.30311900   0.02212000
 H        -4.97044500   2.25227600  -0.10254600
 C        -3.08438400   1.29444600   0.26253700
 C        -2.45867200  -2.51386600   0.32196300
 H        -1.38846200  -2.33960600   0.47300600
 C        -2.96152800  -3.38414600   1.47517700
 H        -2.42622900  -4.33916500   1.49340800
 H        -4.02923800  -3.60649100   1.37316600
 H        -2.81480500  -2.89419800   2.44323400
 C        -2.61116500  -3.21058200  -1.03342400
 H        -2.25851500  -2.54229300  -1.82440300
 H        -3.65538000  -3.47540900  -1.23216000
 H        -2.02030800  -4.13228600  -1.06044200
 C        -2.29436700   2.58882000   0.24033900
 H        -1.31906400   2.40131300   0.70334400
 C        -2.95650400   3.71978400   1.02663400
 H        -3.15241400   3.43172600   2.06438800
 H        -3.90684200   4.02708300   0.57813000
 H        -2.30623200   4.60032600   1.03479100
 C        -2.04281600   2.98537800  -1.21995000
 H        -1.38556000   3.85981100  -1.27795200
 H        -2.98639200   3.23585900  -1.71749800
 H        -1.58309800   2.15551100  -1.76776500
 C         2.46025300   0.04505100   0.40562000
 C         3.08370500   1.29509600   0.26108300
 C         4.45786300   1.30414000   0.02085200
 H         4.96932300   2.25340700  -0.10499500
 C         5.17758000   0.11992200  -0.07021400
 H         6.24843800   0.14874900  -0.25024800
 C         4.52649400  -1.09983200   0.04575600
 H         5.09075100  -2.02228400  -0.05637500
 C         3.15177700  -1.16650700   0.28086600
 C         2.29315900   2.58910500   0.23708000
 H         1.31713100   2.40131400   0.69842600
 C         2.95349800   3.72053500   1.02422400
 H         3.90499000   4.02740400   0.57787600
 H         3.14683100   3.43311800   2.06263900
 H         2.30331500   4.60116400   1.03022900
 C         2.04397000   2.98501600  -1.22377800
 H         2.98831300   3.23536600  -1.71993400
```

H	1.38671100	3.85934600	-1.28322500
H	1.58515800	2.15481800	-1.77184900
C	2.96385400	-3.38329000	1.47752700
H	4.03140000	-3.60585400	1.37430900
H	2.42844900	-4.33822900	1.49672300
H	2.81836800	-2.89299300	2.44559400
C	2.45970700	-2.51336100	0.32462100
H	1.38957400	-2.33945200	0.47664700
C	2.61128400	-3.21022700	-1.03080200
H	3.65544700	-3.47470500	-1.23028900
H	2.25782900	-2.54212300	-1.82158300
H	2.02070300	-4.13212800	-1.05725200
C	-0.00002700	-0.09034800	-0.01910800

MesNHCAsH:

0 1

As	0.00000400	-0.32170100	-1.91963800
H	-0.00018100	-1.82595300	-1.71202300
N	-1.07587500	0.02609900	0.80140400
C	-0.67781000	0.19280500	2.11233200
H	-1.39015600	0.29728100	2.91511500
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C	0.67768900	0.19302200	2.11232200
H	1.39001100	0.29771100	2.91509700
C	-3.15124500	-1.16722800	0.27926400
C	-4.52596700	-1.10091700	0.04404300
H	-5.08977900	-2.02351300	-0.05921600
C	-5.17762400	0.11865300	-0.07054100
H	-6.24847200	0.14718100	-0.25068700
C	-4.45850800	1.30311900	0.02212000
H	-4.97044500	2.25227600	-0.10254600
C	-3.08438400	1.29444600	0.26253700
C	-2.45867200	-2.51386600	0.32196300
H	-1.38846200	-2.33960600	0.47300600
C	-2.96152800	-3.38414600	1.47517700
H	-2.42622900	-4.33916500	1.49340800
H	-4.02923800	-3.60649100	1.37316600
H	-2.81480500	-2.89419800	2.44323400
C	-2.61116500	-3.21058200	-1.03342400
H	-2.25851500	-2.54229300	-1.82440300
H	-3.65538000	-3.47540900	-1.23216000
H	-2.02030800	-4.13228600	-1.06044200
C	-2.29436700	2.58882000	0.24033900
H	-1.31906400	2.40131300	0.70334400
C	-2.95650400	3.71978400	1.02663400
H	-3.15241400	3.43172600	2.06438800
H	-3.90684200	4.02708300	0.57813000
H	-2.30623200	4.60032600	1.03479100
C	-2.04281600	2.98537800	-1.21995000
H	-1.38556000	3.85981100	-1.27795200
H	-2.98639200	3.23585900	-1.71749800
H	-1.58309800	2.15551100	-1.76776500
C	2.46025300	0.04505100	0.40562000
C	3.08370500	1.29509600	0.26108300
C	4.45786300	1.30414000	0.02085200
H	4.96932300	2.25340700	-0.10499500
C	5.17758000	0.11992200	-0.07021400
H	6.24843800	0.14874900	-0.25024800
C	4.52649400	-1.09983200	0.04575600
H	5.09075100	-2.02228400	-0.05637500
C	3.15177700	-1.16650700	0.28086600
C	2.29315900	2.58910500	0.23708000
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H	3.14683100	3.43311800	2.06263900

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C	2.04397000	2.98501600	-1.22377800
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H	4.03140000	-3.60585400	1.37430900
H	2.42844900	-4.33822900	1.49672300
H	2.81836800	-2.89299300	2.44559400
C	2.45970700	-2.51336100	0.32462100
H	1.38957400	-2.33945200	0.47664700
C	2.61128400	-3.21022700	-1.03080200
H	3.65544700	-3.47470500	-1.23028900
H	2.25782900	-2.54212300	-1.82158300
H	2.02070300	-4.13212800	-1.05725200
C	-0.00002700	-0.09034800	-0.01910800

3.5.5. References

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3.6. Author contributions

The syntheses and characterization of compounds **1b** and **2a** were performed by Adinarayana Doddi.

The syntheses (*via* Route 2) of compounds **2b**, **3a**, **3b** and **3c** were performed by Michael Weinhart.

The syntheses (*via* Route 1) and characterization of compounds **2b**, **3a** and **3b** were performed by Adinarayana Doddi.

X-ray structural analyses of **2a** and **2b** were performed by Adinarayana Doddi.

X-ray structural analyses of **2b**·0.5(C_6H_{12}), **3a**, **3b** and **3c** were performed by Michael Weinhart.

The synthesis and characterization of [Na(dioxane)$_x$][AsCO] was performed by Alexander Hinz.

NMR analyses of **3c** and **3a** (*via* Route 2) were performed by Alexander Hinz.

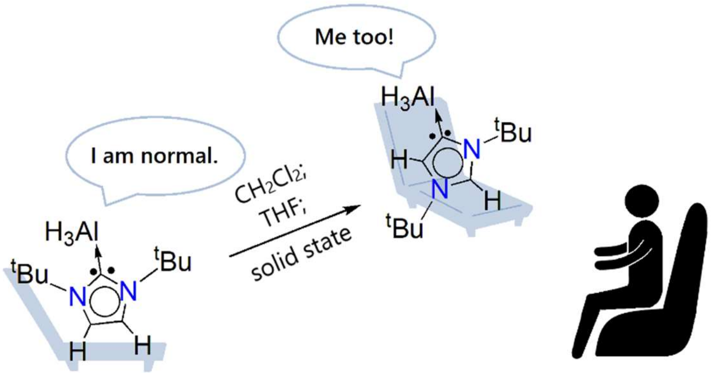
NMR analysis of **3b** (*via* Route 2) was performed by Michael Weinhart.

VT NMR studies of **3b** were performed by Michael Weinhart.

Computational analyses (optimized geometries, NBO, NRT, ELF and electron density) were performed by Alexander Hinz and Dirk Bockfeld.

The manuscript was written by Adinarayana Doddi.

4. Normal to abnormal I^{t}Bu·AlH$_3$ isomerization in solution and in the solid state



Abstract: A complex of an N-heterocyclic carbene I^{t}Bu (1,3-di-tert-butylimidazol-2-ylidene) and aluminum hydride was observed to isomerize into an abnormal carbene complex *a*I^{t}Bu·AlH$_3$ (*a*I^{t}Bu = 1,3-di-tert-butylimidazol-4-ylidene) in a polar solvent, and, for the first time, in the solid state. I^{t}Bu·AlH$_3$ and *a*I^{t}Bu·AlH$_3$ were structurally characterized by single crystal X-ray diffraction analysis. NMR studies and DFT computations indicate that the polarity of the solvent promotes the isomerization process. The possible pathways for the isomerization are discussed on the basis of the DFT computational studies.

4.1. Introduction

Over the past two decades, N-heterocyclic carbenes (NHCs) have received exceptional attention due to their strong σ-donating properties.[1] The NHCs as ligands have been widely used in transition metal chemistry and catalysis.[2] In main group element chemistry, NHCs have been employed as strong Lewis bases for the stabilization of low-valent and low-coordinate main group elements and their moieties.[3] For these purposes, mostly imidazolylidene-type NHCs are used, which coordinate to the metal center *via* the C2 position (**I**, Fig. 1a). Moreover, there has also been a growing interest[4] in so-called *abnormal* (*a*NHC) carbenes (**II**, Fig. 1a), where binding to a metal center occurs *via* the C4 carbon. The first example of a complex containing such an abnormal carbene was reported by Crabtree and co-workers in 2001 (Fig. 1b).[5] Abnormal NHCs are so-called mesoionic compounds, for which no form of resonance without formal charges can be suggested, in contrast to normal NHCs.[6] Stable *a*NHC in the free state can be obtained by blocking the C2 position with a bulky substituent.[7]

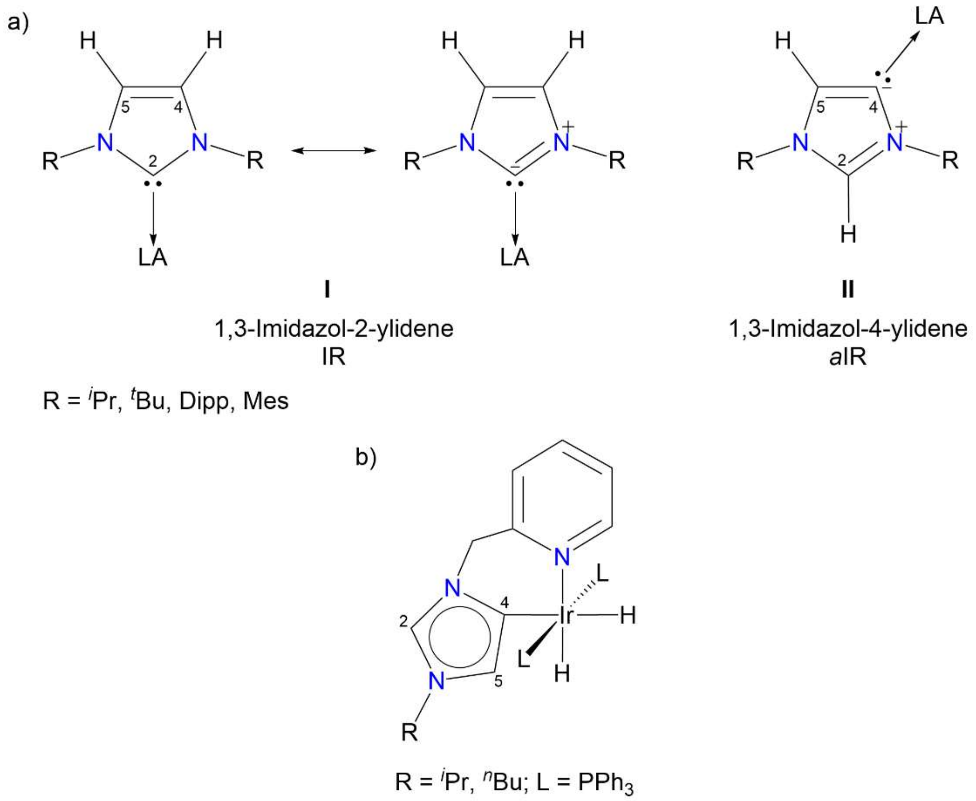
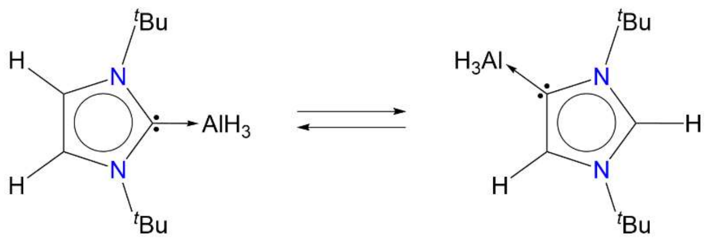


Figure 1: (a) Resonance structures of complexes of NHC (I) and *a*NHC (II) with Lewis acids (LA). (b) The first *a*NHC complex.[5]

As compared to normal NHCs, *a*NHCs exhibit stronger σ-donating properties[6] that could result in an even higher stability of the *a*NHC-complexes. Due to this energetic stabilization, the *a*NHCs complexes of the type II may originate *via* the isomerization of less stable NHC complexes. Recently, Dagorne et al. reported the rearrangement of the sterically congested adducts I^{t}Bu·MMe_3 (M = Al, Ga, In) into their abnormal analogs *a*I^{t}Bu·MMe_3.[8] The isomerization of I^{t}Bu·$AlMe_3$ into *a*I^{t}Bu·$AlMe_3$ was observed to be fast in THF solution (5 min at room temperature). In the case of the nonpolar solvent C_6D_6, the isomerization is slow but could be thermally promoted.[9] Steric relief was proposed to be the driving force for this process and the mechanism of a THF-promoted rearrangement through the dissociation of the complex I^{t}Bu·$AlMe_3$ was suggested.[8]

These findings encouraged us to examine the complex of the less congested Lewis acid AlH_3 and a bulky carbene I^{t}Bu. The reactivity of AlH_3 adducts with different NHCs was studied by the group of Radius,[9] but no normal-to-abnormal isomerization was observed. In the present communication, we report the synthesis and characterization of the two isomers **1** and **1a** (Scheme 1) and studies of the role of the solvent in the isomerization process. Quantum chemical DFT studies are used to determine the relative stability of the isomers in different solvents.

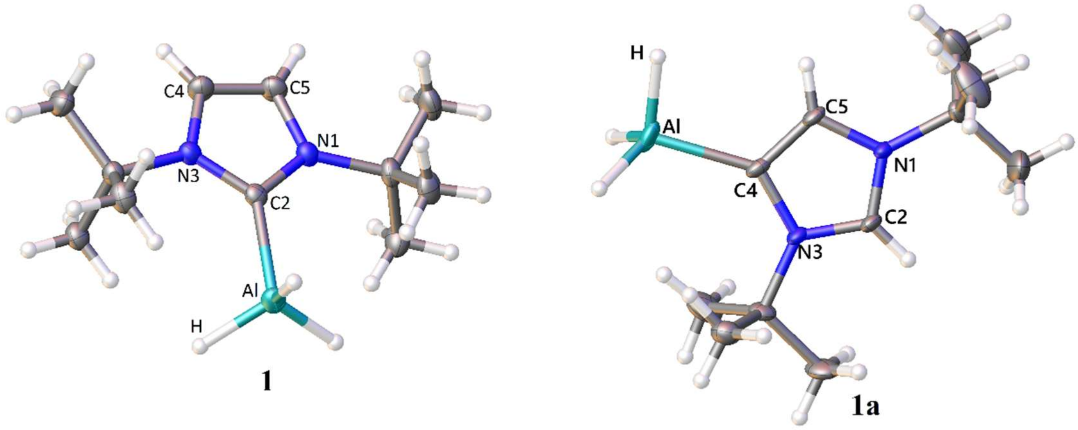


1 **1a**

Scheme 1: Isomerization of **1** into **1a**.

4.2. Results and Discussion

The reaction of I^{t}Bu with a three-fold excess of $LiAlH_4$ in diethyl ether with the subsequent extraction of the complex with toluene yields the expected complex **1** (Fig. 2). According to the ^{1}H NMR spectra, this form is predominant in a nonpolar solvent such as C_6D_6. Nevertheless, the X-ray single crystal structure analysis of the crystals grown from a THF/hexane solution of **1** in the presence of still unremoved I^{t}Bu revealed the formation of the abnormal complex **1a** (Fig. 2). The Al-C4 bond length of 2.026(2) Å is shorter than the Al-C4 bond lengths in the complexes with a normal carbene (2.0556(13) Å in IDipp·AlH_3,[11] 2.034(3) Å in IMes·AlH_3[12] and 2.0405(17) Å in I^{i}Pr·AlH_3[9]), for which no isomerization to an abnormal isomer was observed. The Al-C2 bond length in **1** (2.0838(11) Å) is longer than in IDipp·AlH_3 (2.0556(13) Å), IMes·AlH_3 (2.034(3) Å) and I^{i}Pr·AlH_3 (2.0405(17) Å), which correlates with the relative bulkiness of the ^{t}Bu substituents. The Al-C4 bond is shorter in **1a** than the Al-C2 bond in **1**, which is in agreement with the stronger σ-donating properties of the *a*NHCs. The shorter Al-C bond distance in **1a** agrees with the larger dissociation energy predicted by DFT computations.[13] The Al-C4 bond in **1a** is also shorter than 2.067(3) Å as in *a*I^{t}Bu·$AlMe_3$[10], due to less steric hindrance of the small Lewis acid AlH_3.



1 **1a**

Figure 2: Molecular structures of complexes **1** and **1a** in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental bond distances (Å) and angles (°) for **1**: Al–C2 2.0838(11), Al–H 1.50(2), C2–N1 1.3684(14), C2–N3 1.3694(14), N3–C4 1.3790(15), N1–C5 1.3787(15), C4–C5 1.3406(17), N1–C2–N3 104.45(9), N3–C4–C5 107.28(10); **1a**: Al–C4 2.026(2), Al–H 1.56(3), C2–N1 1.326(3), C2–N3 1.332(3), N3–C4 1.411(2), N1–C5 1.383(3), C4–C5 1.355(3), N1–C2–N3 109.35(17), N3–C4–C5 103.39(16).

In order to understand the role of the solvent in the formation of an abnormal isomer, NMR studies were carried out. The isomers **1** and **1a** can be distinguished by the singlets of the tert-butyl protons: in case of **1**, one singlet at 1.55 ppm for the 18 tert-butyl protons is observed in C_6D_6, while **1a** gives two signals at 1.47 ppm and 0.68 ppm, because the two ^{t}Bu-groups are non-equivalent. The aluminum-bound hydrides appear as very broad signals in the ^{1}H NMR (C_6D_6) spectrum at 5.42 ppm for **1** and 4.34 ppm for **1a**. This broadening occurs due to the direct binding to the ^{27}Al atom (I = 5/2) and the resulting splitting in combination with the quadrupole moment of the aluminum nuclei. ^{1}H NMR spectra measured in different solvents just after the synthesis of **1** shed light on the role of the solvent in the isomerization process. In nonpolar solvents such as C_6D_6, the content of the abnormal isomer **1a** is the lowest, equaling 1.8%. The amount of **1a** increases to 14%, if more polar solvent dichloromethane is used.[13] In contrast to I^{t}Bu·$AlMe_3$, which undergoes fast isomerization into *a*I^{t}Bu·$AlMe_3$ in THF solution (100% conversion after 5 min at room temperature),[8] **1** exhibits a slow isomerization rate in C_6D_6 and in CD_2Cl_2. The NMR spectra were also recorded in d_8-THF after 3 weeks of storing the product under argon and the content of the form **1a** equaled 19%.

The results of the DFT computations, performed at the B3LYP-D3[14]/def2-SVPD[14],[15] level of theory with PCM[16], to account for the solvent effects, are in good qualitative agreement with the experimental NMR results. In the gas phase, **1** is by 16.8 kJ·mol^{-1} more stable than **1a** and the isomerization process is slightly endergonic. However, in the studied solvents, the isomerization is thermodynamically favored, and in THF and dichloromethane **1a** becomes more stable than **1** (Table 1). With the increase of the dielectric constant of the solvent the equilibrium shifts towards the formation of the abnormal isomer **1a**. This trend is in agreement with the higher dipole moment of **1a** (7.35 and 11.93 D for **1** and **1a**, respectively). The higher content of **1a** in THF possibly reflects the direct participation of THF in the normal-to-abnormal isomerization, as it was shown for the I^{t}Bu·AlMe$_3$/*a*I^{t}Bu·AlMe$_3$ isomer pair.[8] In case of the bulky I^{t}Bu·AlR$_3$ adducts with their substantial steric hindrance, a displacement of I^{t}Bu by much less σ-donating Lewis bases (THF, pyridine) occurs and the transient THF·AlR$_3$ complex and free carbene are observed.

Table 1. Computed ΔE (in kJ·mol^{-1}) of isomer **1a** with respect to **1**, standard enthalpies ΔH°$_{298}$, standard Gibbs free energies ΔG°$_{298}$ (in kJ·mol^{-1}), equilibrium constants K$_{298}$ for the process **1** = **1a**. B3LYP-D3/def2-SVPD level of theory, PCM for the solvent.

Medium	ΔE	ΔH°$_{298}$	ΔG°$_{298}$	K$_{298}$
gas phase	16.8	15.8	9.7	0.02
***n*-hexane**	5.7	4.7	–2.6	2.9
benzene	3.1	2.2	–3.9	4.9
THF	–7.3	–8.0	–15.0	426.7
dichloromethane	–8.1	–8.8	–16.0	630.8

In contrast, in our NMR studies, in different solvents, no signals of free I^{t}Bu were detected. Moreover, we found that **1** isomerizes to **1a** even in the solid state. Two hours after the synthesis of **1**, the content of **1a** in the mixture of isomers was only 14%, according to ^{1}H NMR in CD$_2$Cl$_2$. After one month of storage of the product in the solid state in a dry glovebox under argon, the amount of **1a** had increased to up to 89%, and after 81 days, only the isomer **1a** was present in the solid state.[13] This observation is unprecedented, as normal-to-abnormal NHC-complex isomerization in the solid state (without solvent promotion) has not been reported to date.

In order to shed light on the mechanism involved in this solid-state, solvent-free isomerization, additional computational studies were performed at the B3LYP-D3/def2-SVPD level of theory. We considered two possible pathways for the solvent-free isomerization. The first one includes an H-transfer *via* in situ H$_2$ formation and subsequent reaction, apparently showing, however, a very high Gibbs energy of activation (403 kJ·mol^{-1}), which indicates that this reaction pathway is exceptionally slow.[13] The second pathway consists of the dissociation of **1** and an NHC-assisted proton transfer, a dissociation pathway similar to the one that was proposed for the isomerization of IDipp·GaR$_3$ (R = CH$_2$SiMe$_3$).[17] In this case, too, the Gibbs energy of 375 kJ·mol^{-1} is still very high to make the isomerization through this pathway operational. Thus, two possible pathways were examined and rejected on the basis of the DFT computations. The isomerization mechanism remains an intriguing topic for further research.

4.3. Conclusion

For the first time, we observed a solvent-free isomerization of NHC complexes coordinating to AlH_3 in the solid state. The isomerization of **1** both in the solid state and in solution results in a complex of an abnormal NHC **1a**. The molecular structures of both isomers were determined by X-ray single crystal analysis. **1** demonstrated a very slow rate of isomerization in the non-polar solvent benzene. The isomerization is promoted by more polar solvents as for instance THF or CD_2Cl_2. The results of the DFT computations are in agreement with the experimental NMR observations, stressing the influence of the polarity of the solvent on the isomerization process.

4.4. References

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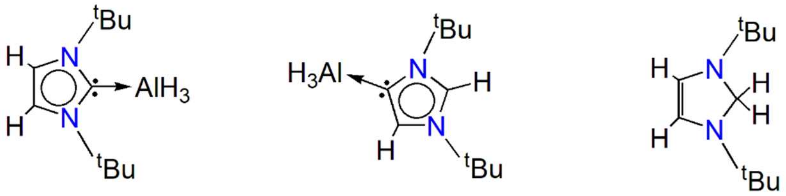
4.5. Supporting Information

4.5.1. Experimental Section

General procedures: All manipulations were performed under dry argon using standard Schlenk and glove-box techniques. All solvents were purified and degassed by standard procedures.[1] The I^{t}Bu was prepared according to literature procedure from the corresponding imidazolium salt.[2] $LiAlH_4$ was obtained from Sigma-Aldrich (95%) and used without further purification. Deuterated solvents (benzene-d^6, dichloromethane-d^2 and tetrahydrofuran-d^8) were purchased from Sigma Aldrich, distilled, degased and stored over activated molecular sieves (4Å). The NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers. ^{1}H NMR spectra were calibrated using residual proton signals of the solvent: (δ ^{1}H(C_6D_5H) = 7.16; δ ^{1}H(THF) = 1.72, 3.58; δ ^{1}H($CHDCl_2$) = 5.32 ppm). ^{13}C NMR spectra were calibrated using the solvent signals (δ ^{13}C(C_6D_6) = 128.06; δ ^{13}C(d_8-THF) = 67.21, 25.31; δ ^{13}C(CD_2Cl_2) = 53.84 ppm). Elemental analyses (C, H, N) were performed on a Vario micro cube.

Synthesis of 1/1a:



1 **1a** I^{t}BuH$_2$

First attempt: 0.5 g (2.78 mmol) I^{t}Bu was dissolved in 5 ml of Et_2O and added to a suspension of 0.32 g (8.33 mmol) $LiAlH_4$ in 12 ml Et_2O at −30 °C. The mixture was stirred and allowed to reach room temperature with additional stirring for 2 days. Ether was removed under vacuum and the product was extracted in 30 ml of toluene and filtered over a celite pad. The resulting white solid was obtained after removing of toluene.

^{1}**H NMR** (400 MHz, C_6D_6, 298 K) showed that during this attempt not all of the I^{t}Bu has reacted and the product mixture consisted of **1** (62% of the mix, δ = 6.41 (s, 2H, NC_2H_2N), 5.42 (br, AlH_3), 1.55 (s, 18H, ^{t}Bu) ppm), I^{t}Bu (35% of the mix, δ = 6.50 (s, 2H, NC_2H_2N), 1.37 (s, 18H, ^{t}Bu) ppm) and the side product I^{t}BuH$_2$ (3% of the mix, δ = 5.49 (s, 2H, NC_2H_2N), 4.25 (s, 2H, NCH_2N), 1.00 (s, 18H, ^{t}Bu) ppm). After the subsequent syntheses (attempts 2 and 3) no free I^{t}Bu was observed. Colorless crystals of **1a** were obtained by dissolving small amount of product mixture in THF layered with *n*-hexane and storing the solution at 6°C for a week (Fig. S11).

Second attempt: 0.1 g (0.56 mmol) I^{t}Bu was dissolved in 5 ml of Et_2O and added to a suspension of 76 mg (2 mmol) $LiAlH_4$ in 10 ml Et_2O at 0 °C. After warming up to room temperature, the mixture was stirred for 1 day. Ether was removed under vacuum and the product was extracted in 30 ml of toluene and filtered over a celite pad. The resulting white solid was obtained after removing of toluene. The product is a mixture of isomers: normal (**1**) and abnormal (**1a**). The side product I^{t}BuH$_2$ (9%) is observed as in the first attempt. The attempt to obtain the crystals of **1** or **1a** from hexane solution at −27 °C failed. The isomers **1** and **1a** can be distinguished by the singlets of the tert-butyl protons: in case of **1** one singlet at 1.55 ppm for 18 tert-butyl protons is observed in C_6D_6, while **1a** gives two singlets at 1.47 and 0.68 ppm since the two ^{t}Bu-groups are non-equivalent.

^{1}**H NMR** (400 MHz, C_6D_6, 298 K) of **1**: δ = 6.41 (s, 2H, NC_2H_2N), 5.42 (br, AlH_3), 1.55 (s, 18H, ^{t}Bu) ppm; **1a**: δ = 7.26 (s, 1H, NCHN), 6.75 (s, 2H, NC_2HN), 4.34 (br, AlH_3), 1.47 (s, 9H, ^{t}Bu), 0.68 (s, 9H, ^{t}Bu) ppm (Fig. S1).

^{13}C NMR (100 MHz, C_6D_6, 298 K) of **1**: δ = 30.61 (CH$_3$-^{t}Bu), 59.94 (C(CH$_3$)$_3$), 117.23 (N*C*H*C*HN) ppm (Fig. S2).

Third attempt: 0.5 g (2.78 mmol) I^{t}Bu was dissolved in 10 ml of Et_2O and added to a suspension of 0.21 g (5.55 mmol) $LiAlH_4$ in 10 ml Et_2O at −50 °C. After warming up to room temperature, the mixture was stirred for 1 day. Ether was removed under vacuum and the product was extracted in 30 ml of toluene and filtered over a celite pad. The resulting white solid was obtained after removing of toluene. The small amount of white product was dissolved again in toluene and within 3 days at 6 °C crystals of **1** were obtained (Fig. S12).

CHN (%) calc. for $C_{11}H_{23}AlN_2$: C 62.83, H 11.02, N 13.32; Found: C 63.15, H 10.20, N 13.33.

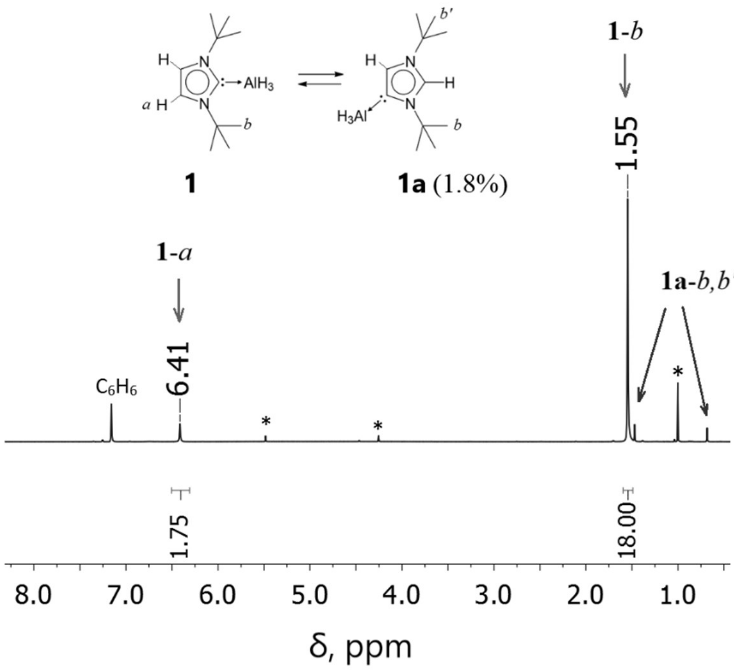


Figure S1: ^{1}H NMR spectrum (C_6D_6, 400 MHz) of product mixture with **1** form predominance. * denotes I^{t}BuH$_2$ (8.5%).

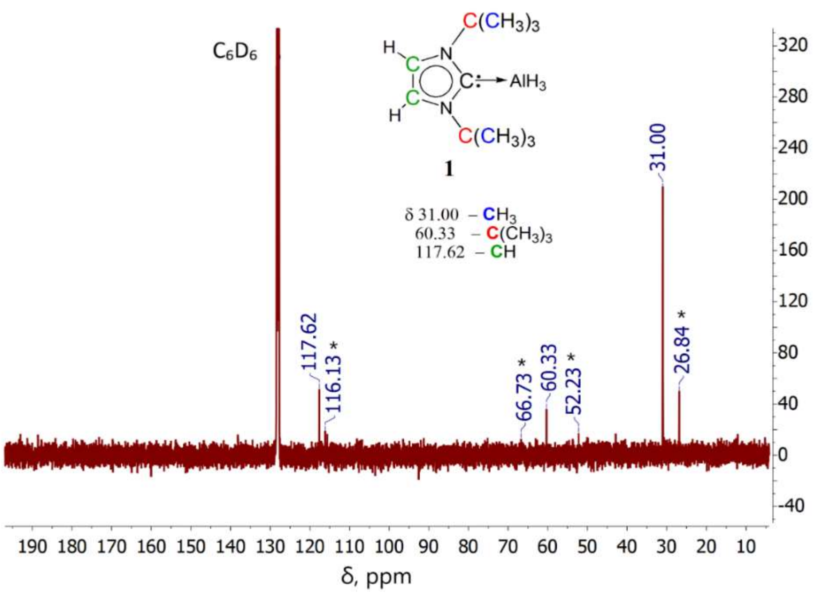


Figure S2: ^{13}C NMR spectrum (C_6D_6, 100 MHz) of product mixture.

The role of the solvent in the isomerization

In order to understand the role of the solvent in the formation of abnormal isomer, the synthesis was repeated and NMR studies were carried out. 0.2 g (1.12 mmol) I*t*Bu was dissolved in 4 ml of Et_2O and added to a suspension of 0.14 mg (4 mmol) $LiAlH_4$ in 10 ml Et_2O at −20 °C. After warming up to room temperature, the mixture was stirred for 1 day. Ether was removed under vacuum and the product was extracted in 40 ml of toluene and filtered to remove LiH and the excess of $LiAlH_4$. The resulting white solid was obtained after removing of toluene. ^{1}H NMR and ^{13}C NMR spectra were measured in C_6D_6 and CD_2Cl_2 just after the synthesis. In nonpolar C_6D_6 the content of abnormal isomer **1a** is the lowest and equals 1.8% (Fig. S3 + S4). Amount of **1a** increases in the case of more polar solvent dichloromethane (14%) (Fig. S5 + S6). NMR measurements were carried out at room temperature ca. 2 hours after the addition of the solvent.

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K) of **1**: δ = 7.20 (s, 2H, NC_2H_2N), 4.41 (br, AlH_3), 1.80 (s, 18H, CH_3-*t*Bu) ppm; **1a**: δ 8.01 (d, $^4J_{H,H}$ = 1.8 Hz, 1H, NC*H*N), 7.28 (d, $^4J_{H,H}$ = 2 Hz, 1H, 1H, NC_2HN), 3.19 (br, AlH_3), 1.73 (s, 9H, CH_3-*t*Bu), 1.60 (s, 9H, CH_3-*t*Bu) ppm.

For comparison the **^{1}H NMR** (400 MHz, CD_2Cl_2, 298 K) for I*t*Bu·$AlMe_3$/*a*I*t*Bu·$AlMe_3$[3]: I*t*Bu·$AlMe_3$: δ = 7.17 ppm (s, 2H, NCHCHN), 1.73 (s, 18H, CH_3-tBu), -0.73 (s, 9H, $AlMe_3$); aI*t*Bu·$AlMe_3$: δ = 7.92 (d, $^4J_{H,H}$ = 2 Hz, 1H, NC*H*N), 7.10 (d, $^4J_{H,H}$ = 2 Hz, 1H, NC*H*CN), 1.65 (s, 9H, CH_3-*t*Bu), 1.59 (s, 9H, CH_3-*t*Bu), -0.96 (s, 9H, $AlMe_3$) ppm.

^{13}C NMR (CD_2Cl_2, 100 MHz, 298 K) of **1**: δ = 31.33 (*C*H_3-*t*Bu), 60.67 (*C*$(CH_3)_3$), 118.51 (N*C*H*C*HN) ppm; **1a**: δ 30.31 (*C*H_3-*t*Bu), 30.47 (*C*H_3-*t*Bu), 58.15 (*C*$(CH_3)_3$), 63.09 (*C*$(CH_3)_3$), 153.91 ($C_{carbene}$) ppm.

For comparison the **^{13}C NMR** (75 MHz, CD_2Cl_2, 298 K) for I^{t}Bu·$AlMe_3$/*a*I^{t}Bu·$AlMe_3$[3]: I^{t}Bu·$AlMe_3$: δ = -0.8 ($AlMe_3$), 31.4 (CH_3-^{t}Bu), 59.1 ($C(CH_3)_3$), 117.4 (N*C*H*C*HN), 174.3 ($C_{carbene}$) ppm; aI^{t}Bu·$AlMe_3$: δ = -6.1 ($AlMe_3$), 29.9 (CH_3-^{t}Bu), 30.4 (CH_3-^{t}Bu), 57.2 ($C(CH_3)_3$), 59.1 ($C(CH_3)_3$), 126.8 (N*C*H*C*N), 128.6 (N*C*HN), 155.9 ($C_{carbene}$) ppm.

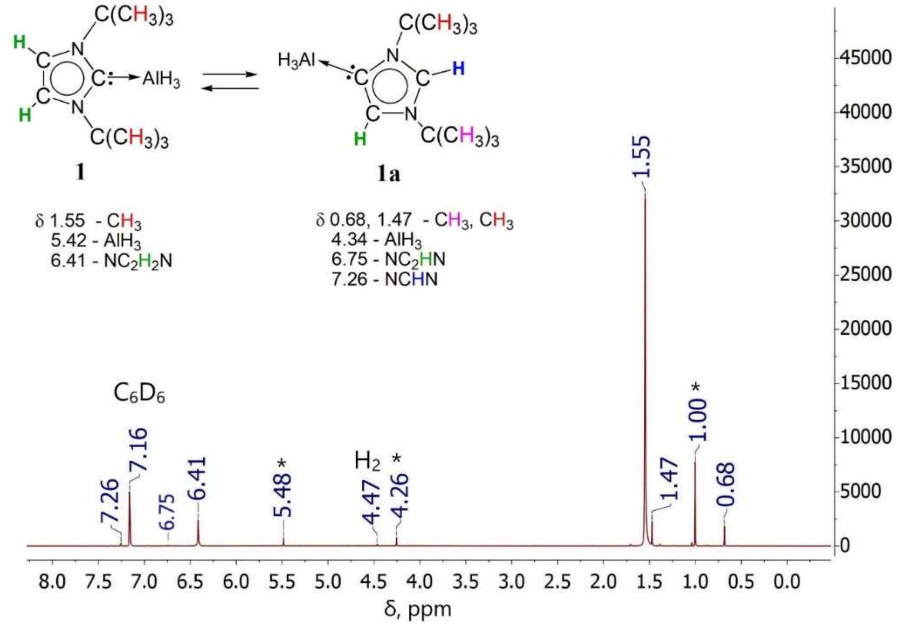


Figure S3: ^{1}H NMR spectrum (C_6D_6, 400 MHz) of product mixture with isomer **1** predominance. * denotes I^{t}BuH$_2$ (8%).

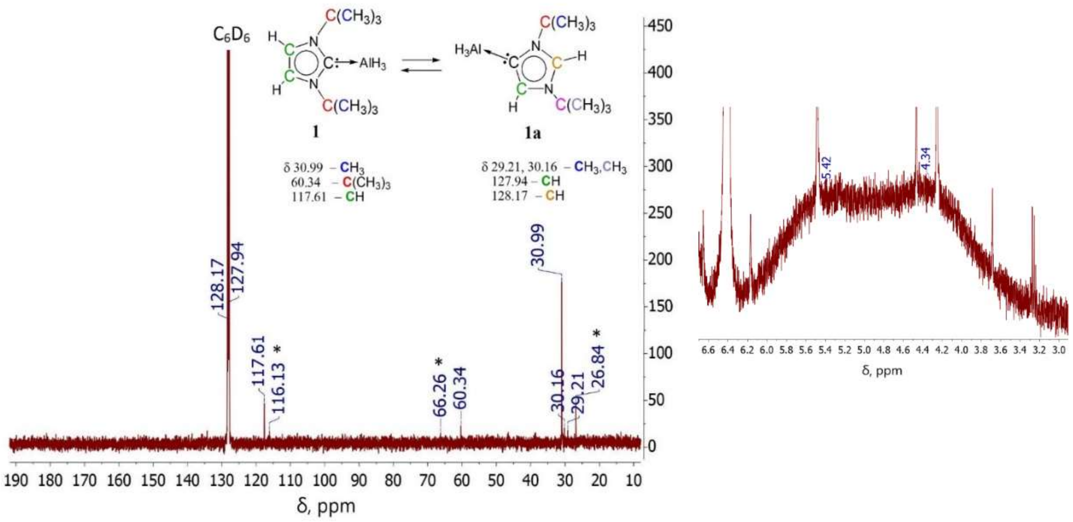


Figure S4: ^{13}C NMR spectrum (C_6D_6, 100 MHz) (left); ^{1}H NMR spectrum (C_6D_6, 400 MHz) of product mixture: fragment with AlH_3 signals (right). * denotes I^{t}BuH$_2$ (8%).

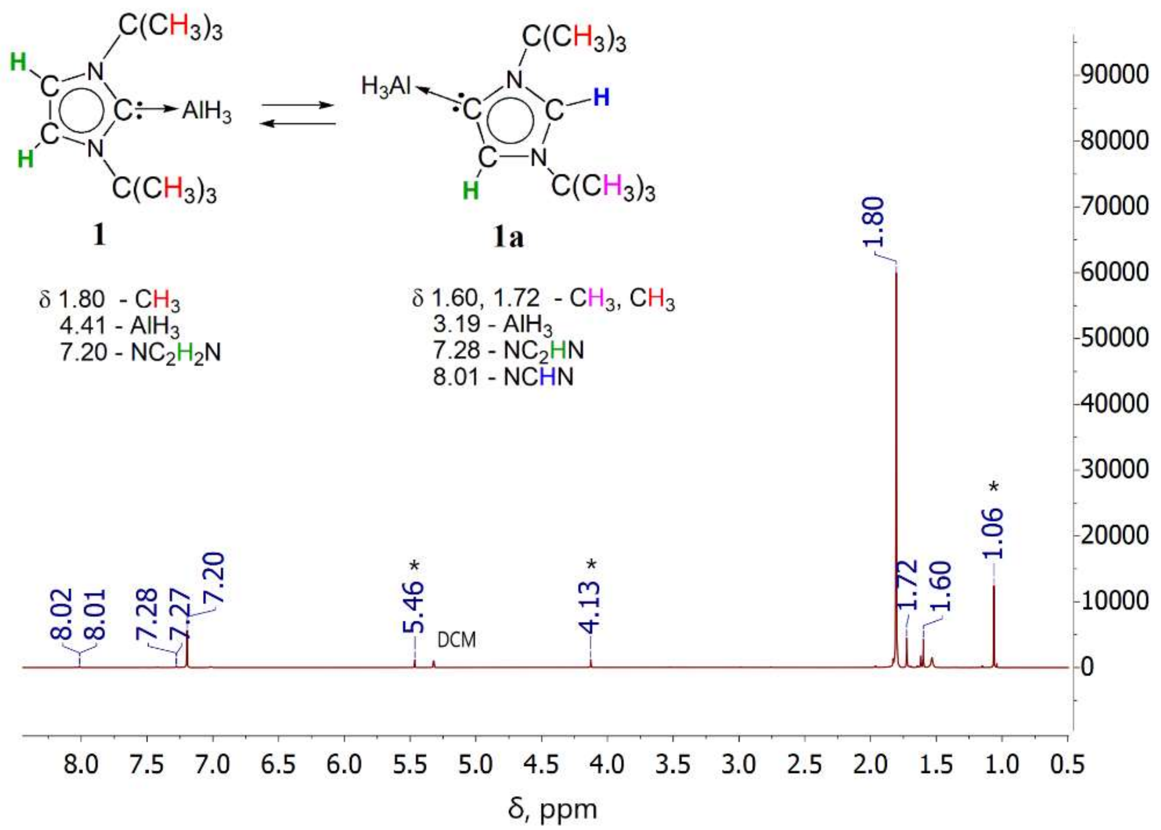


Figure S5: [1]H NMR spectrum (CD_2Cl_2, 400 MHz) or product mixture. * denotes I^{t}BuH$_2$.

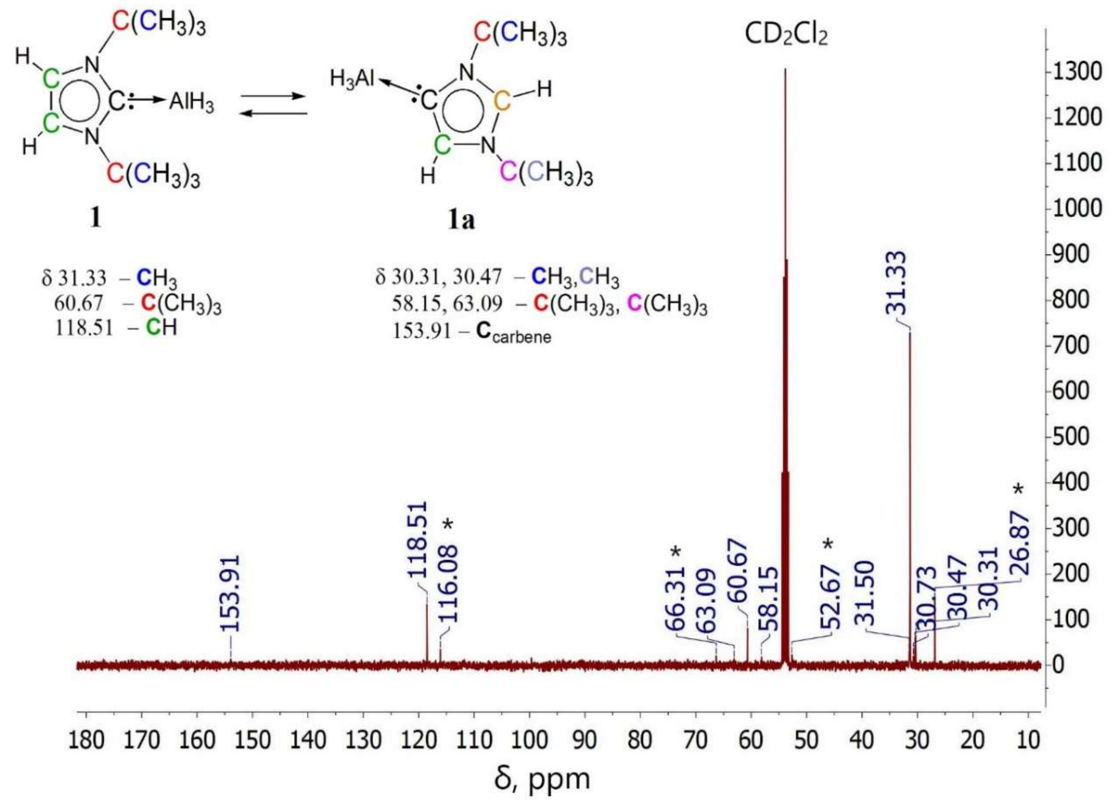


Figure S6: [13]C NMR spectrum (CD_2Cl_2, 100 MHz) of product mixture. * denotes I^{t}BuH$_2$.

The NMR spectra were measured also in d_8-THF after 3 weeks of storing the product under argon.

^{1}H NMR (d_8-THF, 400 MHz, 298 K) of **1**: δ = 7.33 (s, 2H, NC_2H_2N), 4.13 (br, AlH_3), 1.74 (s, 18H, ^{t}Bu) ppm; **1a**: δ 8.39 (s, 1H, NCHN), 7.27 (s, 2H, NC_2HN), 3.34 (br, AlH_3), 1.73 (s, 9H, ^{t}Bu), 1.60 (s, 9H, ^{t}Bu) ppm.

^{13}C NMR (d_8-THF, 100 MHz, 298 K) of **1**: δ = 31.22 (*C*H_3-^{t}Bu), 59.66 (*C*$(CH_3)_3$), 118.14 (N*C*H*C*HN) ppm, **1a**: δ 29.77 (*C*H_3-^{t}Bu), 30.29 (*C*H_3-^{t}Bu), 57.96 (*C*$(CH_3)_3$), 60.27 (*C*$(CH_3)_3$), 128.52 (N*C*H*C*N), 130.92 (N*C*HN) (Fig. S7 +S8).

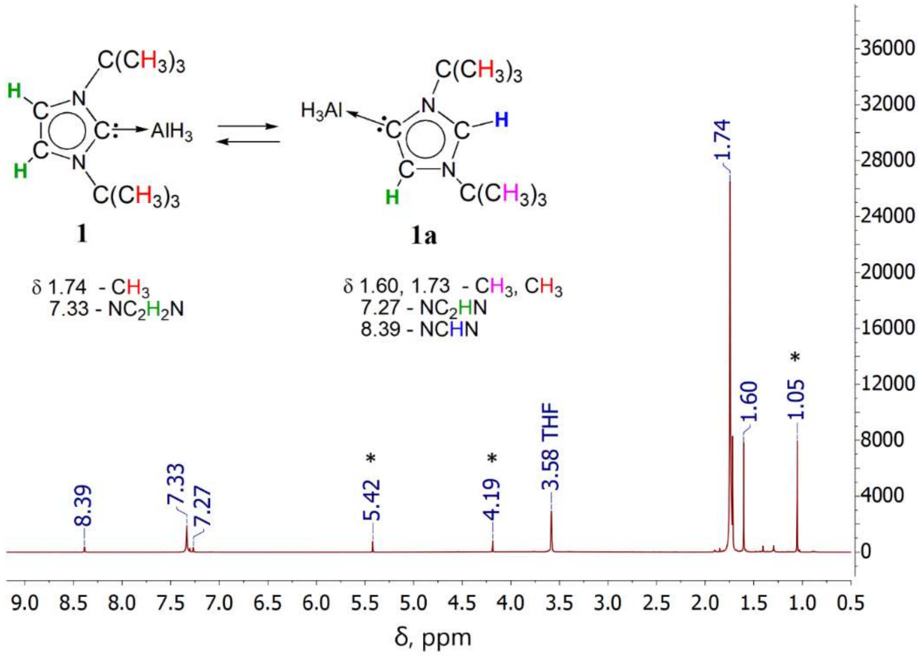


Figure S7: ^{1}H NMR spectrum (d^8-THF, 400 MHz) of product mixture. * denotes I^{t}BuH_2.

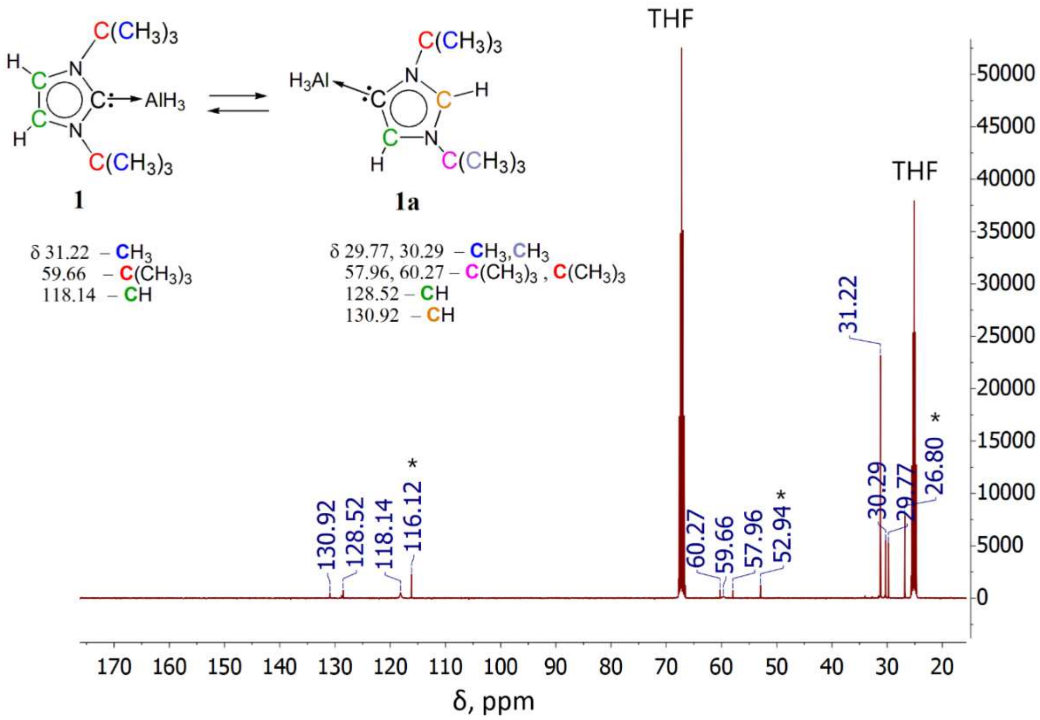


Figure S8: ^{13}C NMR spectrum (d^8-THF, 100 MHz) of product mixture. * denotes I^{t}BuH$_2$.

THF as medium has lower dielectric constant ε = 7.43[4] than the dichloromethane (ε = 8.93)[4] and the content of form **1a** was expected to be lower than in case of CD_2Cl_2 (see DFT computations Table S5), but it equaled 19% (Fig. S5 + S6). This fact points on the specific joint of THF in isomerization process or the isomerization in the solid state during storing.

Isomerization in the solid state

We decided to check if **1** isomerizes into **1a** in the solid state. According to ^{1}H NMR in CD_2Cl_2 NMR after 2 hours after the synthesis and isolation of **1** the content of **1a** in the mixture of isomers was only 14% (NMR control). After 32 days of storage of the product in the solid state under argon the amount of **1a** increased up to 89 %, and after 81 days only isomer **1a** is present in the solid state (Fig. S9, Fig. S10). The signals of ^{t}Bu protons are the most representative (1.80 ppm for **1**, 1.72 and 1.60 ppm for **1a**).

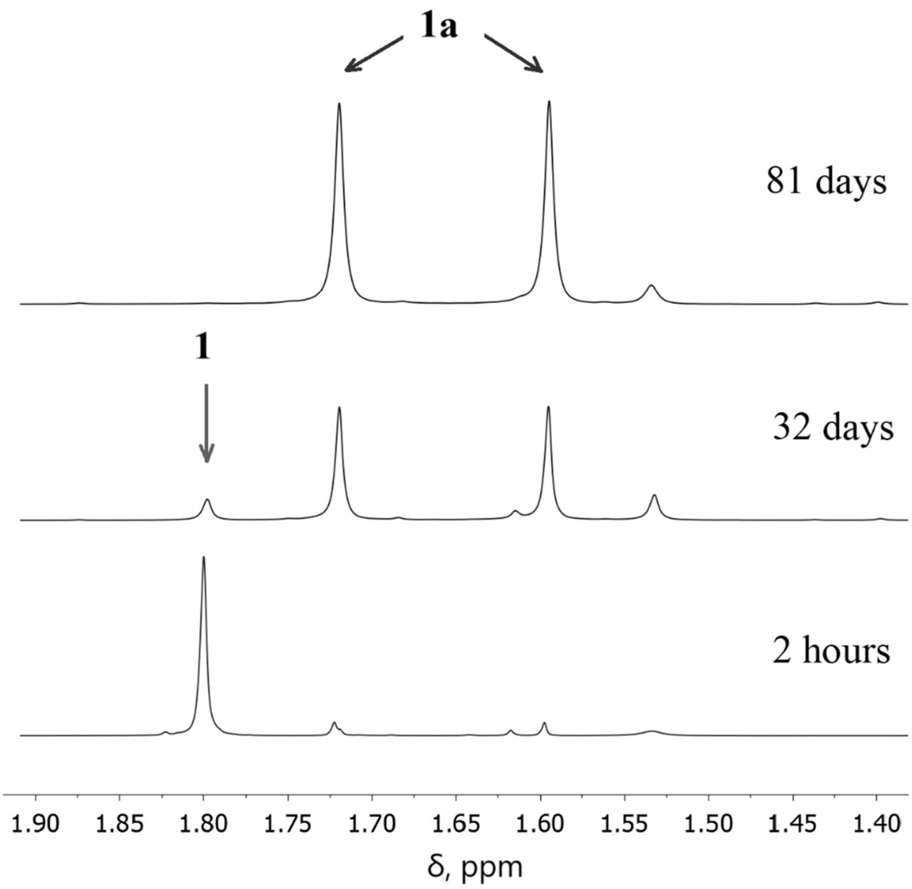


Figure S9: Section of ^{1}H NMR spectra (CD_2Cl_2, 400 MHz): the increase of the contents of **1a** after 32 days and 81 days of storing the product mixture in the solid state under argon.

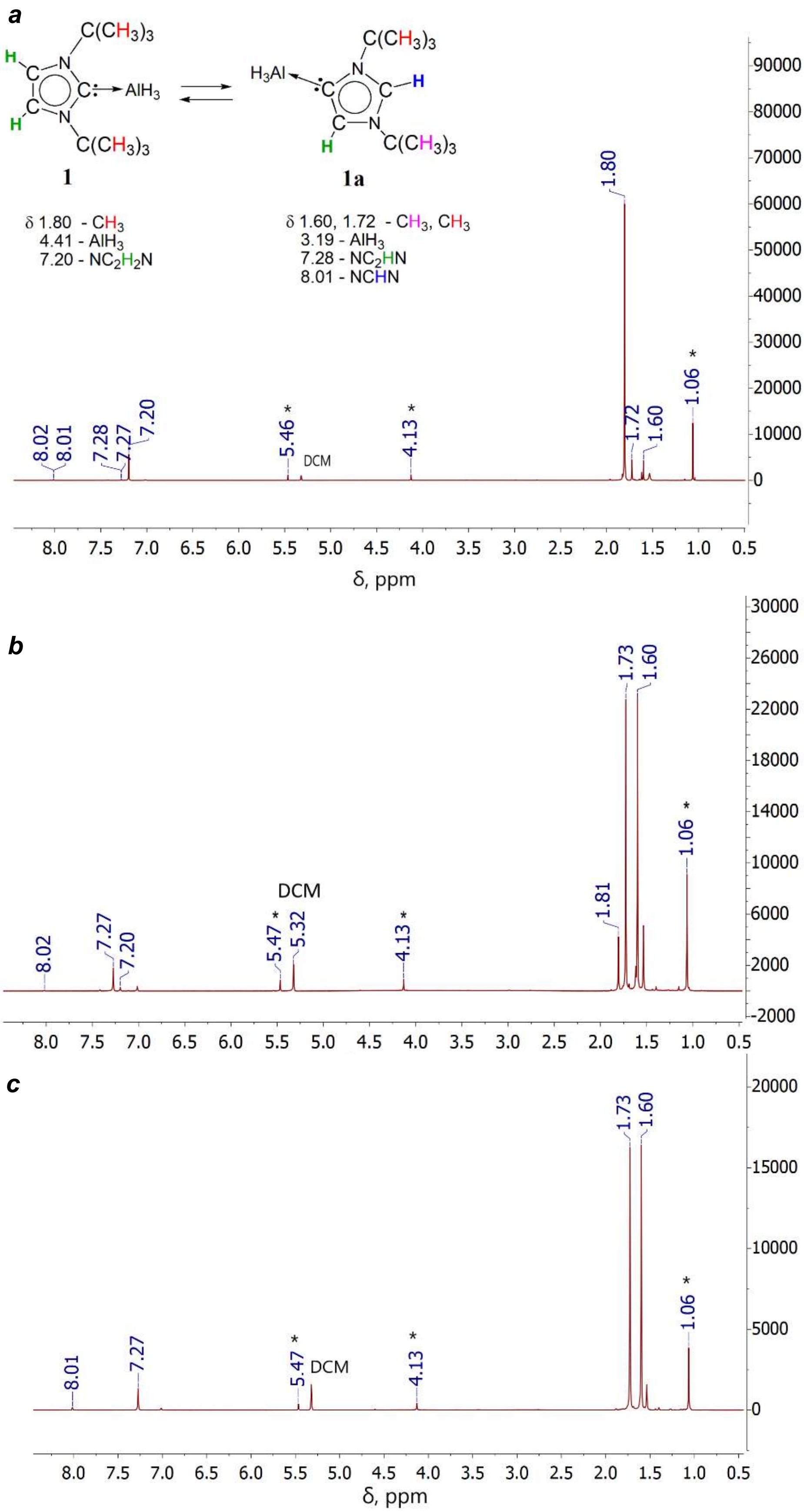


Figure S10: ^{1}H NMR spectra (CD_2Cl_2, 400 MHz) of product mixture: a) 2 hours after synthesis, b) after 32 days, c) after 81 days.

4.5.2. Crystallographic data

The single crystal X-Ray structure analysis was performed on a Rigaku Oxford Diffraction SuperNova and a Rigaku Oxford Diffraction GeminiUltra diffractometers applying Cu-Kα radiation (λ = 1.54178 Å) at 123 K. All crystallographic manipulations were performed under mineral oil. Crystals were selected from the ampule in an inert atmosphere and placed into dehydrated and deoxygenated mineral oil. A selected crystal was mounted on a plastic MiTeGen CryoMounts® loop under a stream of cold N_2. The structure was solved using the Olex2 program[5] and refined anisotropically against F2 using the SHELXT program.[6] Crystallographic data together with the details of the experiment are given in Table S1. All cif-files (CCDC 1966204 (**1**) and 1966205 (**1a**)) are available online from the Cambridge Crystallographic Data Centre.

CCDC-1966204 (**1**) and CCDC-1966205 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Summary of crystallographic data and structure refinement for complex **1** and **1a**.

Compound	**1**	**1a**
Formula	$C_{11}H_{23}AlN_2$	$C_{11}H_{23}AlN_2$
$D_{calc.}$ / g · cm^{-3}	1.038	1.027
μ/mm^{-1}	1.061	1.050
Formula Weight	210.29	210.29
Colour	colorless	colorless
Shape	block	block
Size/mm^3	0.95×0.35×0.29	0.45×0.20×0.13
T/K	122.98(10)	123.0(2)
Crystal System	tetragonal	monoclinic
Space Group	$P4_2/n$	$P2_1/n$
a/Å	13.99950(10)	8.5552(5)
b/Å	13.99950(10)	11.6275(7)
c/Å	13.7306(2)	13.9902(8)
α/°	90	90
β/°	90	102.264(6)
γ/°	90	90
V/Å^3	2691.00(5)	1359.92(14)
Z	8	4
Z'	2	1
Wavelength/Å	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α
Θ_{min}/°	4.467	4.993
Θ_{max}/°	73.444	74.701
Measured Refl.	7413	7331
Independent Refl.	2605	2672
R_{int}	0.0187	0.0731
Parameters	146	146
Restraints	0	0
Largest Peak	0.261	0.438
Deepest Hole	-0.232	-0.461
GooF	1.047	1.058
wR_2 (all data)	0.0877	0.1755
wR_2	0.0867	0.1670
R_1 (all data)	0.0330	0.0649
R_1	0.0317	0.0599

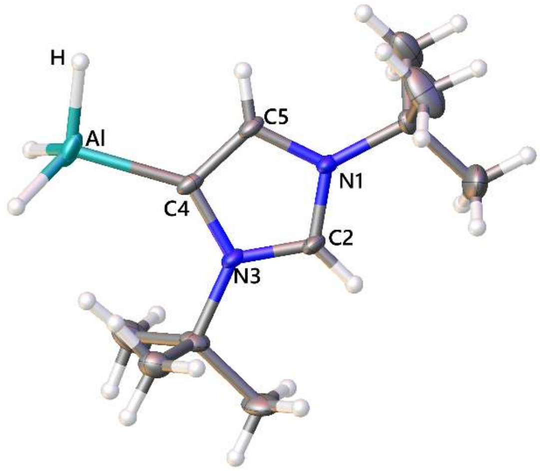
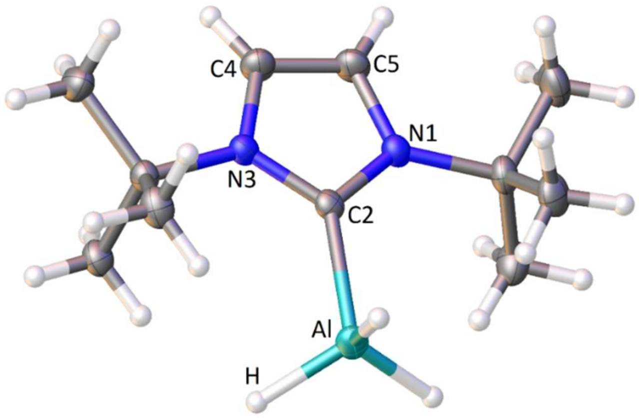


Figure S11: Molecular structure of complex **1a**. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental bond distances [Å] and angles [°]: Al–C4 2.026(2); Al–H 1.56(3), C2–N1 1.326(3), C2–N3 1.332(3), N3–C4 1.411(2), N1–C5 1.383(3), C4–C5 1.355(3), N1–C2–N3 109.35(17), N3–C4–C5 103.39(16).



1

Figure S12: Molecular structure of complex **1**. Anisotropic displacement parameters are depicted at the 50% probability level. Selected experimental bond distances [Å] and angles [°]: Al–C2 2.0838(11); Al–H 1.50(2); C2–N1 1.3684(14); C2–N3 1.3694(14); N3–C4 1.3790(15); N1–C5 1.3787(15); C4–C5 1.3406(17); N1–C2–N3 104.45(9); N3–C4–C5 107.28(10).

4.5.3. Computational data

Computational details

Density functional theory in form of B3LYP-D3[7] functional with conjunction of def2-SVPD[8] basis set was used as implemented in Gaussian-16 software suite[9] to locate minima and transition states on the respective potential energy surfaces of the studied systems. Vibrational frequency computations were performed to verify that obtained stationary points are either true minima (Nimag=0) or transition states (Nimag=1) and to obtain the thermodynamic characteristics. Intrinsic reaction coordinate (IRC[10]) scans were performed to prove that the transition state connects the corresponding reactants and products. In order to take into account solvent effects, the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM)[11] was used.

Mechanistic studies

We considered two pathways of solvent-free isomerization. The first includes H-transfer via in situ H_2 formation and subsequent reaction (pathway 1). The second pathway consists of dissociation and NHC-assisted proton transfer (pathway 2). Computed reaction pathways are depicted in Fig. S12 and Fig. S13.

Pathway 1:

As a starting point for the geometry optimization, geometry of the one asymmetric unit of **1a** that contains two neighboring *a*I^{t}Bu·AlH_3 molecules was used. We succeeded in locating the transition state **TS4** (Fig. S12) featuring the hydrogen expulsion reaction which leads to the intermediate **4**, which was confirmed by the intrinsic reaction coordinate (IRC) scan. In the same manner we located transition state **TS3** and suggested the reaction pathway up to **1** through 8 steps forming 3 intermediates. The reaction starts with interaction of the hydridic H on aluminum in **1** with the hydrogen atom in the NHC backbone of the neighboring molecule. Passing through the transition state **TS1** results in the dihydrogen molecule formation along with intermediate **2**. The formation of **2** is thermodynamically favored (ΔG°_{298} = −31 kJ·mol^{-1}) but the activation barrier is very high (413 kJ·mol^{-1}). Then the reaction with hydrogen leads to cleavage of Al-C bond and formation of ion-pair **3** passing the **TS2**. Next step was suggested in an assumption that hydride in anion of ion-pair **3** interacts with proton in the backbone of the cation of the ion-pair via transition state **TS3**, resulting the hydrogen expulsion and formation of **4**. Finally, **4** reacts with molecular H_2 with cleavage of the Al-C bond via **TS4** and formation of the product **1a** (Fig. S13).

At B3LYP-D3/def2-SVPD level of theory several attempts of localizing **TS2** failed. The Synchronous Transit-guided Quasi-Newton method (QST2 and QST3 options)[12] did not help: the predicted **TS2** reorganizes into the product **3**. **TS2** was localized on a RHF/3-21G* level of theory with subsequent SP-computation on B3LYP-D3/def2-SVPD level of theory.

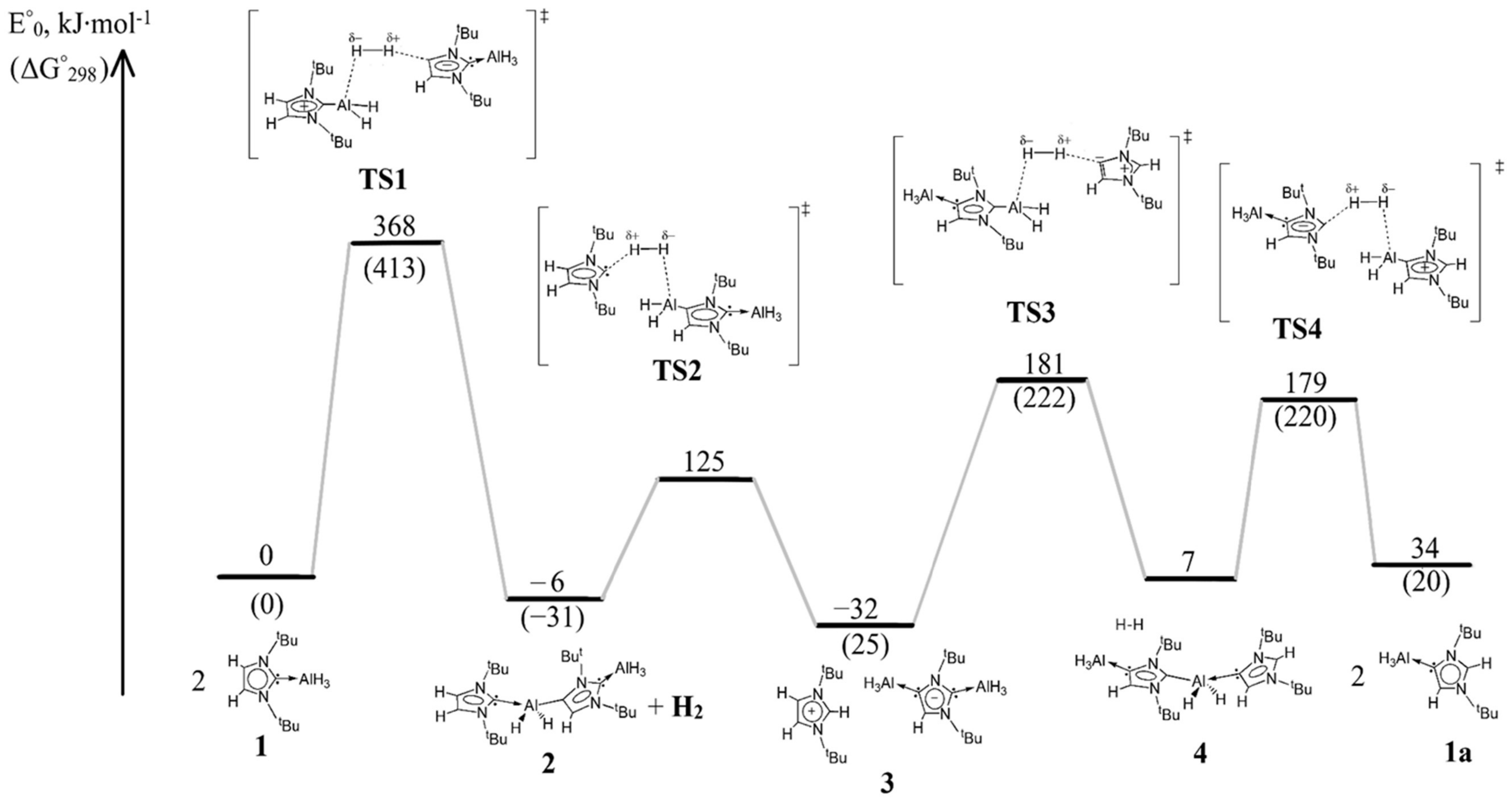


Figure S13. Energy profile for the isomerization process (pathway 1). The relative energies (ΔE°_{298}, in kJ·mol^{-1}) and Gibbs free energy values (ΔG°_{298}, in kJ·mol^{-1}, in parentheses) are given with respect to two isolated molecules of **1**. B3LYP-D3/def2-SVPD level of theory.

Pathway 2:

For pathway 2 the dissociation of one molecule of 1 is considered as a first step (Fig. S14). Then the free carbene I*ᵗ*Bu attacks the hydrogen atom in the NHC backbone of the neighboring molecule 1, passing the TS5 and forming the ion-pair 5. The association of an anion with AlH_3 leads to formation of a more stable ion-pair 3. The dissociation of AlH_3 from C2-carbone of anion leads to the new ion-pair 6. Then the proton in the backbone of cationic part of 6 interacts with the carbene site of anionic part, passing TS6 (TS6′) and forming 1a and *a*I^{t}Bu. The latter forms complex with AlH_3 on the last step. The energy barrier of 425 kJ·mol^{-1} is very high to make the isomerization through this pathway operational.

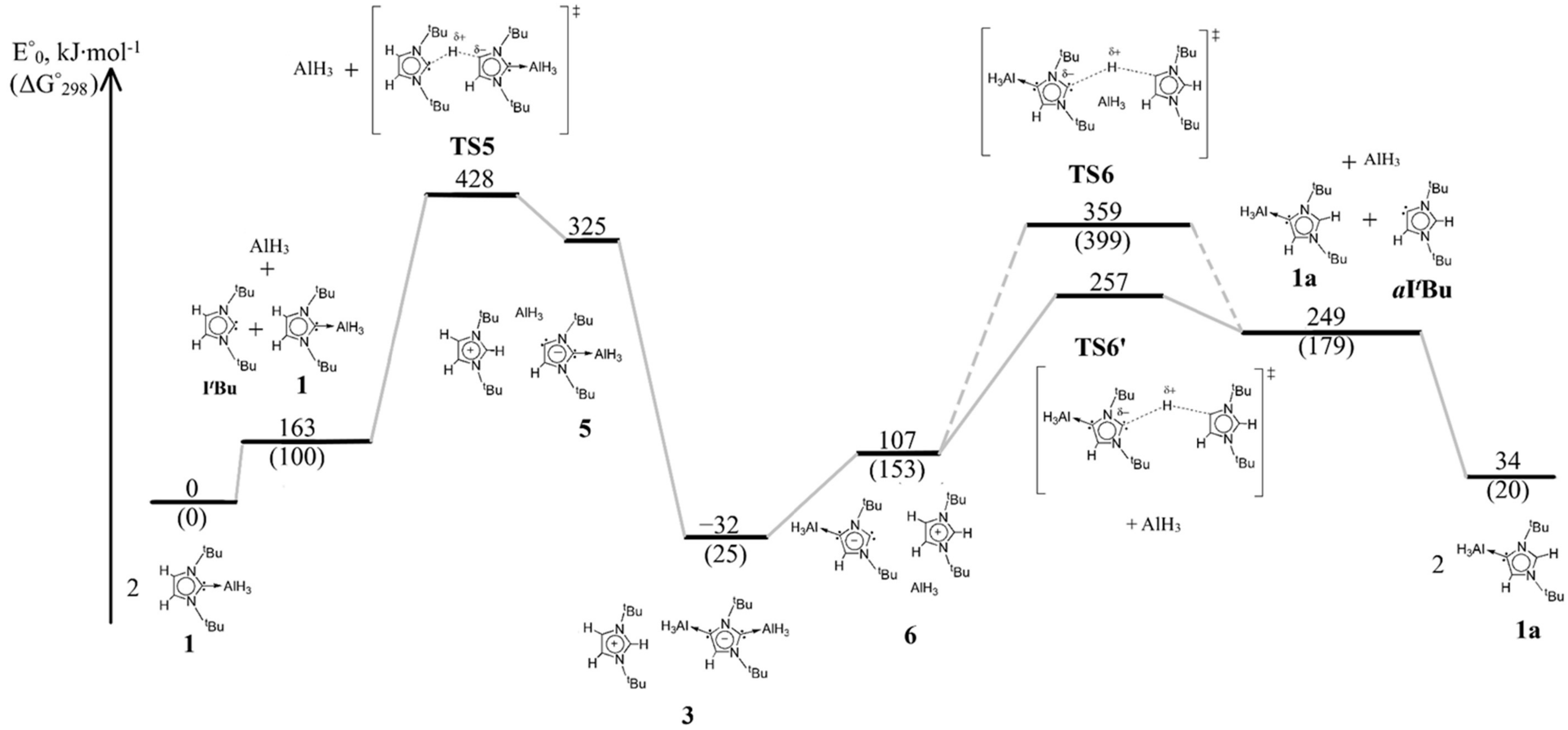


Figure S14. Energy profile for the isomerization process (pathway 2). The relative energies (ΔE°_{0}, in kJ·mol^{-1}) and Gibbs free energy values (ΔG°_{298}, in kJ·mol^{-1}, in parentheses) are given with respect to two isolated molecules of **1**. B3LYP-D3/def2-SVPD level of theory.

Thermodynamic characteristics

Table S2. Total energies E°$_0$, sum of electronic and thermal enthalpies H°$_{298}$, standard Gibbs free energies (Hartree) and standard entropies S°$_{298}$ (cal·mol^{-1}K^{-1}). $^{a)}$ SP energy on B3LYP-D3/def2-SVPD with optimized on RHF/3-21G* geometry.

	B3LYP-D3/def2-SVPD level of theory				RHF/3-21G* level of theory		
Compound	**E°$_0$**	**H°$_{298}$**	**S°$_{298}$**	**G°$_{298}$**	**E°$_0$**	**H°$_{298}$**	**S°$_{298}$**
1	-784.5702435	-784.233327	126.598	-784.293478			
1a	-784.5638492	-784.227324	131.430	-784.289771			
H_2	-1.1738579	-1.160603	31.224	-1.175438			
AlH_3	-244.1458501	-244.123270	49.545	-244.146810			
I^{t}Bu	-540.3622556	-540.052199	118.815	-540.108653			
*a*I^{t}Bu	-540.3357863	-540.025745	118.924	-540.082250			
I^{t}BuH_2	-541.5740532	-541.240872	118.168	-541.297018			
TS1	-1569.0003509	-1568.328925	211.650	-1568.413715			
2	-1567.9739281	-1567.316767	204.045	-1567.413715			
TS2$^{a)}$	-1569.0927777				-1552.9072531	-1552.189447	214.757
3	-1569.1527897	-1568.476936	211.831	-1568.577584			
TS3	-1569.0715338	-1568.399416	216.520	-1568.502292			
4	-1569.1379301	-1568.400758	215.706	-1568.503246			
TS4	-1569.0724876	-1568.400758	215.706	-1568.503246			
TS5$^{a)}$	-1324.8315682				-1310.518006	-1309.827722	193.472
5$^{a)}$	-1569.0169065				-1552.8699562	-1552.149126	226.906
6	-1569.0999114	-1568.425537	217.381	-1568.528822			
TS6	-1569.0037432	-1568.334568	211.167	-1568.434900			
TS6'$^{a)}$	-1324.8969215				-1310.5049524	-1309.915808	198.651

Table S3. Total energies E°$_0$, sum of electronic and thermal enthalpies H°$_{298}$ (Hartree) and standard entropies S°$_{298}$ (cal·mol^{-1}K^{-1}) of **1** and **1a** in gas phase and in different solvents. B3LYP-D3/def2-SVPD level of theory.

Medium	**Compound**	**E°$_0$**	**H°$_{298}$**	**S°$_{298}$**
gas phase	**1**	-784.570244	-784.233327	126.598
	1a	-784.5638492	-784.227324	131.43
n-hexane (ε = 1.8819	**1**	-784.5750926	-784.238259	126.34
	1a	-784.5729135	-784.236457	132.216
C_6H_6 (ε = 2.2706)	**1**	-784.576367	-784.239567	126.335
	1a	-784.5751887	-784.23872	131.258
THF (ε = 7.4257)	**1**	-784.5820578	-784.245467	126.47
	1a	-784.5848261	-784.248497	132.121
DCM (ε = 8.93)	**1**	-784.5826012	-784.246041	126.491
	1a	-784.5857036	-784.249407	132.211

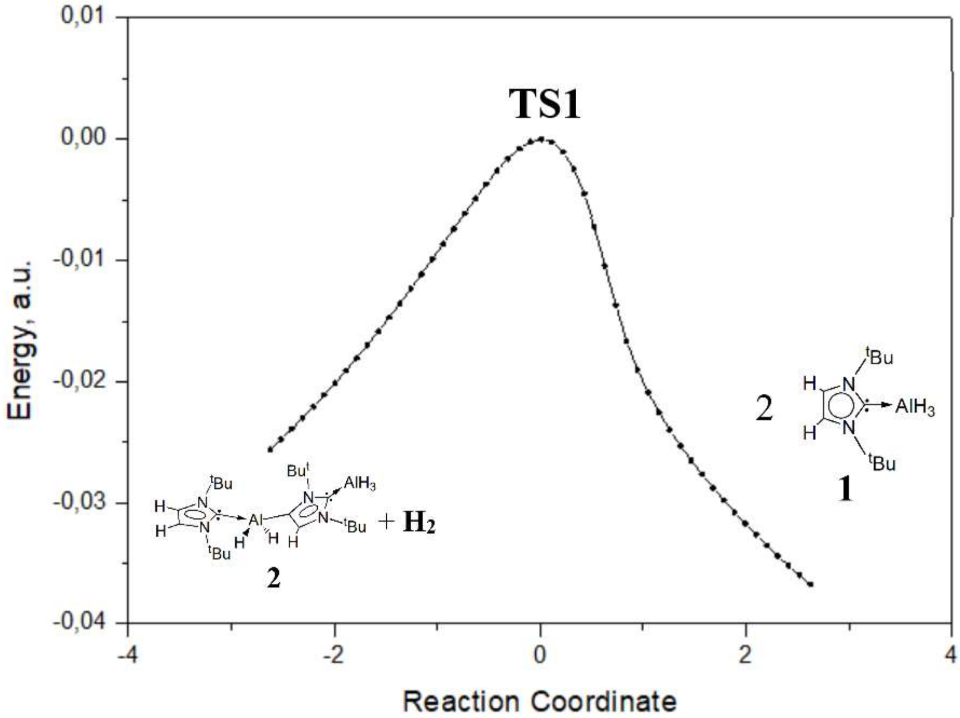
Table S4. Computed energies ΔE°$_0$ (in kJ·mol$_{-1}$), standard enthalpies ΔH°$_{298}$, standard entropies ΔS°$_{298}$ (cal·mol^{-1}K^{-1}) and Gibbs free energies ΔG°$_{298}$ (in kJ·mol^{-1}) for processes (1) – (4) in the gas phase. B3LYP-D3/def2-SVPD, PCM level of theory.

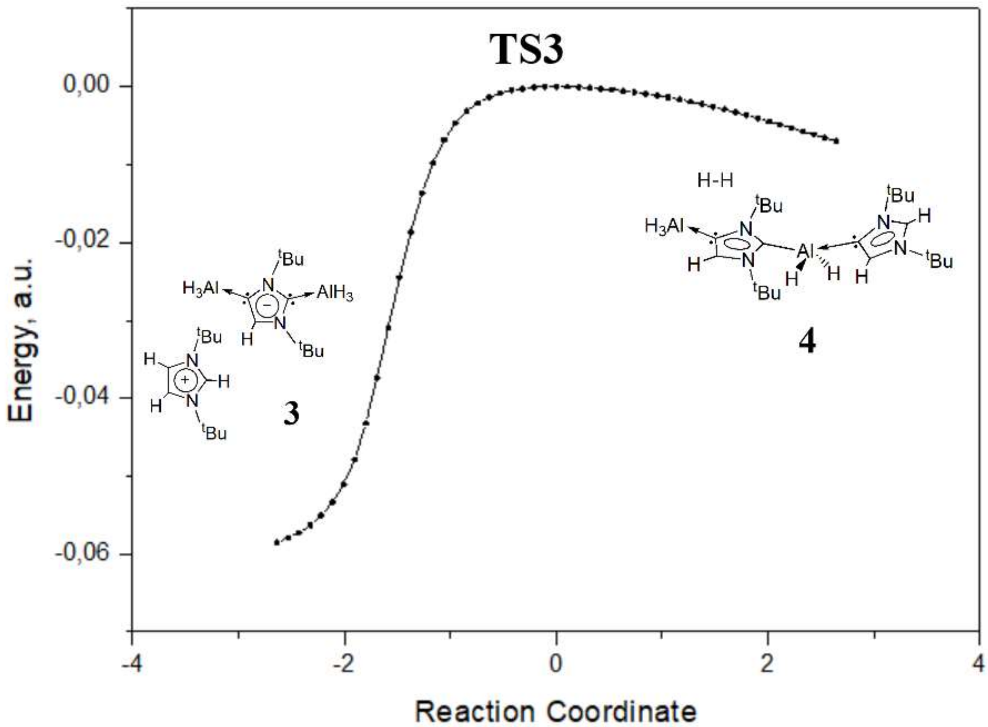
Process		**ΔE°$_0$**	**ΔH°$_{298}$**	**ΔS°$_{298}$**	**ΔG°$_{298}$**
(1)	**1** = I^{t}Bu + AlH_3	163.1	151.9	174.7	99.8
(2)	**1a** = *a*I^{t}Bu + AlH_3	215.8	205.6	155.0	159.4
(3)	I^{t}Bu = *a*I^{t}Bu	69.5	69.5	0.5	69.3
(4)	**1** = **1a**	16.8	15.8	20.2	9.7

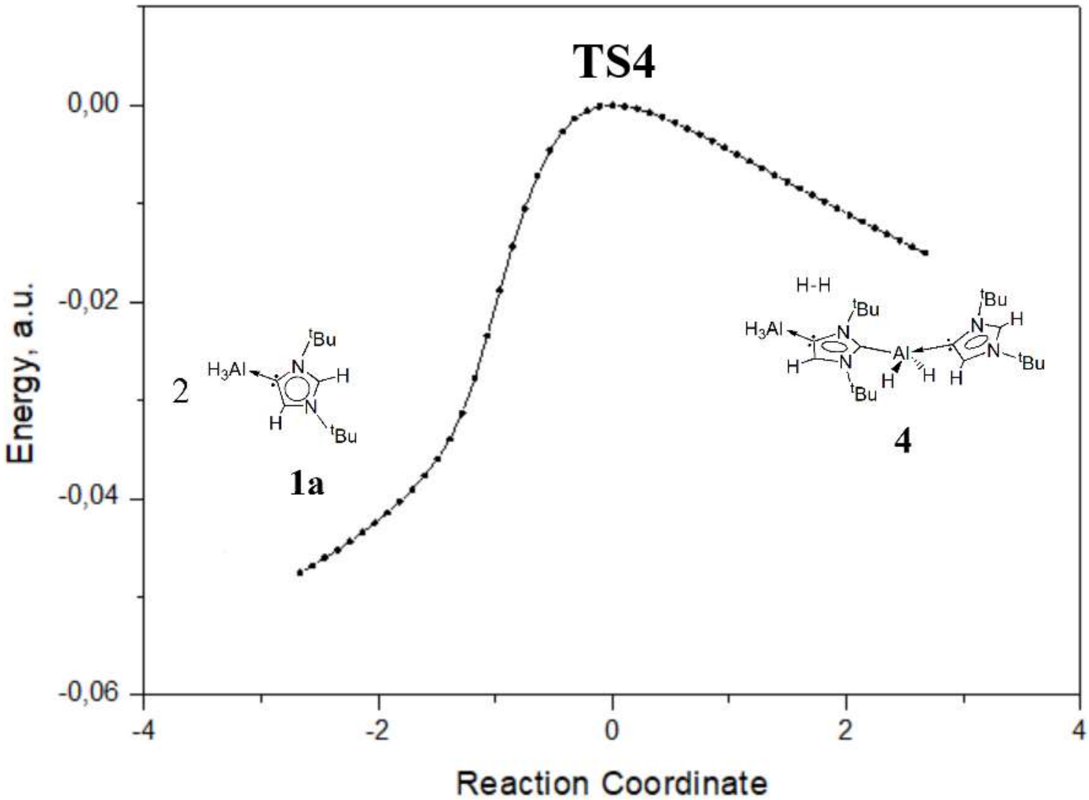
Table S5. Computed ΔE°_0 (in kJ·mol^{-1}) of isomer **1a** with respect to **1**, standard enthalpies ΔH°_{298}, standard Gibbs free energies ΔG°_{298} (in kJ·mol^{-1}), equilibrium constants K_{298} for the process **1** = **1a** and dielectric permittivity of the solvent ε[4] and dipole moments μ[4]. B3LYP-D3/def2-SVPD level of theory, PCM for solvents.

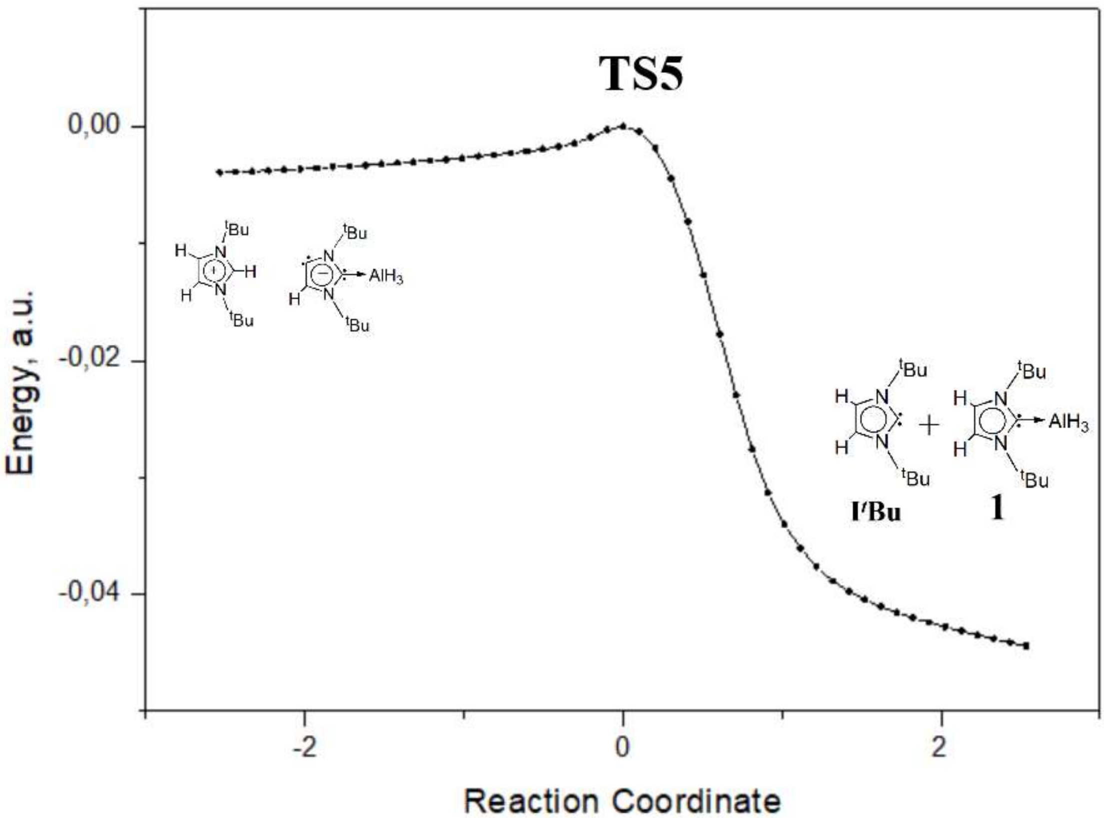
Medium	**ΔE°_0**	**ΔH°_{298}**	**ΔG°_{298}**	**K_{298}**	**ε**	**μ**
gas phase	16.8	15.8	9.7	0.02		
n-hexane	5.7	4.7	–2.6	2.9	1.8819	0.08
benzene	3.1	2.2	–3.9	4.9	2.2706	0
THF	–7.3	–8.0	–15.0	426.7	7.4257	1.75
dichloromethan	–8.1	–8.8	–16.0	630.8	8.93	1.14

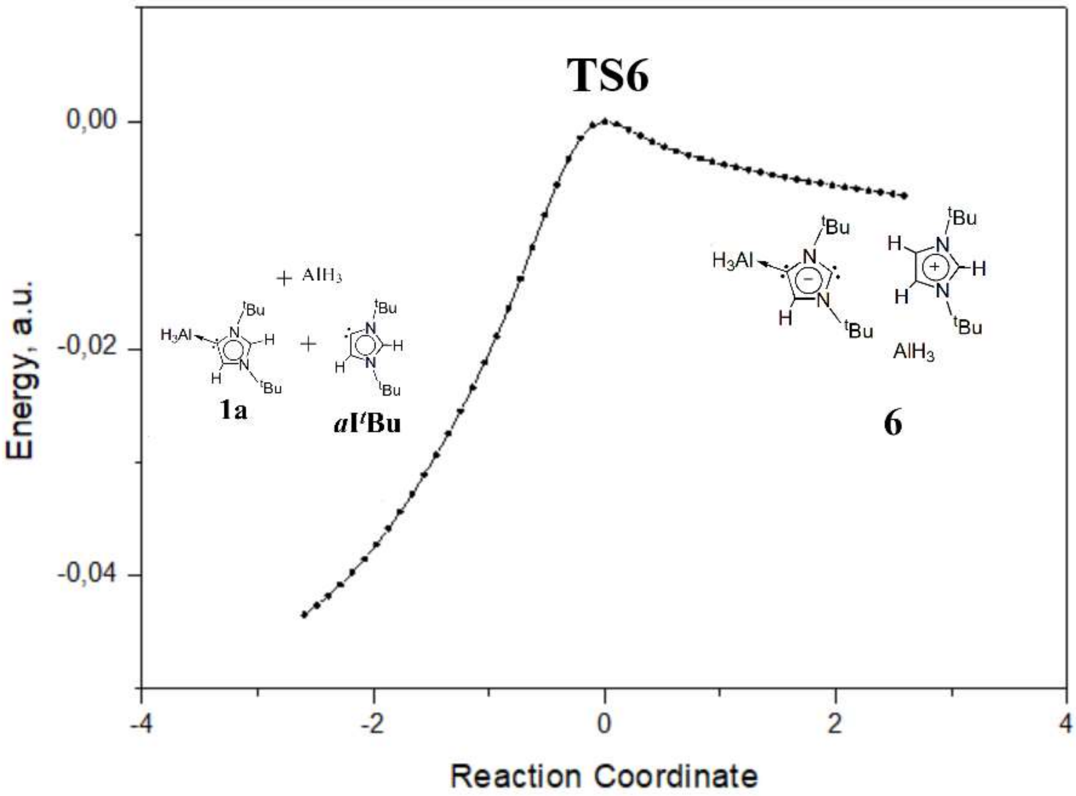
IRC scans


TS1
0,01
0,00
-0,01
-0,02
-0,03
-0,04
Energy, a.u.
-4
-2
0
2
4
Reaction Coordinate
+ H2
2
2
1


TS3
0,00
-0,02
-0,04
-0,06
Energy, a.u.
-4
-2
0
2
4
Reaction Coordinate
H-H
3
4


TS4
Energy, a.u.
Reaction Coordinate
0,00
-0,02
-0,04
-0,06
-4
-2
0
2
4
2
1a
4
H-H


TS5
Energy, a.u.
Reaction Coordinate
0,00
-0,02
-0,04
-2
0
2
I^tBu
1


TS6
Energy, a.u.
Reaction Coordinate
1a
aI^tBu
6
AlH3

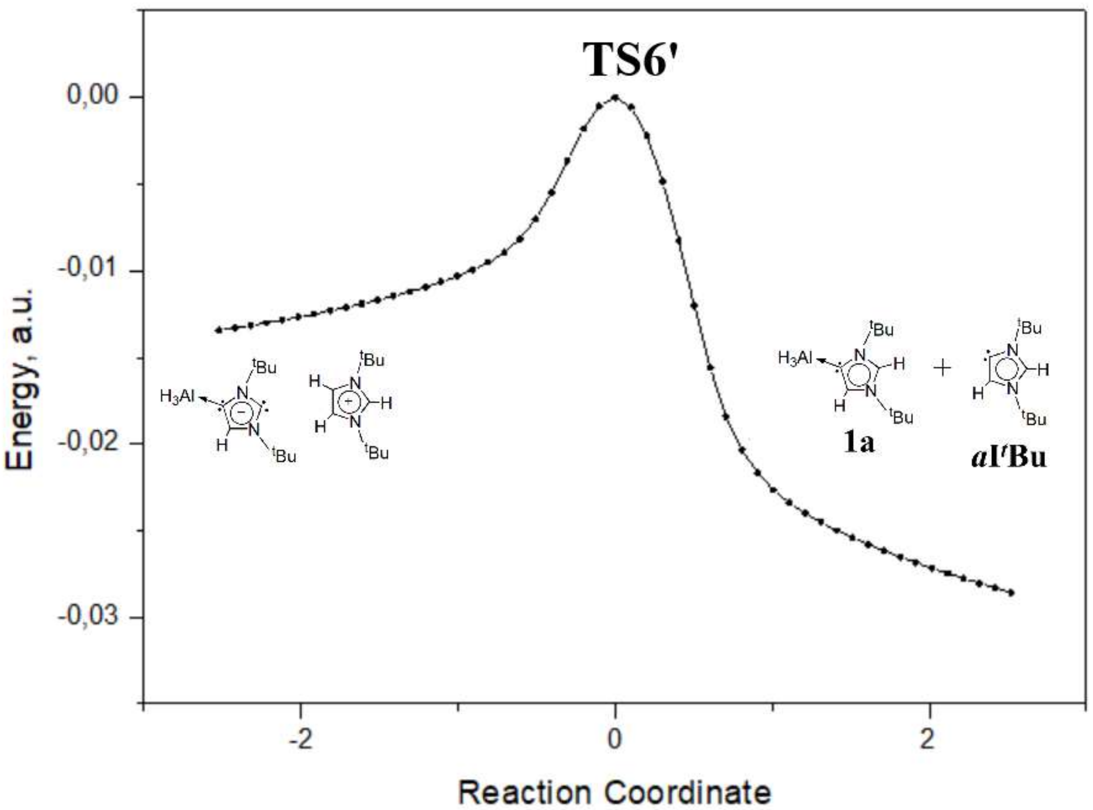

TS6'
Energy, a.u.
Reaction Coordinate
1a
aI^tBu

Table S8. Summary of reaction path following. Energies reported relative to the TS energy (ΔE, a.u.)

TS1		TS3	
ΔE	Reaction Coordinate	ΔE	Reaction Coordinate
-0.02561	-2.62159	-0.05850	-2.63909
-0.02477	-2.51670	-0.05795	-2.53387
-0.02390	-2.41183	-0.05727	-2.42884
-0.02300	-2.30697	-0.05633	-2.32368
-0.02207	-2.20212	-0.05506	-2.21824
-0.02111	-2.09724	-0.05335	-2.11279
-0.02012	-1.99235	-0.05109	-2.00772
-0.01910	-1.88743	-0.04787	-1.90297
-0.01805	-1.78249	-0.04321	-1.79748
-0.01698	-1.67753	-0.03734	-1.69175
-0.01586	-1.57258	-0.03091	-1.58598
-0.01472	-1.46760	-0.02452	-1.48020
-0.01354	-1.36264	-0.01868	-1.37442
-0.01235	-1.25765	-0.01372	-1.26866
-0.01111	-1.15287	-0.00978	-1.16294
-0.00989	-1.04865	-0.00681	-1.05726
-0.00864	-0.94455	-0.00467	-0.95160
-0.00737	-0.83981	-0.00316	-0.84593
-0.00612	-0.73488	-0.00210	-0.74023
-0.00489	-0.62986	-0.00136	-0.63451
-0.00371	-0.52486	-0.00084	-0.52877
-0.00259	-0.41984	-0.00048	-0.42302
-0.00160	-0.31485	-0.00025	-0.31727
-0.00078	-0.20986	-0.00010	-0.21151
-0.00021	-0.10494	-0.00002	-0.10576
0.00000	0.00000	0.00000	0.00000
-0.00025	0.10499	-0.00002	0.10575
-0.00105	0.20995	-0.00007	0.21149
-0.00245	0.31494	-0.00016	0.31726
-0.00451	0.41995	-0.00026	0.42302
-0.00725	0.52497	-0.00040	0.52880
-0.01045	0.62998	-0.00055	0.63457
-0.01372	0.73495	-0.00072	0.74035
-0.01665	0.83976	-0.00092	0.84612
-0.01902	0.94418	-0.00114	0.95190
-0.02091	1.04872	-0.00138	1.05768
-0.02254	1.15350	-0.00164	1.16346
-0.02399	1.25838	-0.00193	1.26924

-0.02531	1.36329	-0.00224	1.37502
-0.02653	1.46823	-0.00257	1.48081
-0.02767	1.57321	-0.00293	1.58659
-0.02876	1.67820	-0.00329	1.69238
-0.02979	1.78319	-0.00368	1.79817
-0.03078	1.88817	-0.00408	1.90396
-0.03174	1.99302	-0.00449	2.00974
-0.03264	2.09784	-0.00490	2.11553
-0.03353	2.20276	-0.00532	2.22132
-0.03438	2.30777	-0.00574	2.32710
-0.03520	2.41277	-0.00616	2.43288
-0.03599	2.51777	-0.00658	2.53865
-0.03675	2.62278	-0.00699	2.64441

TS4		**TS5**	
ΔE	Reaction Coordinate	ΔE	Reaction Coordinate
-0.04757	-2.66990	-0.00395	-2.53590
-0.04682	-2.56307	-0.00390	-2.43426
-0.04603	-2.45631	-0.00384	-2.33260
-0.04521	-2.34961	-0.00378	-2.23094
-0.04435	-2.24286	-0.00371	-2.12926
-0.04343	-2.13602	-0.00364	-2.02765
-0.04247	-2.02915	-0.00357	-1.92606
-0.04143	-1.92229	-0.00349	-1.82453
-0.04031	-1.81546	-0.00341	-1.72291
-0.03906	-1.70868	-0.00333	-1.62125
-0.03764	-1.60195	-0.00324	-1.51957
-0.03598	-1.49527	-0.00314	-1.41789
-0.03395	-1.38881	-0.00304	-1.31620
-0.03132	-1.28268	-0.00294	-1.21452
-0.02777	-1.17606	-0.00283	-1.11284
-0.02344	-1.06918	-0.00271	-1.01117
-0.01880	-0.96224	-0.00258	-0.90951
-0.01438	-0.85529	-0.00245	-0.80787
-0.01048	-0.74834	-0.00230	-0.70626
-0.00719	-0.64140	-0.00214	-0.60471
-0.00458	-0.53447	-0.00196	-0.50327
-0.00266	-0.42756	-0.00175	-0.40230
-0.00135	-0.32066	-0.00145	-0.30335
-0.00054	-0.21378	-0.00094	-0.20306

-0.00012	-0.10691	-0.00031	-0.10162
0.00000	0.00000	0.00000	0.00000
-0.00010	0.10688	-0.00043	0.10170
-0.00036	0.21377	-0.00189	0.20338
-0.00075	0.32071	-0.00449	0.30507
-0.00122	0.42764	-0.00817	0.40677
-0.00177	0.53459	-0.01272	0.50846
-0.00236	0.64151	-0.01780	0.61015
-0.00299	0.74845	-0.02295	0.71183
-0.00365	0.85525	-0.02762	0.81344
-0.00432	0.96213	-0.03133	0.91477
-0.00501	1.06892	-0.03402	1.01567
-0.00570	1.17569	-0.03605	1.11700
-0.00639	1.28203	-0.03763	1.21848
-0.00708	1.38855	-0.03885	1.31990
-0.00778	1.49533	-0.03976	1.42117
-0.00846	1.60226	-0.04047	1.52231
-0.00915	1.70911	-0.04105	1.62350
-0.00984	1.81595	-0.04155	1.72491
-0.01051	1.92273	-0.04200	1.82638
-0.01118	2.02947	-0.04241	1.92797
-0.01184	2.13618	-0.04279	2.02951
-0.01249	2.24289	-0.04315	2.13105
-0.01313	2.34964	-0.04349	2.23255
-0.01376	2.45645	-0.04381	2.33408
-0.01439	2.56330	-0.04412	2.43564
-0.01500	2.67019	-0.04441	2.53725
TS6		**TS6′**	
ΔE	Reaction Coordinate	ΔE	Reaction Coordinate
-0.04347	-2.59480	-0.01344	-2.52329
-0.04265	-2.49112	-0.01330	-2.42217
-0.04178	-2.38848	-0.01316	-2.32105
-0.04080	-2.28569	-0.01301	-2.21994
-0.03972	-2.18216	-0.01285	-2.11882
-0.03853	-2.07843	-0.01268	-2.01771
-0.03725	-1.97457	-0.01250	-1.91659
-0.03587	-1.87068	-0.01231	-1.81549
-0.03439	-1.76675	-0.01212	-1.71438
-0.03281	-1.66279	-0.01191	-1.61336
-0.03113	-1.55883	-0.01169	-1.51247
-0.02936	-1.45488	-0.01146	-1.41161

-0.02749	-1.35092	-0.01121	-1.31068
-0.02552	-1.24696	-0.01094	-1.20964
-0.02343	-1.14299	-0.01064	-1.10871
-0.02124	-1.03904	-0.01032	-1.00775
-0.01892	-0.93510	-0.00995	-0.90698
-0.01646	-0.83123	-0.00951	-0.80646
-0.01384	-0.72743	-0.00895	-0.70611
-0.01106	-0.62359	-0.00815	-0.60551
-0.00825	-0.51969	-0.00703	-0.50488
-0.00560	-0.41576	-0.00549	-0.40426
-0.00329	-0.31181	-0.00364	-0.30332
-0.00146	-0.20786	-0.00183	-0.20224
-0.00034	-0.10392	-0.00050	-0.10114
0.00000	0.00000	0.00000	0.00000
-0.00023	0.10372	-0.00055	0.10115
-0.00072	0.20743	-0.00220	0.20227
-0.00128	0.31102	-0.00486	0.30339
-0.00179	0.41470	-0.00827	0.40451
-0.00224	0.51847	-0.01203	0.50562
-0.00263	0.62207	-0.01559	0.60667
-0.00296	0.72552	-0.01842	0.70740
-0.00326	0.82858	-0.02034	0.80739
-0.00353	0.93186	-0.02168	0.90804
-0.00378	1.03563	-0.02266	1.00865
-0.00403	1.13955	-0.02340	1.10921
-0.00426	1.24347	-0.02400	1.20995
-0.00448	1.34740	-0.02452	1.31084
-0.00469	1.45133	-0.02499	1.41178
-0.00489	1.55527	-0.02541	1.51266
-0.00508	1.65920	-0.02580	1.61358
-0.00527	1.76313	-0.02617	1.71458
-0.00545	1.86705	-0.02652	1.81566
-0.00562	1.97095	-0.02685	1.91673
-0.00579	2.07484	-0.02717	2.01781
-0.00595	2.17872	-0.02747	2.11889
-0.00611	2.28259	-0.02776	2.21998
-0.00626	2.38646	-0.02804	2.32106
-0.00640	2.49034	-0.02832	2.42215
-0.00654	2.59422	-0.02858	2.52323

Cartesian coordinates for the optimized geometries

B3LYP-D3/def2-SVPD level of theory, gas phase.

H_2

H	0.000000000	0.000000000	0.380080000
H	0.000000000	0.000000000	-0.380080000

AlH_3

Al	0.000000000	0.000000000	0.000000000
H	0.000000000	1.584301000	0.000000000
H	1.372045000	-0.792151000	0.000000000
H	-1.372045000	-0.792151000	0.000000000

I^{t}Bu

N	1.068692000	-0.213795000	-0.000012000
C	0.000004000	0.632250000	-0.000109000
C	0.678815000	-1.549641000	0.000211000
C	-0.678825000	-1.549634000	0.000211000
N	-1.068695000	-0.213790000	0.000006000
H	-1.371671000	-2.382359000	0.000346000
H	1.371658000	-2.382367000	0.000354000
C	2.489564000	0.217087000	-0.000016000
C	3.170909000	-0.335490000	-1.264634000
C	3.170634000	-0.334646000	1.265118000
H	2.665516000	0.042202000	2.164133000
H	3.150124000	-1.432398000	1.292121000
H	4.221895000	-0.017241000	1.295601000
H	3.150554000	-1.433262000	-1.290860000
H	4.222136000	-0.017981000	-1.295161000
H	2.665909000	0.040649000	-2.164013000
C	-2.489562000	0.217102000	-0.000029000
C	-3.170710000	-0.334751000	1.265012000
C	-3.170840000	-0.335347000	-1.264740000
H	-2.665806000	0.040902000	-2.164053000
H	-3.150455000	-1.433116000	-1.291083000
H	-4.222073000	-0.017857000	-1.295280000
H	-3.150239000	-1.432507000	1.291898000
H	-4.221961000	-0.017317000	1.295477000
H	-2.665625000	0.041983000	2.164094000
C	2.566352000	1.747219000	-0.000529000
H	2.072964000	2.168415000	0.882601000
H	3.623267000	2.047028000	-0.000513000
H	2.073164000	2.167810000	-0.884062000
C	-2.566342000	1.747235000	-0.000391000
H	-2.073002000	2.168338000	0.882811000
H	-2.073103000	2.167914000	-0.883852000
H	-3.623256000	2.047049000	-0.000402000

*a*I^{t}Bu

N	-1.088795000	-0.299292000	0.000026000
C	0.004004000	0.484562000	0.000107000
C	-0.768415000	-1.666269000	-0.000079000
C	0.613906000	-1.628321000	-0.000029000
N	1.083787000	-0.307539000	0.000178000
H	1.313216000	-2.454744000	-0.000054000
C	-2.497506000	0.187984000	-0.000074000
C	-3.181363000	-0.360197000	1.261674000
C	-3.181044000	-0.359907000	-1.262121000
H	-2.703356000	0.042183000	-2.166632000
H	-3.097752000	-1.452596000	-1.282020000
H	-4.242019000	-0.073032000	-1.269229000
H	-3.097987000	-1.452881000	1.281383000
H	-4.242362000	-0.073403000	1.268530000
H	-2.703967000	0.041759000	2.166399000
C	2.484560000	0.195985000	-0.000002000
C	2.706423000	1.039538000	-1.267220000
C	3.454310000	-0.991517000	0.000770000
H	3.322489000	-1.616089000	0.893194000
H	3.322924000	-1.616940000	-0.891119000
H	4.482765000	-0.610714000	0.000818000
H	2.509816000	0.440002000	-2.165512000
H	3.745021000	1.396078000	-1.304865000
H	2.048264000	1.917968000	-1.288107000
C	-2.542320000	1.720550000	0.000097000
H	-2.063930000	2.142110000	-0.895315000
H	-3.589623000	2.045758000	0.000054000
H	-2.064065000	2.141897000	0.895680000
C	2.706305000	1.041001000	1.266261000
H	2.048265000	1.919543000	1.286072000
H	2.509554000	0.442532000	2.165233000
H	3.744927000	1.397498000	1.303606000
H	0.037073000	1.565201000	0.000187000

I^{t}BuH$_2$

N	0.044318000	0.688355000	-1.157849000
C	-0.759587000	0.276283000	0.000000000
C	1.364540000	0.820788000	-0.671581000

C	1.364540000	0.820788000	0.671581000
N	0.044318000	0.688355000	1.157849000
H	2.195023000	1.034699000	1.333369000
H	2.195023000	1.034699000	-1.333369000
C	-0.210864000	0.021173000	-2.453103000
C	0.285424000	-1.440754000	-2.450782000
C	0.511670000	0.813900000	-3.554645000
H	0.197428000	1.865551000	-3.533785000
H	1.602348000	0.775222000	-3.437636000
H	0.272736000	0.392646000	-4.540371000
H	1.365353000	-1.481357000	-2.254645000
H	0.090532000	-1.916781000	-3.421751000
H	-0.220522000	-2.035086000	-1.677925000
C	-0.210864000	0.021173000	2.453103000
C	0.511670000	0.813901000	3.554645000
C	0.285424000	-1.440753000	2.450782000
H	-0.220521000	-2.035086000	1.677925000
H	1.365353000	-1.481357000	2.254645000
H	0.090532000	-1.916781000	3.421751000
H	1.602348000	0.775222000	3.437636000
H	0.272736000	0.392647000	4.540371000
H	0.197428000	1.865551000	3.533785000
C	-1.723169000	0.063967000	-2.727398000
H	-2.093763000	1.095989000	-2.664919000
H	-1.932696000	-0.322313000	-3.733240000
H	-2.286389000	-0.553745000	-2.015109000
C	-1.723169000	0.063967000	2.727398000
H	-2.093763000	1.095989000	2.664919000
H	-2.286389000	-0.553745000	2.015109000
H	-1.932696000	-0.322312000	3.733240000
H	-1.745981000	0.758688000	0.000000000
H	-0.925306000	-0.828638000	0.000000000

1

N	-1.085145000	-0.569759000	-0.014838000
C	0.000002000	0.267199000	0.004748000
C	-0.677282000	-1.889729000	-0.023760000
C	0.677227000	-1.889749000	-0.023762000
N	1.085124000	-0.569789000	-0.014844000
H	1.353384000	-2.730270000	-0.037288000
H	-1.353463000	-2.730233000	-0.037282000
C	-2.541135000	-0.174999000	0.007440000
C	-2.877716000	0.378217000	1.400659000
C	-3.414452000	-1.413150000	-0.258458000
H	-3.178650000	-1.882898000	-1.222919000
H	-3.337651000	-2.162243000	0.540542000
H	-4.460059000	-1.087467000	-0.294161000
H	-2.675334000	-0.379914000	2.169785000
H	-3.944389000	0.637860000	1.442677000
H	-2.298811000	1.280372000	1.618484000
C	2.541119000	-0.175050000	0.007436000
C	2.812494000	0.842560000	-1.109411000
C	3.414431000	-1.413201000	-0.258480000
H	3.337640000	-2.162298000	0.540517000
H	3.178615000	-1.882944000	-1.222941000
H	4.460038000	-1.087520000	-0.294195000
H	2.535314000	0.424186000	-2.085880000
H	3.883699000	1.082492000	-1.123213000
H	2.270015000	1.779497000	-0.964341000
C	-2.812510000	0.842593000	-1.109424000
H	-2.535334000	0.424201000	-2.085886000
H	-3.883714000	1.082527000	-1.123227000
H	-2.270029000	1.779532000	-0.964371000
C	2.877702000	0.378153000	1.400659000
H	2.298798000	1.280307000	1.618491000
H	2.675317000	-0.379984000	2.169779000
H	3.944376000	0.637792000	1.442680000
H	-1.326932000	2.866934000	0.781435000
Al	0.000052000	2.409997000	0.011040000
H	1.327155000	2.866854000	0.781280000
H	-0.000031000	2.748666000	-1.560807000

TS1

N	-3.181353000	-1.088183000	0.387001000
C	-4.356913000	-0.385561000	0.332243000
N	-4.011687000	0.816966000	-0.226935000
Al	0.231138000	-0.343052000	-0.782238000
C	-2.082463000	-0.332168000	-0.066777000
C	-2.645879000	0.859450000	-0.435271000
H	-2.153086000	1.720512000	-0.867046000
C	-4.918071000	1.960112000	-0.597863000
C	-3.037030000	-2.500100000	0.888519000
C	-2.945437000	-2.473007000	2.422915000
H	-3.866226000	-2.069300000	2.863897000
H	-2.796809000	-3.494229000	2.808187000
H	-2.089387000	-1.857130000	2.743149000
C	-4.210853000	-3.363101000	0.400260000
H	-4.306987000	-3.302391000	-0.694111000
H	-4.022368000	-4.411655000	0.676876000
H	-5.167452000	-3.081680000	0.852403000
C	-1.753299000	-3.119113000	0.314876000
H	-0.844766000	-2.658161000	0.722337000
H	-1.725284000	-4.182036000	0.596887000
H	-1.721467000	-3.048603000	-0.780488000

C	-4.202734000	2.869431000	-1.615605000
H	-3.870288000	2.308480000	-2.502292000
H	-4.912833000	3.640488000	-1.947529000
H	-3.338178000	3.393748000	-1.182416000
C	-6.188254000	1.420951000	-1.271750000
H	-6.804555000	0.823432000	-0.590962000
H	-6.804345000	2.267382000	-1.611838000
H	-5.930305000	0.802160000	-2.144615000
C	-5.235129000	2.778008000	0.664402000
H	-4.303352000	3.148530000	1.121232000
H	-5.860128000	3.645812000	0.400587000
H	-5.780578000	2.169485000	1.397078000
H	-0.060040000	1.031093000	-1.514237000
H	-0.752247000	-0.579522000	0.710847000
H	0.226356000	-1.724608000	-1.532159000
C	2.283430000	0.047918000	-0.149092000
N	3.363495000	-0.796180000	-0.156261000
N	2.721877000	1.170053000	0.510610000
H	0.130475000	-0.721675000	1.030641000
C	4.439192000	-0.213408000	0.488304000
C	4.039465000	1.013231000	0.902967000
H	4.604631000	1.763539000	1.439268000
C	1.971438000	2.465597000	0.721365000
C	3.432148000	-2.170167000	-0.777930000
C	3.105000000	-2.052505000	-2.274726000
H	2.084426000	-1.688975000	-2.440032000
H	3.185052000	-3.042864000	-2.747922000
H	3.815691000	-1.372836000	-2.770122000
C	2.470429000	-3.108942000	-0.032684000
H	2.726521000	-3.149457000	1.037348000
H	2.552412000	-4.124799000	-0.447591000
H	1.426813000	-2.793080000	-0.136416000
C	4.857422000	-2.731247000	-0.640411000
H	5.604801000	-2.101097000	-1.145927000
H	4.881433000	-3.719125000	-1.121269000
H	5.152995000	-2.873304000	0.410100000
C	2.766068000	3.366803000	1.682820000
H	2.923413000	2.888691000	2.661911000
H	2.186546000	4.285258000	1.849867000
H	3.737856000	3.673029000	1.268670000
C	0.599863000	2.197021000	1.359672000
H	-0.111407000	1.740945000	0.662583000
H	0.154465000	3.153952000	1.668431000
H	0.693050000	1.554608000	2.247118000
C	1.839201000	3.174489000	-0.635828000
H	2.833765000	3.377690000	-1.062873000
H	1.317819000	4.135117000	-0.503479000
H	1.263282000	2.563584000	-1.342575000
Al	-6.244016000	-0.884107000	1.198842000
H	-6.906034000	0.512169000	1.645230000
H	-5.920695000	-1.792460000	2.485935000
H	-7.074742000	-1.641373000	0.045871000
H	5.401995000	-0.690598000	0.613370000

2

N	1.232739000	-1.280230000	0.051229000
C	2.515931000	-0.924349000	-0.264712000
N	2.890967000	-0.068919000	0.730011000
Al	-1.063136000	-0.076950000	1.927454000
C	0.736145000	-0.554861000	1.151648000
C	1.817846000	0.173270000	1.565977000
H	1.876753000	0.861865000	2.397066000
C	4.231143000	0.563948000	0.952415000
C	0.467768000	-2.403947000	-0.591437000
C	-0.605947000	-1.826039000	-1.524210000
H	-0.139570000	-1.217679000	-2.306628000
H	-1.159359000	-2.645900000	-2.000569000
H	-1.325202000	-1.213877000	-0.972706000
C	1.403535000	-3.334268000	-1.376483000
H	2.258725000	-3.645701000	-0.765469000
H	0.837885000	-4.231688000	-1.658199000
H	1.772880000	-2.882416000	-2.299647000
C	-0.162886000	-3.249958000	0.528663000
H	-0.838726000	-2.681180000	1.169804000
H	-0.730791000	-4.073842000	0.077698000
H	0.620779000	-3.679697000	1.166366000
C	4.477218000	0.655268000	2.471251000
H	4.358772000	-0.326458000	2.948341000
H	5.503911000	1.000528000	2.641805000
H	3.809534000	1.370375000	2.966857000
C	5.338348000	-0.308438000	0.347486000
H	5.295193000	-0.340567000	-0.743935000
H	6.312650000	0.114485000	0.623745000
H	5.280261000	-1.333369000	0.735067000
C	4.218879000	1.972311000	0.337384000
H	3.412381000	2.574716000	0.777877000
H	5.174643000	2.474778000	0.540329000
H	4.075640000	1.913216000	-0.746613000
H	-0.834664000	1.056443000	3.028792000
H	-1.868410000	-1.337260000	2.461528000
C	-2.215550000	0.753075000	0.317123000
N	-3.414338000	0.263171000	-0.141880000
N	-1.794447000	1.610975000	-0.667501000

C	-3.676509000	0.741362000	-1.409653000
C	-2.663850000	1.578417000	-1.737530000
H	-2.519390000	2.151963000	-2.640180000
C	-0.597517000	2.535072000	-0.698888000
C	-4.390694000	-0.631053000	0.584082000
C	-4.540091000	-0.144707000	2.033311000
H	-3.611875000	-0.238427000	2.600405000
H	-5.295086000	-0.759028000	2.540281000
H	-4.873280000	0.901261000	2.052463000
C	-3.912902000	-2.087114000	0.489377000
H	-3.805344000	-2.385624000	-0.561603000
H	-4.652115000	-2.746108000	0.963280000
H	-2.958844000	-2.226175000	0.999776000
C	-5.772486000	-0.521319000	-0.086709000
H	-6.122951000	0.518235000	-0.132837000
H	-6.487841000	-1.090511000	0.517311000
H	-5.789105000	-0.955071000	-1.094643000
C	-0.979363000	3.805659000	-1.484778000
H	-1.104818000	3.622714000	-2.558593000
H	-0.163499000	4.530276000	-1.382429000
H	-1.895638000	4.262314000	-1.088279000
C	0.558069000	1.819293000	-1.406465000
H	0.836515000	0.910144000	-0.878436000
H	1.437615000	2.472882000	-1.448048000
H	0.288099000	1.543510000	-2.433042000
C	-0.224408000	2.968712000	0.718846000
H	-1.078765000	3.428428000	1.230921000
H	0.585873000	3.705178000	0.656697000
H	0.135236000	2.144384000	1.331054000
Al	3.302558000	-0.898465000	-2.242049000
H	4.021808000	0.537817000	-2.335901000
H	1.973149000	-0.894555000	-3.153914000
H	4.285972000	-2.145785000	-2.456587000
H	-4.552013000	0.478818000	-1.982670000

3

N	-2.139800000	-1.098118000	0.349009000
C	-2.854878000	0.061790000	0.234250000
N	-2.480384000	0.586290000	-0.967415000
Al	0.431794000	-2.406921000	-1.018707000
C	-1.208365000	-1.252960000	-0.694064000
C	-1.458341000	-0.179533000	-1.507218000
H	-0.964642000	0.084623000	-2.432752000
C	-3.132916000	1.707184000	-1.718238000
C	-2.447402000	-2.194864000	1.335968000
C	-1.389431000	-2.242612000	2.446306000
H	-1.408201000	-1.318901000	3.033566000
H	-1.611913000	-3.082526000	3.118199000
H	-0.387814000	-2.398927000	2.030334000
C	-3.842125000	-1.992085000	1.946001000
H	-4.604971000	-1.871263000	1.167437000
H	-4.092239000	-2.880500000	2.539643000
H	-3.887587000	-1.132858000	2.620504000
C	-2.469812000	-3.527235000	0.564934000
H	-1.488773000	-3.814039000	0.174091000
H	-2.802108000	-4.324100000	1.242788000
H	-3.169627000	-3.474781000	-0.279158000
C	-4.542298000	1.969942000	-1.172188000
H	-4.526039000	2.394690000	-0.164925000
H	-5.043278000	2.695622000	-1.825744000
H	-5.135868000	1.047900000	-1.155524000
C	-2.272423000	2.975600000	-1.625900000
H	-1.263169000	2.793338000	-2.018061000
H	-2.730527000	3.773618000	-2.225656000
H	-2.202365000	3.315804000	-0.587835000
C	-3.268197000	1.270460000	-3.191078000
H	-3.801178000	0.313829000	-3.265686000
H	-3.839694000	2.030689000	-3.737973000
H	-2.297630000	1.167740000	-3.690781000
H	1.310979000	-1.479261000	-2.030460000
H	1.275601000	-2.433288000	0.388236000
H	0.156383000	-3.890846000	-1.560229000
C	2.914847000	0.037050000	0.347973000
N	4.045921000	0.122958000	-0.370411000
N	2.515415000	1.273545000	0.675610000
H	2.374010000	-0.885860000	0.565815000
C	4.357918000	1.459901000	-0.529668000
C	3.402054000	2.177867000	0.125613000
H	3.288388000	3.246833000	0.242706000
C	1.286489000	1.657162000	1.460856000
C	4.811592000	-1.017007000	-0.984164000
C	4.440101000	-1.077540000	-2.472381000
H	3.363996000	-1.257574000	-2.589933000
H	4.991329000	-1.897176000	-2.951732000
H	4.705727000	-0.141341000	-2.982558000
C	4.429892000	-2.317228000	-0.270652000
H	4.655260000	-2.261155000	0.803209000
H	5.018337000	-3.136091000	-0.700110000
H	3.370619000	-2.565981000	-0.396051000
C	6.310566000	-0.742466000	-0.792708000
H	6.650815000	0.138710000	-1.351470000
H	6.876031000	-1.602912000	-1.170043000
H	6.556036000	-0.606782000	0.268849000

C	1.715891000	2.614600000	2.580095000
H	2.455641000	2.143753000	3.240702000
H	0.832135000	2.870440000	3.176925000
H	2.133775000	3.552551000	2.192152000
C	0.656188000	0.401144000	2.052675000
H	0.328111000	-0.289458000	1.272105000
H	-0.234689000	0.690320000	2.619469000
H	1.344170000	-0.124289000	2.728164000
C	0.310752000	2.327764000	0.490105000
H	0.735062000	3.239460000	0.048727000
H	-0.608369000	2.597282000	1.023612000
H	0.042731000	1.633972000	-0.313260000
Al	-3.470927000	1.244146000	1.869221000
H	-2.925224000	2.709591000	1.450555000
H	-2.565717000	0.688942000	3.085594000
H	-5.053458000	1.172074000	2.103325000
H	5.223303000	1.795865000	-1.083475000

TS3

N	-3.200438000	-1.161648000	0.281900000
C	-4.427257000	-0.695953000	-0.003092000
N	-4.361622000	0.636800000	-0.107081000
H	-5.322984000	-1.284956000	-0.127110000
Al	0.447162000	0.481626000	-0.273638000
C	-2.269168000	-0.116931000	0.366071000
C	-3.037245000	0.999525000	0.121836000
H	-2.726223000	2.035438000	0.074039000
C	-5.474672000	1.576465000	-0.419137000
C	-2.843904000	-2.605440000	0.419088000
C	-2.015992000	-2.773960000	1.701136000
H	-2.586385000	-2.441180000	2.578107000
H	-1.754151000	-3.831407000	1.833619000
H	-1.088125000	-2.198952000	1.655354000
C	-4.113683000	-3.460526000	0.517123000
H	-4.715981000	-3.413792000	-0.400463000
H	-3.823403000	-4.507750000	0.659315000
H	-4.736326000	-3.164975000	1.372874000
C	-2.031101000	-3.006756000	-0.821396000
H	-1.175919000	-2.338237000	-0.958882000
H	-1.664117000	-4.036144000	-0.714985000
H	-2.652593000	-2.950430000	-1.725345000
C	-5.121802000	2.314934000	-1.720778000
H	-5.001820000	1.604381000	-2.548815000
H	-5.924987000	3.018360000	-1.976719000
H	-4.190133000	2.884499000	-1.618890000
C	-6.783256000	0.798784000	-0.599289000
H	-7.062612000	0.256850000	0.314335000
H	-7.588647000	1.507267000	-0.824549000
H	-6.721961000	0.089053000	-1.435236000
C	-5.609855000	2.562295000	0.752765000
H	-4.687545000	3.136735000	0.901684000
H	-6.422559000	3.271415000	0.547857000
H	-5.838550000	2.028363000	1.684310000
H	-0.194762000	1.923163000	-0.272203000
H	-0.647487000	-0.062407000	1.231094000
H	0.120500000	-0.522030000	-1.446207000
C	2.451535000	0.416429000	0.159135000
N	3.284476000	-0.672249000	0.060345000
N	3.293826000	1.486085000	0.294707000
H	0.119581000	0.031057000	1.546184000
C	4.633975000	-0.313127000	0.059388000
Al	6.472055000	-1.203896000	-0.291743000
C	4.600934000	1.048541000	0.215730000
H	5.447976000	1.716034000	0.263282000
C	2.924192000	2.923378000	0.509620000
C	2.852627000	-2.106449000	-0.072712000
C	2.756291000	-2.446645000	-1.567864000
H	2.005874000	-1.822123000	-2.067252000
H	2.470153000	-3.501129000	-1.689874000
H	3.732019000	-2.295729000	-2.045854000
C	1.514117000	-2.341595000	0.639032000
H	1.548311000	-1.987668000	1.676935000
H	1.302581000	-3.417287000	0.649902000
H	0.673273000	-1.879686000	0.116953000
C	3.886237000	-3.017533000	0.607755000
H	4.827282000	-3.067830000	0.055123000
H	3.480017000	-4.036806000	0.648982000
H	4.102320000	-2.682907000	1.629431000
C	4.174659000	3.723976000	0.914899000
H	4.648892000	3.308553000	1.813049000
H	3.865744000	4.752015000	1.138220000
H	4.917835000	3.771230000	0.109874000
C	1.912731000	3.023622000	1.663866000
H	0.968653000	2.523341000	1.435009000
H	1.684627000	4.080014000	1.859104000
H	2.337275000	2.585089000	2.576233000
C	2.378141000	3.511737000	-0.802427000
H	3.123004000	3.402273000	-1.601343000
H	2.167089000	4.581919000	-0.669040000
H	1.449589000	3.024697000	-1.113486000
H	7.383655000	0.109830000	-0.549086000
H	6.272406000	-2.144018000	-1.597559000
H	6.913711000	-2.052222000	1.009517000

4

N	-2.257124000	-0.581766000	0.167705000
C	-3.487532000	-0.103134000	0.394890000
N	-3.698646000	0.958785000	-0.391457000
H	-4.201258000	-0.506560000	1.095073000
Al	0.185008000	0.263358000	-1.843608000
C	-1.609372000	0.195961000	-0.806285000
C	-2.549097000	1.145431000	-1.138727000
H	-2.457904000	1.958108000	-1.847577000
C	-4.906195000	1.832489000	-0.437465000
C	-1.712712000	-1.826553000	0.814311000
C	-0.373064000	-1.490409000	1.472010000
H	-0.488254000	-0.697051000	2.220429000
H	0.040675000	-2.376867000	1.964286000
H	0.358794000	-1.165871000	0.736397000
C	-2.684435000	-2.334901000	1.886232000
H	-3.657155000	-2.629135000	1.468159000
H	-2.244005000	-3.226978000	2.344704000
H	-2.836817000	-1.596155000	2.685277000
C	-1.561738000	-2.881648000	-0.290327000
H	-0.970052000	-2.497247000	-1.125751000
H	-1.055399000	-3.766015000	0.113161000
H	-2.545733000	-3.181188000	-0.676189000
C	-5.974895000	1.291206000	0.518058000
H	-5.628531000	1.292818000	1.560308000
H	-6.858454000	1.936904000	0.462484000
H	-6.287280000	0.274808000	0.242954000
C	-4.480109000	3.245890000	-0.007209000
H	-3.717852000	3.656896000	-0.680286000
H	-5.349050000	3.916308000	-0.027818000
H	-4.071157000	3.234507000	1.011367000
C	-5.440637000	1.831116000	-1.878272000
H	-5.718223000	0.815615000	-2.188933000
H	-6.330112000	2.470951000	-1.941211000
H	-4.696519000	2.217453000	-2.585358000
H	0.008857000	1.656468000	-2.618454000
H	0.299719000	-5.103158000	1.670029000
H	0.198281000	-1.041528000	-2.751946000
C	1.777192000	0.329723000	-0.511746000
N	2.546575000	-0.742346000	-0.136190000
N	1.836464000	1.188642000	0.556019000
H	0.897804000	-4.684787000	1.888827000
C	2.972539000	-0.654202000	1.193807000
Al	3.538181000	-2.011279000	2.643451000
C	2.527326000	0.580462000	1.588859000
H	2.652147000	1.035366000	2.560212000
C	1.462872000	2.644086000	0.558142000
C	3.009000000	-1.841068000	-1.059986000
C	3.222413000	-1.268160000	-2.471324000
H	2.294252000	-0.939358000	-2.943753000
H	3.649639000	-2.052253000	-3.109472000
H	3.928395000	-0.428118000	-2.438629000
C	1.996266000	-2.993066000	-1.055669000
H	1.821323000	-3.338076000	-0.030022000
H	2.397579000	-3.833876000	-1.636722000
H	1.052024000	-2.690886000	-1.513596000
C	4.368442000	-2.363529000	-0.569261000
H	5.077472000	-1.543706000	-0.403828000
H	4.778757000	-3.030004000	-1.338721000
H	4.292510000	-2.939941000	0.356564000
C	2.015675000	3.312274000	1.828074000
H	1.545313000	2.921299000	2.739488000
H	1.796124000	4.385183000	1.774509000
H	3.102799000	3.195528000	1.910885000
C	-0.060932000	2.828497000	0.539986000
H	-0.477256000	2.600325000	-0.441903000
H	-0.305564000	3.874291000	0.769023000
H	-0.540890000	2.185508000	1.288340000
C	2.107678000	3.310494000	-0.668789000
H	3.198650000	3.194175000	-0.635254000
H	1.871949000	4.383633000	-0.672176000
H	1.734705000	2.875034000	-1.601269000
H	3.121094000	-1.202040000	3.984345000
H	5.097128000	-2.405324000	2.567408000
H	2.563310000	-3.283491000	2.358766000

TS4

N	-3.174559000	-1.000928000	-0.346291000
C	-4.406179000	-0.479756000	-0.440756000
N	-4.313544000	0.850626000	-0.542259000
H	-5.330451000	-1.035449000	-0.438044000
Al	-0.138270000	0.234740000	-0.419510000
C	-2.213250000	0.023184000	-0.384611000
C	-2.965816000	1.169558000	-0.506821000
H	-2.620536000	2.192859000	-0.577599000
C	-5.430145000	1.832954000	-0.676391000
C	-2.886465000	-2.467972000	-0.208662000
C	-2.180943000	-2.690250000	1.136556000
H	-2.828926000	-2.387001000	1.969606000
H	-1.935860000	-3.753354000	1.252615000
H	-1.249357000	-2.123816000	1.205025000
C	-4.197931000	-3.264784000	-0.229667000
H	-4.742831000	-3.136891000	-1.175085000

H	-3.955413000	-4.328951000	-0.134546000
H	-4.856769000	-3.003327000	0.610059000
C	-2.007466000	-2.901488000	-1.390138000
H	-1.073697000	-2.333203000	-1.434823000
H	-1.758868000	-3.965643000	-1.288796000
H	-2.539880000	-2.758206000	-2.339805000
C	-6.773079000	1.094991000	-0.674298000
H	-6.935715000	0.547661000	0.264077000
H	-7.579645000	1.830160000	-0.772319000
H	-6.856064000	0.397967000	-1.519123000
C	-5.357818000	2.797795000	0.517820000
H	-4.406066000	3.342600000	0.538367000
H	-6.167544000	3.535118000	0.444282000
H	-5.466195000	2.253788000	1.465113000
C	-5.243386000	2.582890000	-2.005005000
H	-5.269838000	1.885900000	-2.852591000
H	-6.051067000	3.315431000	-2.130443000
H	-4.289492000	3.123620000	-2.032026000
H	-0.106068000	1.806280000	-0.584245000
H	-0.255148000	-0.211728000	1.414569000
H	0.375766000	-0.816010000	-1.471194000
C	2.172291000	0.202742000	0.608098000
N	3.077008000	-0.690495000	0.103816000
N	2.844770000	1.387103000	0.645961000
H	0.596256000	-0.104711000	1.268280000
C	4.287359000	-0.085447000	-0.268495000
Al	6.042789000	-0.623504000	-1.223173000
C	4.102727000	1.225593000	0.089772000
H	4.802346000	2.044609000	-0.015754000
C	2.423290000	2.657744000	1.296569000
C	2.891904000	-2.174680000	0.078796000
C	2.912961000	-2.670841000	-1.374781000
H	2.081921000	-2.233559000	-1.941491000
H	2.813857000	-3.765658000	-1.390396000
H	3.850046000	-2.401400000	-1.874533000
C	1.569811000	-2.579054000	0.743069000
H	1.487019000	-2.181318000	1.762534000
H	1.532199000	-3.673905000	0.801106000
H	0.706824000	-2.260479000	0.154044000
C	4.033473000	-2.808376000	0.894501000
H	5.019710000	-2.570885000	0.483520000
H	3.916013000	-3.901140000	0.896784000
H	4.000856000	-2.452167000	1.933833000
C	3.551320000	3.100704000	2.250803000
H	3.765219000	2.313602000	2.985658000
H	3.240368000	4.007007000	2.787448000
H	4.479523000	3.331531000	1.716502000
C	1.152931000	2.449672000	2.130972000
H	0.281937000	2.242105000	1.504414000
H	0.944609000	3.370373000	2.690725000
H	1.285729000	1.631887000	2.850654000
C	2.192760000	3.726557000	0.215940000
H	3.103408000	3.883079000	-0.376270000
H	1.921374000	4.682334000	0.686308000
H	1.386013000	3.422543000	-0.459947000
H	6.786562000	0.812779000	-1.322672000
H	5.645837000	-1.255587000	-2.660441000
H	6.835785000	-1.698696000	-0.308643000

1a

N	0.800466000	-0.347407000	0.000419000
C	-0.432869000	-0.872613000	0.005216000
C	0.731638000	1.052821000	-0.022657000
C	-0.621898000	1.311881000	-0.030897000
N	-1.331214000	0.119925000	-0.015490000
H	-1.108305000	2.277405000	-0.048841000
C	2.065665000	-1.153161000	0.014058000
C	2.852134000	-0.786674000	1.280944000
C	2.858762000	-0.819463000	-1.257787000
H	2.287730000	-1.101209000	-2.153266000
H	3.093053000	0.249075000	-1.321328000
H	3.801277000	-1.383145000	-1.255205000
H	3.087064000	0.283020000	1.316922000
H	3.794055000	-1.351060000	1.298432000
H	2.275844000	-1.044088000	2.180363000
C	-2.810505000	-0.083782000	0.001723000
C	-3.196017000	-0.957004000	-1.203451000
C	-3.509742000	1.276165000	-0.098899000
H	-3.267250000	1.920316000	0.755602000
H	-3.241791000	1.799977000	-1.025242000
H	-4.594135000	1.115761000	-0.101806000
H	-2.885217000	-0.479510000	-2.141572000
H	-4.284804000	-1.095568000	-1.226440000
H	-2.734525000	-1.951824000	-1.150135000
C	1.733503000	-2.651685000	0.032117000
H	1.175137000	-2.962661000	-0.862075000
H	2.675194000	-3.211961000	0.040372000
H	1.172437000	-2.940989000	0.931892000
C	-3.188597000	-0.769830000	1.324662000
H	-2.716063000	-1.756713000	1.416395000
H	-2.878268000	-0.156004000	2.179945000
H	-4.276344000	-0.911504000	1.373172000
H	1.052157000	3.868548000	-0.060200000

Al	2.087758000	2.628932000	-0.043268000
H	2.973598000	2.501655000	1.299558000
H	2.974859000	2.466360000	-1.381388000
H	-0.681387000	-1.922898000	0.024260000

6

N	1.780725000	0.424912000	1.274536000
C	2.041224000	-0.913824000	1.234353000
C	2.039686000	1.099149000	0.057929000
C	2.491731000	0.094368000	-0.756461000
N	2.475369000	-1.107522000	-0.045250000
H	2.797492000	0.164997000	-1.792582000
C	1.308121000	1.109052000	2.508036000
C	-0.090742000	1.703218000	2.264868000
C	2.305262000	2.223979000	2.865718000
H	3.302386000	1.797389000	3.035625000
H	2.388182000	2.972162000	2.069114000
H	1.982854000	2.735783000	3.783163000
H	-0.081492000	2.426715000	1.443775000
H	-0.445675000	2.212519000	3.171378000
H	-0.802636000	0.906044000	2.023580000
C	3.042239000	-2.398695000	-0.515064000
C	2.107963000	-3.545356000	-0.103064000
C	4.423338000	-2.576324000	0.137969000
H	5.078093000	-1.733280000	-0.120294000
H	4.318860000	-2.610426000	1.229427000
H	4.897511000	-3.505929000	-0.207482000
H	1.908717000	-3.507118000	0.972841000
H	2.573446000	-4.508818000	-0.349418000
H	1.157111000	-3.481628000	-0.648029000
C	1.234370000	0.111007000	3.671525000
H	2.211923000	-0.339613000	3.873242000
H	0.893318000	0.643600000	4.570131000
H	0.539346000	-0.708884000	3.458232000
C	3.181051000	-2.388709000	-2.044055000
H	2.224597000	-2.158641000	-2.532759000
H	3.930496000	-1.662823000	-2.383259000
H	3.504399000	-3.381376000	-2.380654000
H	1.599031000	2.642642000	-2.288862000
Al	1.799560000	2.978182000	-0.700875000
H	0.368294000	3.572551000	-0.193254000
H	3.014621000	3.962975000	-0.335762000
H	0.143627000	-1.125067000	-0.281545000
N	-1.923977000	-0.679515000	0.219287000
C	-2.725085000	0.341236000	-0.098064000
C	-0.732667000	-0.517033000	-0.469461000
C	-0.847673000	0.643779000	-1.203115000
N	-2.104432000	1.155850000	-0.958468000
H	-0.097473000	1.153199000	-1.799203000
C	-2.308766000	-1.818264000	1.129579000
C	-1.110894000	-2.757609000	1.275669000
C	-3.490552000	-2.550859000	0.476632000
H	-4.374481000	-1.904797000	0.388546000
H	-3.221051000	-2.910083000	-0.523619000
H	-3.765215000	-3.413856000	1.095667000
H	-0.864645000	-3.233169000	0.320080000
H	-1.378365000	-3.548576000	1.985243000
H	-0.216988000	-2.242266000	1.654066000
C	-2.705752000	2.414088000	-1.533485000
C	-4.117730000	2.073136000	-2.032567000
C	-1.830736000	2.881184000	-2.699537000
H	-0.822336000	3.158308000	-2.370286000
H	-1.759639000	2.109402000	-3.477538000
H	-2.294679000	3.769383000	-3.143124000
H	-4.089282000	1.245295000	-2.752274000
H	-4.540079000	2.955473000	-2.527762000
H	-4.797610000	1.807225000	-1.211650000
C	-2.700084000	-1.237125000	2.495174000
H	-3.535320000	-0.528334000	2.421245000
H	-3.019172000	-2.056563000	3.150210000
H	-1.850593000	-0.731530000	2.966269000
C	-2.734109000	3.464378000	-0.415417000
H	-3.341187000	3.124429000	0.435376000
H	-1.714120000	3.681234000	-0.073066000
H	-3.178900000	4.390133000	-0.802391000
H	-3.731630000	0.476111000	0.269721000
Al	-1.236218000	-1.591143000	-2.894012000
H	-2.758493000	-1.136692000	-2.788750000
H	-0.256026000	-0.890602000	-3.915508000
H	-0.839256000	-2.966837000	-2.209626000

TS6

N	1.698267000	0.616489000	1.047358000
C	1.726961000	-0.700581000	0.687103000
C	2.370179000	1.450907000	0.133640000
C	2.885162000	0.559890000	-0.778053000
N	2.497059000	-0.731050000	-0.432886000
H	3.512263000	0.771059000	-1.639370000
C	1.131637000	1.096868000	2.342194000
C	-0.067352000	2.022490000	2.085806000
C	2.237225000	1.850176000	3.103543000
H	3.110265000	1.195284000	3.248940000
H	2.562616000	2.749657000	2.563927000
H	1.862565000	2.156344000	4.093152000

H	0.207453000	2.866461000	1.438817000
H	-0.442582000	2.425892000	3.038963000
H	-0.889287000	1.473231000	1.603723000
C	3.049298000	-1.966158000	-1.055306000
C	2.254242000	-3.189689000	-0.585119000
C	4.513832000	-2.097204000	-0.594999000
H	5.107107000	-1.226011000	-0.911429000
H	4.565209000	-2.167480000	0.502355000
H	4.970226000	-3.001400000	-1.027139000
H	2.303593000	-3.303870000	0.506103000
H	2.673820000	-4.092602000	-1.053523000
H	1.196649000	-3.126607000	-0.873675000
C	0.685049000	-0.099005000	3.190228000
H	1.520475000	-0.780308000	3.401868000
H	0.279655000	0.270792000	4.144713000
H	-0.096781000	-0.676806000	2.687622000
C	2.982553000	-1.849682000	-2.585791000
H	1.947612000	-1.703687000	-2.925199000
H	3.597021000	-1.018299000	-2.960809000
H	3.365161000	-2.775057000	-3.042529000
H	3.319594000	3.574866000	-1.568237000
Al	2.385503000	3.471098000	-0.253496000
H	0.819849000	3.806948000	-0.600882000
H	2.868064000	4.331653000	1.023738000
H	0.340148000	-1.254799000	0.398251000
N	-2.041106000	-0.843599000	0.476670000
C	-2.685178000	0.239124000	0.035160000
C	-0.798446000	-0.948932000	-0.178267000
C	-0.759029000	0.176097000	-0.998600000
N	-1.926256000	0.882798000	-0.868037000
H	0.071186000	0.524641000	-1.605694000
C	-2.636762000	-1.831669000	1.447131000
C	-1.593433000	-2.908829000	1.763221000
C	-3.869771000	-2.473275000	0.788593000
H	-4.639315000	-1.723839000	0.547003000
H	-3.596268000	-2.997529000	-0.137360000
H	-4.314650000	-3.200607000	1.483666000
H	-1.305580000	-3.462647000	0.860357000
H	-2.033183000	-3.617846000	2.479536000
H	-0.686274000	-2.486166000	2.213526000
C	-2.344664000	2.127833000	-1.614630000
C	-3.691422000	1.828739000	-2.290936000
C	-1.278150000	2.450583000	-2.664903000
H	-0.313304000	2.698588000	-2.196697000
H	-1.154380000	1.625195000	-3.382619000
H	-1.603552000	3.338965000	-3.224538000
H	-3.615382000	0.943623000	-2.940060000
H	-3.987623000	2.692391000	-2.903766000
H	-4.494482000	1.655853000	-1.557260000
C	-3.038166000	-1.071811000	2.721754000
H	-3.821760000	-0.323473000	2.525505000
H	-3.441261000	-1.783563000	3.456855000
H	-2.175354000	-0.561868000	3.171122000
C	-2.455233000	3.275213000	-0.600944000
H	-3.178835000	3.043893000	0.197049000
H	-1.473792000	3.492330000	-0.155392000
H	-2.801872000	4.181771000	-1.118534000
H	-3.678997000	0.551514000	0.338184000
Al	-1.280327000	-2.307885000	-2.119964000
H	-2.740074000	-1.669649000	-2.291599000
H	-0.179560000	-1.916252000	-3.192507000
H	-1.210594000	-3.741338000	-1.427874000

RHF/3-21G* for **TS2, 5, TS5 and TS6'**, gas phase.

TS2

N	2.516178000	-1.241219000	-0.127330000
C	3.528211000	-0.329667000	-0.175762000
N	3.280821000	0.529487000	0.855426000
Al	-0.113608000	-1.553340000	1.683625000
C	1.587374000	-0.933503000	0.901441000
C	2.097593000	0.169135000	1.482662000
H	1.695710000	0.720198000	2.293219000
C	4.098332000	1.705797000	1.320974000
C	2.367819000	-2.422838000	-1.049139000
C	1.816625000	-1.943247000	-2.402333000
H	2.500366000	-1.264001000	-2.884485000
H	1.662563000	-2.796895000	-3.052861000
H	0.864272000	-1.447334000	-2.251320000
C	3.714383000	-3.154665000	-1.189672000
H	4.087664000	-3.431131000	-0.211297000
H	3.561344000	-4.055336000	-1.772430000
H	4.458446000	-2.566013000	-1.693786000
C	1.376034000	-3.432466000	-0.453186000
H	0.364435000	-3.053680000	-0.447282000
H	1.380855000	-4.314348000	-1.081950000
H	1.658385000	-3.725979000	0.548364000

C	5.586388000	1.325252000	1.380957000
H	6.000094000	1.130712000	0.407904000
H	6.139047000	2.149907000	1.815597000
H	5.720679000	0.448423000	2.002089000
C	3.836666000	2.905584000	0.396367000
H	2.778433000	3.142458000	0.394510000
H	4.383359000	3.767767000	0.761488000
H	4.157495000	2.694889000	-0.610760000
C	3.668493000	2.088637000	2.753634000
H	3.748293000	1.244342000	3.427414000
H	4.336455000	2.866109000	3.101699000
H	2.662241000	2.485870000	2.788194000
H	-0.691871000	-0.394416000	2.610449000
H	-1.246111000	-1.420664000	0.137414000
H	-0.508036000	-3.057870000	1.988236000
C	-3.326792000	0.269028000	-0.176877000
N	-4.631324000	-0.024858000	0.097339000
N	-3.377130000	1.525583000	-0.694718000
H	-1.837084000	-0.896394000	0.094273000
C	-5.470694000	1.041740000	-0.241894000
C	-4.693295000	2.003787000	-0.733688000
H	-4.952141000	2.965468000	-1.102088000
C	-2.220437000	2.329865000	-1.163626000
C	-5.063499000	-1.313020000	0.705002000
C	-4.486099000	-1.406373000	2.126297000
H	-3.406743000	-1.363502000	2.103619000
H	-4.786533000	-2.339560000	2.588140000
H	-4.847531000	-0.582801000	2.730454000
C	-4.557758000	-2.471297000	-0.170405000
H	-4.945098000	-2.372774000	-1.177341000
H	-4.893211000	-3.414748000	0.243984000
H	-3.478821000	-2.480862000	-0.214039000
C	-6.598121000	-1.372925000	0.774947000
H	-6.997046000	-0.593669000	1.413205000
H	-6.886195000	-2.328019000	1.195975000
H	-7.039699000	-1.291305000	-0.211242000
C	-2.445151000	2.706837000	-2.639044000
H	-2.559002000	1.811040000	-3.236767000
H	-1.592896000	3.266261000	-3.005433000
H	-3.329138000	3.320423000	-2.762572000
C	-0.930614000	1.512498000	-1.040015000
H	-0.737179000	1.240117000	-0.013048000
H	-0.102937000	2.113716000	-1.396620000
H	-0.983732000	0.611856000	-1.636295000
C	-2.113652000	3.592906000	-0.290805000
H	-3.002130000	4.206981000	-0.375347000
H	-1.262027000	4.184269000	-0.605407000
H	-1.984033000	3.313670000	0.747467000
Al	5.113174000	-0.138898000	-1.634673000
H	5.396431000	1.437162000	-1.772526000
H	4.559509000	-0.727532000	-3.022688000
H	6.330815000	-0.978276000	-0.992025000
H	-6.522721000	1.025228000	-0.110485000

TS5

N	3.028344000	1.227348000	0.321607000
C	2.370775000	0.124421000	-0.086710000
C	4.378478000	1.121309000	-0.011219000
C	4.540584000	-0.052006000	-0.624737000
N	3.287713000	-0.665429000	-0.677350000
H	5.418928000	-0.491068000	-1.022946000
H	5.093125000	1.870906000	0.211646000
C	2.393723000	2.419203000	0.980001000
C	1.512098000	3.135765000	-0.054209000
C	3.491327000	3.371779000	1.478692000
H	4.157146000	2.876321000	2.175343000
H	4.066059000	3.788386000	0.660256000
H	3.012886000	4.193067000	1.996480000
H	2.100399000	3.418464000	-0.919484000
H	1.092709000	4.031367000	0.388838000
H	0.698147000	2.496145000	-0.363823000
C	3.045338000	-2.031187000	-1.248389000
C	4.125800000	-2.338955000	-2.299902000
C	1.669952000	-2.060496000	-1.927289000
H	0.869545000	-1.837963000	-1.238982000
H	1.636252000	-1.337924000	-2.734384000
H	1.507046000	-3.048284000	-2.341385000
H	4.159440000	-1.565054000	-3.057036000
H	3.874861000	-3.276313000	-2.779849000
H	5.107279000	-2.452392000	-1.856681000
C	1.555974000	1.937854000	2.171190000
H	2.175539000	1.391839000	2.872741000
H	1.130078000	2.796291000	2.676691000
H	0.747422000	1.306580000	1.836885000
C	3.125538000	-3.051763000	-0.103183000
H	4.097179000	-3.007904000	0.374976000
H	2.364660000	-2.850466000	0.636533000
H	2.975190000	-4.051560000	-0.492756000
N	-1.579816000	-0.559656000	0.819626000
C	-2.779107000	-0.225122000	0.252507000
C	-0.466341000	-0.139783000	0.032089000
C	-1.052470000	0.427518000	-1.039473000
H	-0.587215000	0.855115000	-1.890748000

H	1.104228000	-0.076314000	0.051968000
C	-1.392832000	-1.313109000	2.098130000
C	-1.631114000	-0.384134000	3.301324000
C	0.050922000	-1.840762000	2.163060000
H	0.257168000	-2.473828000	1.311054000
H	0.773297000	-1.039381000	2.189666000
H	0.156156000	-2.428883000	3.067696000
H	-0.951381000	0.457875000	3.255804000
H	-1.449035000	-0.927071000	4.222652000
H	-2.645445000	-0.019530000	3.313044000
C	-3.368607000	0.914256000	-1.976693000
C	-4.486590000	-0.094671000	-2.289304000
C	-2.576082000	1.129369000	-3.284267000
H	-1.836109000	1.913004000	-3.186476000
H	-2.093162000	0.214295000	-3.604146000
H	-3.277077000	1.433463000	-4.051597000
H	-4.055641000	-1.050374000	-2.561087000
H	-5.072380000	0.276440000	-3.122651000
H	-5.152921000	-0.237857000	-1.457582000
C	-2.318041000	-2.543352000	2.140640000
H	-2.169114000	-3.146318000	1.253139000
H	-2.074269000	-3.138151000	3.013875000
H	-3.357539000	-2.276048000	2.207911000
C	-3.925554000	2.273830000	-1.521321000
H	-4.524995000	2.166033000	-0.631947000
H	-3.105462000	2.953954000	-1.319841000
H	-4.542487000	2.696069000	-2.307175000
H	-4.633861000	-0.425681000	2.668401000
Al	-4.748471000	-0.471548000	1.062935000
H	-5.633435000	0.770317000	0.542330000
H	-5.245523000	-1.900804000	0.492024000
N	-2.453410000	0.369679000	-0.921476000

5

N	4.057971000	-0.376228000	1.056448000
C	3.270000000	-0.608039000	-0.011255000
C	5.145665000	0.385821000	0.668549000
C	5.013169000	0.615528000	-0.668547000
N	3.847303000	-0.011206000	-1.071401000
H	5.662062000	1.153977000	-1.344875000
H	5.928981000	0.691522000	1.347687000
C	3.716433000	-0.776910000	2.460761000
C	2.790472000	0.301273000	3.045163000
C	5.010400000	-0.885176000	3.276324000
H	5.724374000	-1.571372000	2.801608000
H	5.494077000	0.089454000	3.423067000
H	4.767708000	-1.278526000	4.270076000
H	3.270145000	1.288478000	3.015196000
H	2.556804000	0.058119000	4.090176000
H	1.850997000	0.344727000	2.481811000
C	3.232292000	0.062856000	-2.436798000
C	4.345415000	0.241773000	-3.476038000
C	2.271134000	1.260277000	-2.451177000
H	1.460479000	1.109018000	-1.729392000
H	2.795874000	2.191307000	-2.203152000
H	1.826267000	1.369457000	-3.448743000
H	4.844681000	1.215828000	-3.390092000
H	3.902449000	0.192966000	-4.477394000
H	5.097398000	-0.554309000	-3.394823000
C	3.003984000	-2.133985000	2.419416000
H	3.641303000	-2.901052000	1.960560000
H	2.767383000	-2.445857000	3.443818000
H	2.061719000	-2.064313000	1.864239000
C	2.468676000	-1.240184000	-2.695466000
H	3.135734000	-2.109278000	-2.626381000
H	1.646608000	-1.359856000	-1.980131000
H	2.039695000	-1.209726000	-3.704322000
N	-2.456890000	-1.142592000	-0.356528000
C	-3.576179000	-0.441223000	0.023882000
C	-1.326006000	-0.336490000	-0.531732000
C	-1.800560000	0.915337000	-0.260252000
H	-1.244657000	1.840601000	-0.257753000
H	2.142718000	-1.014079000	0.033957000
C	-2.376859000	-2.629759000	-0.531557000
C	-2.365628000	-3.294073000	0.855176000
C	-1.075123000	-2.990719000	-1.266296000
H	-1.050413000	-2.548565000	-2.268204000
H	-0.182256000	-2.667549000	-0.722795000
H	-1.036334000	-4.082540000	-1.372560000
H	-1.497945000	-2.947235000	1.432439000
H	-2.293947000	-4.385390000	0.746175000
H	-3.282082000	-3.066483000	1.407828000
C	-3.960035000	2.063512000	0.425163000
C	-5.256539000	2.103265000	-0.397342000
C	-3.163343000	3.343668000	0.085760000
H	-2.269032000	3.425094000	0.724358000
H	-2.902505000	3.360923000	-0.985266000
H	-3.793658000	4.212979000	0.296764000
H	-5.029025000	2.071317000	-1.470967000
H	-5.802273000	3.031274000	-0.179024000
H	-5.919488000	1.268638000	-0.157776000
C	-3.544257000	-3.131073000	-1.395650000
H	-3.590971000	-2.566663000	-2.335992000

H	-3.391817000	-4.192828000	-1.632030000
H	-4.509817000	-3.047373000	-0.892014000
C	-4.230382000	2.060370000	1.938163000
H	-4.842645000	1.197840000	2.216722000
H	-3.281474000	2.026190000	2.491515000
H	-4.770112000	2.973890000	2.225363000
H	-5.333568000	-2.639766000	1.131138000
Al	-5.509186000	-1.179430000	0.485520000
H	-6.164289000	-0.166670000	1.550481000
H	-6.285795000	-1.175381000	-0.927184000
N	-3.155256000	0.858340000	0.062967000
Al	0.978099000	4.093620000	0.000435000
H	0.656108000	3.991651000	-1.546105000
H	2.010875000	3.060716000	0.623365000
H	0.485518000	5.329880000	0.853317000

TS6′

N	-2.542082000	-1.552508000	-1.329872000
C	-2.927455000	-0.313532000	-0.944437000
C	-1.638178000	-2.153044000	-0.398248000
C	-1.481778000	-1.198589000	0.537951000
N	-2.255826000	-0.073392000	0.202174000
H	-0.887307000	-1.237399000	1.414425000
C	-3.036702000	-2.250360000	-2.547590000
C	-4.159843000	-3.219234000	-2.140438000
C	-1.883291000	-3.021495000	-3.209902000
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H	-3.787157000	-3.938212000	-1.424155000
H	-4.526044000	-3.750576000	-3.012513000
H	-4.982600000	-2.668115000	-1.697556000
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C	-2.332895000	2.382535000	0.098881000
C	-1.161143000	1.244913000	1.985123000
H	-1.186314000	0.457822000	2.726663000
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H	-1.848879000	-5.142424000	-0.367651000
H	0.510110000	-4.149668000	-1.191012000
H	-4.098798000	0.471494000	-1.395462000
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H	-4.723250000	4.982999000	-2.807325000
H	-3.394814000	2.167442000	-2.898681000
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H	-4.203731000	1.600165000	-4.347648000
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C	-10.064939000	1.081048000	-1.610329000
C	-9.038137000	0.329799000	0.559124000
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H	-8.913474000	1.356784000	0.878934000
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H	-9.999010000	2.116899000	-1.297939000
H	-11.022398000	0.695994000	-1.284607000
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H	-8.986294000	-1.286753000	-2.518484000
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H	-10.045770000	-1.618130000	-1.150360000
H	-8.096913000	2.346883000	-2.692700000

4.5.4. References

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4.6. Author contributions

The syntheses of compounds **1** and **1a** were performed by Michael Weinhart.

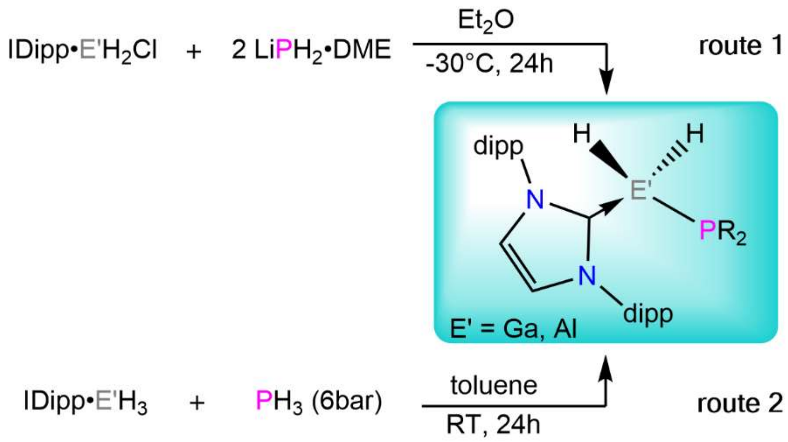
The NMR studies in different solvents of **1** and **1a** were performed by Anna M. Chernysheva.

X-ray structural analyses of **1** and **1a** were performed by Michael Weinhart.

Computational studies were performed by Anna M. Chernysheva.

The manuscript was written by Anna M. Chernysheva.

5. Phosphanylalanes and –gallanes stabilized only by a Lewis Base



Abstract: The synthesis and characterization of the first parent phosphanylalane and –gallane stabilized only by a Lewis-base (LB) were reported. The corresponding substituted compounds such as IDipp•GaH_2PCy_2 (**1**) (IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene) were obtained by the reaction of $LiPCy_2$ with IDipp•GaH_2Cl. However, the LB-stabilized parent compounds IDipp•GaH_2PH_2 (**3**) and IDipp•AlH_2PH_2 (**4**) were prepared via a salt metathesis of $LiPH_2$•DME with IDipp•E'H_2Cl (E' = Ga, Al) or by H_2-elimination reactions of IDipp•E'H_3 (E' = Ga, Al) and PH_3, respectively. The compounds could be isolated as crystalline solids and completely characterized. Supporting DFT computations gave insight into the reaction pathways as well as into the stability of these compounds with respect to their decomposition behavior.

5.1. Introduction

In current main group chemistry, the development of new synthetic routes to functional materials is an important topic. In this context, unsaturated compounds such as $H_2EE'H_2$ (E = group 15 element, E' = group 13 element) are interesting as they are isoelectronic to hydrocarbons, just as ethene in the given example. Due to the polarity of the bond between the group 13 and the group 15 atom, different reactivity and functionalities compared to hydrocarbons can be observed. Therefore they are studied e.g. as single source precursors for binary and composite 13/15 materials for micro- and optoelectronic devices[1] as well as in the fabrication of semiconducting materials, layers and inorganic materials.[1,2] Besides H_2NBH_2, which could be isolated in an Ar matrix,[3] it was only possible to study the parent compounds of the type $H_2EE'H_2$ by DFT calculations,[4] because of their instability to form polymers due to the existing donor and acceptor orbitals and their high tendency to H_2 eliminations. Therefore, a combination of a donor (Lewis base = LB) and an acceptor (Lewis acid = LA) was needed for the electronic stabilization of these compounds.[5] For boron-based systems, various synthetic routes[6] and different types of stabilization (types **A** and **B**, Figure 1)[7] as well as their reactivity[8] and polymerization[9] (type **D**) were investigated. With regard to the heavier analogs Al and Ga, the current research is more focused on the use as FLPs (frustrated Lewis-pairs)[10] and in solid-state chemistry.[11] In the context of the parent compounds, up to now we have only succeeded in stabilizing type **A** compounds.[5] In contrast to the corresponding boron derivatives, it has so far not been possible to receive type **B** compounds except for organo substituted compounds such as, dmap•$AlMe_2P(SiMe_3)_2$ (dmap = 4-dimethylaminopyridine).[12] Moreover, LA/LB-stabilized phosphanylalanes and –gallanes of type **A** have a strong tendency to a pentacoordinated environment at the group 13 element atom, and therefore readily undergo H_2-elimination reactions to form polymers.

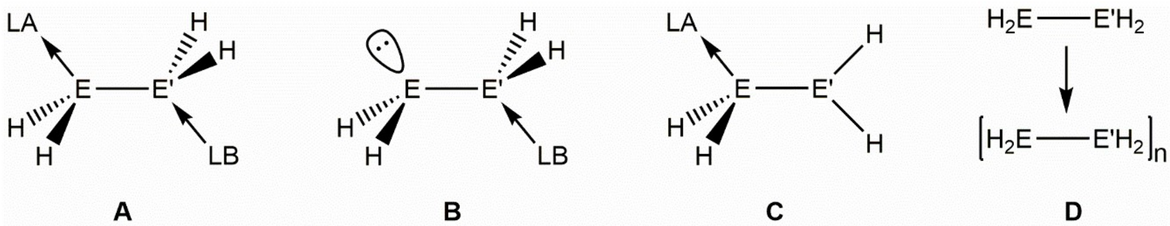


Figure 1: Different types of stabilization of parent compounds of the pentelyltrielanes.

Depending on the solvent, the reaction temperatures and the used LB, we were able to control the polymerization process and isolate and characterize different oligomers, as for instance the dimer **A1**, the trimer **A2** and other four-membered ring species such as **A3** (Figure 2).[13] Still the question arises, if one could avoid the formation of these oligomers and, moreover, stabilize for the first time type **B** compounds. A possible way could be to prevent a pentacoordinated environment at the group 13 element by using a bulky but also strong donating LB.[14]

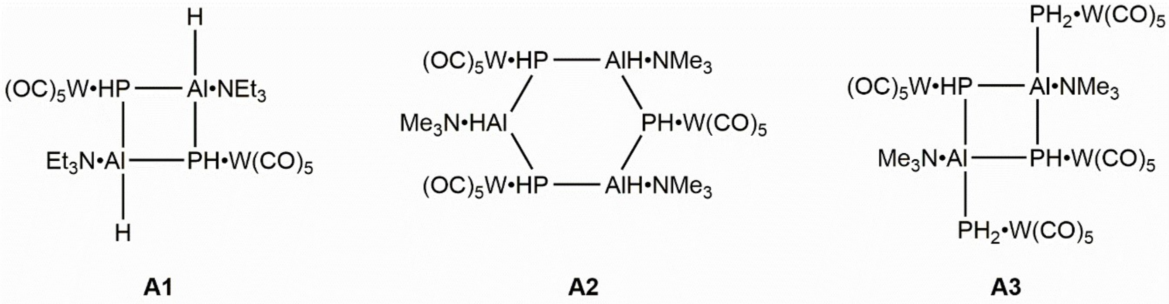


Figure 2: Different oligomeric products of the reaction between PH2·W(CO)5 and AlH2·NMe3/AlH2·NEt3.

Herein, we report the synthesis and characterization of different substituted phosphanylalanes and –gallanes stabilized only by a LB as well as the first Lewis-base-stabilized parent phosphanylalane and –gallane (type **B**).

5.2. Results and Discussion

In order to select the most promising LB for the stabilization, quantum chemical computations were carried out for several Lewis bases: NMe_3, Py, dmap (4-dimethylaminopyridine) and IDipp (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene). One of the decomposition pathways of the Lewis-base-stabilized compounds LB•E'H_2PH_2 is the LB elimination with the formation of $(E'H_2PH_2)_n$ polymers (E' = Al, Ga). We modeled the oligomer formation (Equation 1), as the trimer was shown to be a good energetic model compound for the stability studies of long-chain oligomers.[15]

$$LB{\bullet}EH_2PH_2 = \tfrac{1}{3}\,(EH_2PH_2)_3 + LB \qquad (1)$$

Quantum chemical computations indicate that, in terms of stabilization with respect to the oligomer formation (Equation 1), the order of Lewis bases is NMe_3<Py<dmap<Dipp (Table 1) with IDipp providing the best energetic stabilization. Note that decomposition of PH_2GaH_2•NMe_3 and PH_2GaH_2•Py is predicted to be exergonic already at room temperature, while PH_2GaH_2•IDipp is expected to be stable even in boiling toluene (ΔG^o_{383} = 14.2 kJ mol^{-1}).

Kinetic stability with respect to LB elimination depends on the activation energy of the dissociation (Equation 2). Since complex formation proceeds without energy barrier, the standard enthalpy of the complex dissociation can be taken as an estimation of the activation energy.

$$LB{\bullet}EH_2PH_2 = EH_2PH_2 + LB \qquad (2)$$

Table 1. Thermodynamic characteristics of gas phase reactions. Standard enthalpies ΔH^o_{298} and standard Gibbs energies ΔG^o_{298} in kJ mol^{-1}, standard entropies ΔS^o_{298} in J mol^{-1} K^{-1}. B3LYP/def2-TZVP level of theory.

	E = Al			E = Ga		
Process	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
$PH_2EH_2 \cdot NMe_3 = {}^1/_3(PH_2EH_2)_3 + NMe_3$	13.7	40.4	1.7	0.6	37.6	-10.6
$PH_2EH_2 \cdot Py = {}^1/_3(PH_2EH_2)_3 + Py$	17.8	25.6	10.2	1.1	26.4	-6.8
$PH_2EH_2 \cdot dmap = {}^1/_3(PH_2EH_2)_3 + dmap$	36.1	33.8	26.0	15.7	31.0	6.5
$PH_2EH_2 \cdot IDipp = {}^1/_3(PH_2EH_2)_3 + IDipp$	52.1	78.5	28.7	40.7	69.0	20.1
$IDipp \cdot MH_3 + PH_3 = H_2 + IDipp \cdot MH_2PH_2$	-16.0	-39.0	-4.3	-14.6	-36.7	-3.7
$IDipp \cdot MH_3 + PHCy_2 = H_2 + IDipp \cdot MH_2PCy_2$	25.9	-81.1	50.1	23.5	-82.3	48.0

The enthalpies of processes of complex dissociation increase in the order NMe_3<Py<dmap<IDipp (Table S4), indicating the increase in kinetic stabilization. Thus, the N-heterocyclic carbene IDipp provides the best energetic stabilization both from a thermodynamic and a kinetic point of view.

After identifying the IDipp as the prominent LB, we considered the thermodynamic favorability of possible synthetic pathways leading to LB•EH_2PH_2. Two alternative pathways toward the parent phosphanylalanes and -gallanes stabilized only by a LB were regarded (Equations 3 and 4).

$$IDipp \cdot EH_3 + PH_3 = H_2 + IDipp \cdot EH_2PH_2 \quad (3)$$

$$IDipp \cdot EH_2X + LiPH_2 \cdot dme = LiX(s) + dme + IDipp \cdot EH_2PH_2 \quad (4)$$

(E = Al, Ga; X= Cl, I)

As can be seen from the data in Table 1, reactions of IDipp•MH_3 with phosphine are exothermic and slightly exergonic for both Al and Ga. Thus, the H_2 elimination synthetic pathway is thermodynamically allowed in this case. In contrast, the reaction with $PHCy_2$ instead of phosphine is both endothermic and endergonic and is thermodynamically prohibited. These data are in good agreement with the experimental observations: the reaction proceeds in the case of PH_3, but not so in case of $PHCy_2$ (*vide infra*). In contrast, the alternative metathesis pathway is highly exothermic and exergonic and thermodynamically allowed in all cases (ΔG^o_{298} values for equation 4 are in the range -140 – -208 kJ mol^{-1}, see Table S6 for details). The formation of solid LiX (X = Cl, I) is a driving force for the metathesis reaction.

Lewis acidity trends: From the results of the quantum chemical computations, we can evaluate the influence of the substituent R in the Lewis acid EH_2R on its Lewis acidity with respect to IDipp as a reference Lewis base. For both aluminum and gallium, the stability of the complexes decreases in the order Cl > I > H >PH_2 > PCy_2. For the same R substituent, the aluminum complexes are more stable compared to the gallium analogs. The overall order of the stability of complexes with IDipp with respect to the dissociation is AlH_2Cl> AlH_2I> AlH_3> AlH_2PH_2 > GaH_2Cl> GaH_2I> GaH_3> AlH_2PCy_2 > GaH_2PH_2 > GaH_2PCy_2. Thus, compounds bearing PCy_2 substituents are the weakest with respect to the dissociation by means of the liberation of IDipp (Table S5).

The IDipp (1,3-Bis-(2,6-diisopropylphenyl)imidazole-2-ylidene) stabilized compound IDipp•GaH_2PCy_2 (**1**) (Cy = cyclohexyl) can be synthesized by the reaction between IDipp•GaH_2Cl and $LiPCy_2$ in Et_2O at –30°C. Crystals of **1** can be isolated in a yield of 55% at –30°C. As a solid, **1** is stable at ambient temperatures in an inert atmosphere. The molecular ion peak of **1** can be detected at 656.337m/z in the mass spectrum (LIFDI-MS). Its ^{1}H NMR spectrum shows a doublet at δ = 4.04 ppm ($^2J_{P,H}$ = 7.91 Hz) for the GaH_2-moiety. The ^{31}P NMR spectrum of a solution of **1** in C_6D_6 shows a broadened singlet at δ = –56.13 ppm that is highfield shifted compared to the compound [{$H_2Ga(\mu\text{-}PCy_2)$}$_3$] (δ = –32.7 ppm).[16] This shift results because of the stabilization from the NHC which increases the shielding of the phosphorus atom.

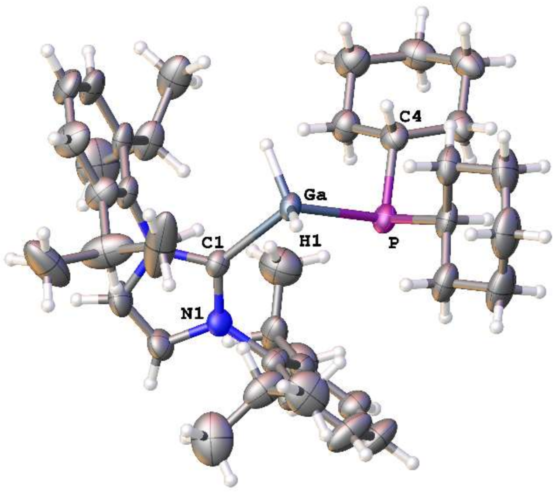
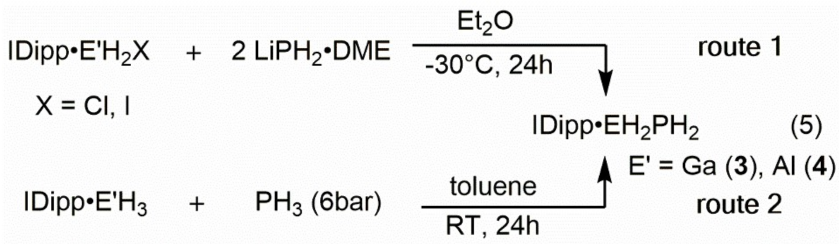


Figure 3: Molecular structure of **1** in the solid state. Selected bond lengths [Å] and angles [°]: Ga–P 2.4051(2), Ga–C1 2.090(2), H1–Ga–P–C4 125.6, C1–Ga–P 112.34(5).

The X-ray structure analysis of **1** (Figure 3) shows a P–Ga bond length of 2.3724(6) Å that is shorter than the Ga–P bond in IMes•$GaEt_2P(H)Si$*t*$BuPh_2$ (Ga–P = 2.4051(2) Å, IMes = 1,3-Bis-(2,4,6-trimethylphenyl)imidazole-2-ylidene) characterized by *von Hänisch et al.* because of less bulkier substituents on the phosphorus atom and the Ga atom, respectively.[17] Likewise, the Ga–C1 bond in **1** (2.090(2) Å) is shorter, too, compared to IMes•$GaEt_2P(H)Si$*t*$BuPh_2$ (Ga–C_{NHC} = 2.1254(7) Å) because of the stronger donation by IDipp as opposed to IMes. The conformation of **1** is an eclipsed one with a torsion angle of H1–Ga–P–C4 = 125.6° (Figure 3). The C1–Ga–P angle of **1** (112.34(5)°) is much wider compared to IMes•$GaEt_2P(H)Si$*t*$BuPh_2$ (C_{NHC}–Ga–P = 99.1(2)°) because of the steric demand of the isopropyl-moieties of the IDipp. Reactions between IDipp•GaH_3 and $PHCy_2$ were performed in toluene at –30°C, room temperature and 100°C for 24 hours. In neither of these reactions the formation of compound **1** could be identified, supporting the results of the previously discussed computations (Table 1). The Al analog IDipp•AlH_2PCy_2 (**2**) is accessible by the reaction between IDipp•AlH_2Cl and $LiPCy_2$ in Et_2O at –30°C. Numerous attempts to crystallize **2** failed because of its extreme sensitivity towards hydrolysis. The ^1H NMR spectrum of crude **2** in C_6D_6 shows IDippH as the major component which cannot be separated due to similar solubility. None the less it was possible to assign compound **2** to the signals in the ^1H NMR spectrum as a minor component. The ^{31}P NMR spectrum of **2** in C_6D_6 shows a singlet at –66.24 ppm (Figure S12) that is highfield shifted compared to **1**. This is consistent with the spectra of **3** and **4** in which the signal for the Al analog is likewise shifted highfield (*vide infra*). In contrast to the substituted phosphanylalanes and –gallanes, the NHC-stabilized parent compounds can be synthesized via two different routes (Eq. 5).



Route 1 is on the lines of the synthesis of the substituted compounds (**1** and **2**), a reaction between IDipp•E'H_2Cl (E' = Ga, Al) and the parent phosphanide $LiPH_2$•DME in Et_2O at –30°C. The other synthesis is the H_2-elimination route between IDipp•E'H_3 and PH_3 (6 bar) in toluene at room temperature (route 2), which was not possible for the substituted derivatives. Compound **3** (IDipp•GaH_2PH_2) can be isolated at –30°C in a crystalline yield of 67% via route 1 and of 23% via route 2. It can be stored at ambient temperatures under an inert atmosphere without showing any decomposition. The molecular ion peak of **3** was detected at 493.205 m/z (LIFDI-MS). The ^1H NMR spectrum of **3** shows a broad singlet at δ = 4.21 ppm for the GaH_2 moiety and a doublet of triplets at δ = 0.54 ppm ($^1J_{P,H}$ = 170.8 Hz, $^3J_{H,H}$ = 3.68 Hz) for the PH_2 moiety. The ^{31}P NMR spectrum reveals a triplet of triplets at δ = –277.10 ppm ($^1J_{P,H}$ = 170.8 Hz, $^2J_{P,H}$ = 19.05 Hz). The molecular structure of **3** (Figure 4) shows a P–Ga bond (2.3373(6) Å) which is slightly shorter than in **1** (2.4051(2) Å) as well as the Ga–C1 bond (2.0507(2) Å, **1**: 2.090(2) Å). In contrast to **1**, which has an eclipsed conformation, compound **3** possesses a staggered-like conformation (torsion angle of H1–Ga–P–H3 = 164.1°) because of the less bulkier H substituents on the phosphorus atom, which results in a smaller C1–Ga–P angle as well (109.19(5)°).

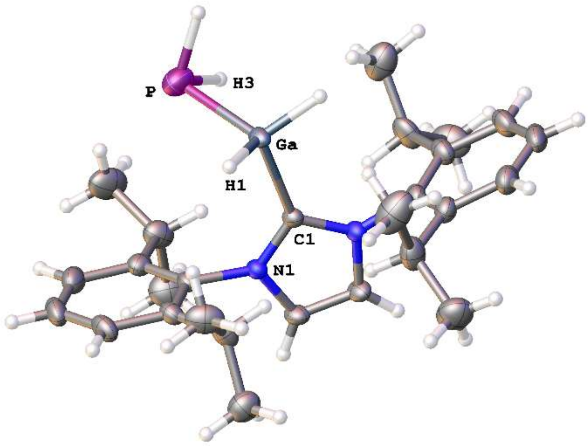


Figure 4: Molecular structure of **3** in the solid state. Selected bond lengths [Å] and angles [°]: Ga–P 2.3373(6), Ga–C1 2.0507(2), H1–Ga–P–H3 164.1, C1–Ga–P 109.19(5).

The aluminum analog IDipp•AlH_2PH_2 (**4**) can also be synthesized via salt metathesis and H_2 elimination reactions. Compound **4** can be isolated as a colorless crystalline solid at –30°C in 55% yield (route 1) and 20% yield (route 2), respectively. This reveals that the H_2 elimination route is less efficient in comparison with the salt elimination reaction. **4** can be stored under an inert atmosphere at room temperature without showing any decomposition. The LIFDI-MS and FD-MS spectrum does not show a molecular ion peak due to decomposition during the ionization process. The ^{1}H NMR spectrum of **4** reveals a broad singlet at δ = 3.64 ppm for the AlH_2 moiety and a triplet of triplets at δ = 0.22 ppm ($^{1}J_{P,H}$ = 169.6 Hz, $^{3}J_{H,H}$ = 3.09 Hz) for the PH_2 moiety. The ^{31}P NMR spectrum of **4** shows a triplet of triplets at δ = –285.7 ppm ($^{1}J_{P,H}$ = 169.6 Hz, $^{2}J_{P,H}$ = 18.7 Hz) which is highfield shifted compared to **3**.

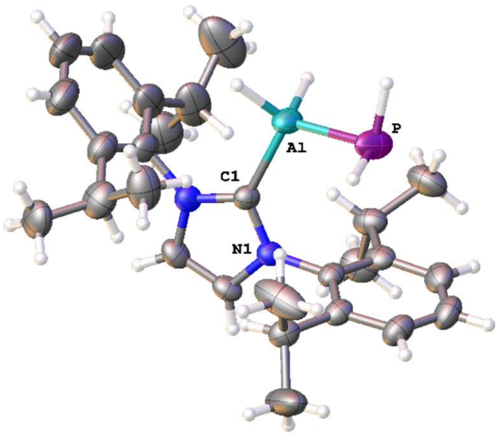


Figure 5: Molecular structure of **4** in the solid state. Selected bond lengths [Å] and angles [°]: Al–P 2.3131(10), Al–C1 2.056(2), C1–Al–P 113.17(7).

The P–Al bond in **4** (2.3131(10) Å; Figure 5) is slightly shorter than the P–Al bond in [{(CO)$_5$W}H$_2$PAlH$_2$•NMe$_3$] (2.377(1) Å).[18] The Al–C1 (2.056(2) Å) bond length is in good agreement with the Ga–C1 bond in **3** (2.0507(2) Å). The C1–Al–P angle (113.17(7)°) is slightly wider than the C1–Ga–P angle in compound **3** (109.19(5)°) and the C1–Ga–P angle in **1** (112.34(5)°). It was not possible to freely refine the H substituents on the phosphorus atom and therefore it is not possible to provide any information about the torsion angle and the conformation of **4**.

5.3. Conclusion

The results have shown for the first time that it is possible to synthesize monomeric phosphanylalanes and –gallanes stabilized only by a Lewis-base if a strong donating and sterically demanding LB is used. Besides the derivatives, which are organosubstituted on the P atom, also the parent compounds were isolated representing the unprecedented examples of only LB-stabilized parent phosphanylalanes and –gallanes. While the parent compounds can be synthesized via salt metathesis and H_2 elimination, the organosubstituted compounds can only be accessed via a salt metathesis reaction. The energetic differences in the reaction pathways and the different stability of these complexes were computed by DFT methods. Moreover, the salt elimination route was applied for the first time to access stabilized phosphanylalanes and –gallanes. Further investigations will be directed at using the novel compounds as precursors for CVD-processes to obtain 13/15 materials.

5.4. References

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5.5. Supporting Information

5.5.1. Experimental section

General procedures: All reactions and subsequent manipulations were performed under an argon atmosphere in a Braun glovebox or using standard Schlenk techniques. NMR spectra were recorded on a Bruker Avance 400 and a Bruker Avance 300. Deuterated solvents (C_6D_6, acetone-d_6) were distilled, and oxygen removed via freeze-pump-thaw procedure prior use. Chemical shifts are listed in parts per million (ppm) and were referenced to external standards (^{1}H and ^{13}C: $Si(CH_3)_3$, ^{31}P: 85% H_3PO_4 ^{27}Al: $Al(NO_3)_3$). Coupling constants are quoted in Hertz. Elemental analysis (CHN) were determined using in-house facility. LIFDI-MS and FD-MS spectra were recorded with a Jeol AccuTOF GCX.

IDipp (1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene)[1] and $LiGaH_4$[2] were prepared according to published procedures. $GaCl_3$ was purchased from Sigma Aldrich and sublimated prior use. $LiAlH_4$ and iodine was purchased from Sigma Aldrich and used as received. All solvents were purified with a MBRAUN SPS-800 and oxygen removed via freeze-pump-thaw procedure before use.

Synthesis of IDipp·GaH$_2$Cl

A slurry of IDipp·GaCl$_3$ (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene) (180 mg, 0.3 mmol, 1 eq) in 10 mL toluene was added slowly to a solution of IDipp·GaH$_3$ (280 mg, 0.61 mmol, 2 eq) in 10 mL toluene. The slightly gray suspension was warmed to 55 °C and stirred for 6 hours. After filtration over a celite pad the solvent was removed *in vacuo* to afford IDipp·GaH$_2$Cl as a white powder (280 mg, 62 %).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 1.00 (d, 12H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-C*H*$_3$), 1.39 (d, 12H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-C*H*$_3$), 2.67 (sept, 4H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-C*H*), 4.66 (s, 2H, Ga*H*$_2$), 6.44 (s, 2H, NC*H*C*H*N), 7.08 (d, 4H, $^3J_{H,H}$ = 7.73 Hz, aryl-C$_{meta}$*H*), 7.22 (t, 2H, $^3J_{H,H}$ = 7.73 Hz, aryl-C$_{para}$*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 23.1 (*i*Pr-*C*H$_3$), 25.4 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H(CH$_3$)$_2$), 124.2 (N*C*H*C*HN), 124.4 (aryl-*C*$_{meta}$H), 131.0 (aryl-*C*$_{para}$H), 134.1 (aryl-*C*$_{ipso}$), 145.7 (aryl-*C*$_{ortho}$), 174.4 (N*C*N).

Synthesis of IDipp·AlH$_2$Cl

A solution of IDipp (1.06 g, 2.74 mmol, 1 eq) in 10 mL Et$_2$O was added dropwise to a suspension of (NMe$_3$)$_2$·AlH$_2$Cl (500 mg, 2.74 mmol, 1 eq) in 10 mL Et$_2$O at -60 °C. The suspension was stirred for 3 hours at room temperature. After removing the solvent the off-white residue was suspended in toluene and filtered over a celite pad. The solution was concentrated and stored at -30 °C to afford IDipp·AlH$_2$Cl as colorless crystals (700 mg, 56 %).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 0.97 (d, 6H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 1.00 (d, 6H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 1.41 (d, 12H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 2.68 (sept, 4H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*), 3.86 (s br, 2H, Al*H*$_2$Cl), 6.43 (s, 2H, NC*H*C*H*N), 7.08 (d, 4H, $^3J_{H,H}$ = 7.83 Hz, aryl-C$_{meta}$*H*), 7.22 (t, 2H, $^3J_{H,H}$ = 7.83 Hz, aryl-C$_{para}$*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 22.9 (*i*Pr-*C*H$_3$), 25.5 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H(CH$_3$)$_2$), 124.2 (N*C*H*C*HN), 124.3 (aryl-*C*$_{meta}$H), 131.2 (aryl-*C*$_{para}$H), 133.7 (aryl-*C*$_{ipso}$), 145.6 (aryl-*C*$_{ortho}$), 150.0 (N*C*N).

^{27}Al NMR (104.26 MHz, C_6D_6, 298 K): δ = 118.0 (s, *Al*H$_2$Cl).

^{27}Al{^{1}H} NMR (104.26 MHz, C_6D_6, 298 K): δ = 117.0 (s, *Al*H$_2$Cl).

Synthesis of IDipp·GaH$_2$PCy$_2$ (1)

A solution of IDipp·GaH$_2$Cl (50 mg, 0.1 mmol, 1 eq) in 5 mL Et$_2$O was added to a solution of LiPCy$_2$ (Cy = C_6H_{11}) (41 mg, 0.2 mmol, 2 eq) in 10 mL Et$_2$O at -30 °C. The yellow suspension was warmed up to room temperature overnight whereby the color changed to white. The solvent was removed and the white residue suspended in *n*-hexane. After filtration the solution was concentrated and stored at -30 °C to afford **1** as colorless needles (14 mg, 23 %).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 1.03 (d, 12H, $^3J_{H,H}$ = 6.92 Hz, *i*Pr-C*H*$_3$), 1.18-1.33 (m, 11H, P(C_6*H*$_{11}$)$_2$), 1.53 (d, 12H, $^3J_{H,H}$ = 6.92 Hz, *i*Pr-C*H*$_3$), 1.63-1.95 (m, 11H P(C_6*H*$_{11}$)$_2$), 2.78 (sept, 4H, *i*Pr-C*H*), 4.04 (d, 2H, $^2J_{P,H}$ = 8.96 Hz, Ga*H*$_2$), 6.47 (s, 2H, NC*H*C*H*N), 7.14 (d, 4H, $^3J_{H,H}$ = 7.72 Hz, aryl-C_{meta}*H*), 7.25 (t, 2H, $^3J_{H,H}$ = 7.72 Hz, aryl-C_{para}*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 22.8 (*i*Pr-*C*H$_3$), 25.2 (*i*Pr-*C*H$_3$), 27.0 (*C*$_6$H$_{11}$), 28.1 (*C*$_6$H$_{11}$), 28.7 (*i*Pr-*C*H(CH$_3$)$_2$), 31.7 (*C*$_6$H$_{11}$), 31.9 (*C*$_6$H$_{11}$), 32.3 (*C*$_6$H$_{11}$), 33.0 (*C*$_6$H$_{11}$), 123.8 (aryl-C_{meta}H), 123.9 (N*C*H*C*HN), 130.2 (aryl-C_{para}H), 135.1 (aryl-C_{ipso}), 145.5 (aryl-C_{ortho}).

^{31}P NMR (161.98 MHz, C_6D_6, 298 K): δ = -56.13 (s, *P*Cy$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, 298 K): δ = -56.13 (s, *P*Cy$_2$).

CHN: Anal. Calcd. (%) for $C_{39}H_{60}GaN_2P$ (657.62 g/mol): C 71.23, H 9.20, N 4.26; Found: C 66.95, H 8.54, N 5.05. Found values differ from calculated values due to leave of gaseous decomposition products prior measurement.

LIFDI-MS (m/z): 656.3370 [M-H]$^+$ (100%).

Synthesis of IDipp·AlH$_2$PCy$_2$ (2)

A solution of IDipp·AlH$_2$Cl (50 mg, 0.11 mmol, 1 eq) in 10 mL Et_2O was added to a suspension of LiPCy$_2$ (Cy = C_6H_{11}) (45 mg, 0.22 mmol, 2 eq) in 10 mL Et_2O at -30 °C. The yellow suspension was stirred at -20 °C for 20 hours. The solvent of the resulting clear solution was removed *in vacuo* and the white residue was suspended in *n*-hexane. After filtration over a celite pad the solution was concentrated and stored at 6 °C to afford **2** as an off-white powder (30 mg, 44 %). Numerous attempts to crystalize **2** weren't successful. Grown crystals were checked and identified as IDippH which forms as a side product of the hydrolysis of compound **2**. By comparison the ^{31}P NMR spectra with the spectra of the gallium analog (**1**) it was possible to prove the formation of compound **2**.

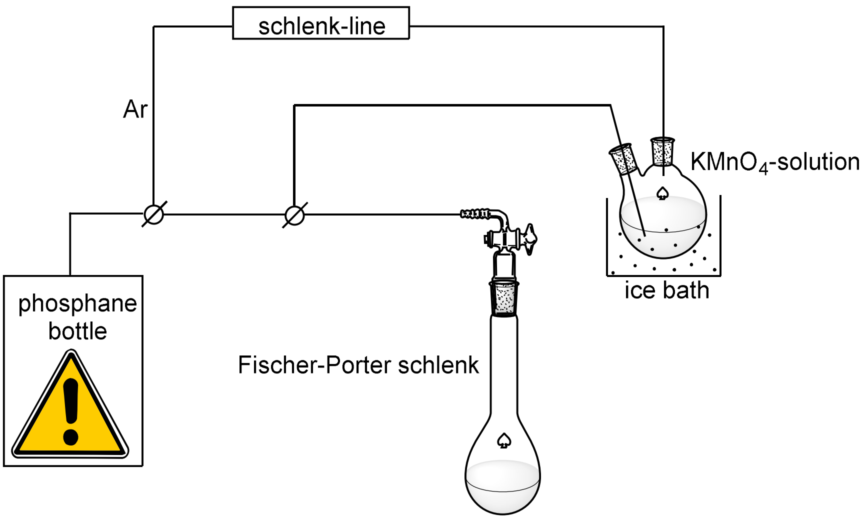
^{31}P NMR (161.98 MHz, C_6D_6, 298 K): -27.41 (d, 1H, $^1J_{P,H,}$ = 193.9 Hz, H*P*Cy$_2$), -66.24 (s, *P*Cy$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, 298 K): δ = -27.41 (s, H*P*Cy$_2$), -66.24 (s, *P*Cy$_2$).

Synthesis of IDipp·GaH_2PH_2 (3)

Route 1: A solution of IDipp·GaH_2Cl (30 mg, 0.06 mmol, 1 eq) in 5 mL Et_2O was added to a suspension of $LiPH_2$·DME (16 mg, 0.12 mmol, 2 eq) in 10 mL Et_2O at -30 °C. The slightly yellow suspension was stirred for 18 hours at -30 °C. After removing the solvent *in vacuo* the yellow residue was suspended in *n*-hexane and filtered over a celite pad. The clear solution was concentrated and stored at -30 °C to afford **3** as colorless needles (20 mg, 67 %).

Route 2: A pressure of 6 bar of PH_3 was put on a Fischer- Porter schlenk filled with IDipp·GaH_3 (50 mg, 0.11 mmol) in 10 mL toluene using the construction shown below. The reaction mixture was stirred for 3 days at room temperature. After the reaction the excess of PH_3 got destroyed with $KMnO_4$ and the toluene solution was concentrated and stored at -30 °C. It was only possible to isolate compound **3** as an off-white powder. (12 mg, 23 %).



^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 0.54 (dt, 2H, $^1J_{P,H}$ = 170.8 Hz, $^3J_{H,H}$ = 3.68 Hz, P*H*$_2$), 1.00 (d, 12H, $^3J_{H,H}$ = 6.95 Hz, *i*Pr-C*H*$_3$), 1.43 (d, 12H, $^3J_{H,H}$ = 6.95 Hz, *i*Pr-C*H*$_3$), 2.69 (sept, 4H, $^3J_{H,H}$ = 6.95 Hz, *i*Pr-C*H*), 4.21 (s, 2H, Ga*H*$_2$), 6.45 (s, 2H, NC*H*C*H*N), 7.10 (d, 4H, $^3J_{H,H}$ = 7.74 Hz, aryl-C_{meta}*H*), 7.23 (t, 2H, $^3J_{H,H}$ = 7.74 Hz, aryl-C_{para}*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 23.4 (*i*Pr-*C*H$_3$), 24.9 (*i*Pr-*C*H$_3$), 29.0 (*i*Pr-*C*H(CH$_3$)$_2$), 123.6 (N*C*H*C*HN), 124.1 (aryl-C_{meta}H), 130.6 (aryl-C_{para}H), 135.2 (aryl-C_{ipso}), 145.6 (aryl-C_{ortho}), 181.6 (N*C*N).

^{31}P NMR (161.98 MHz, C_6D_6, 298 K): δ = -277.10 (tt, 2H, $^1J_{P,H}$ = 170.8 Hz, $^2J_{P,H}$ = 19.05 Hz, *P*H$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, 298 K): δ = -277.10 (s, *P*H$_2$).

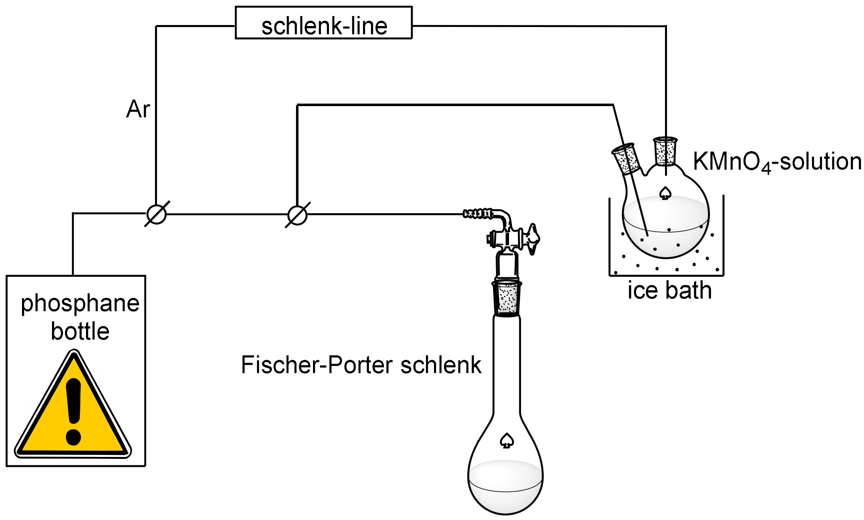
CHN: Anal. Calcd. (%) for $C_{27}H_{40}GaN_2P$ (493.33 g/mol): C 65.74, H 8.17, N 5.68; Found: C 69.60, H 8.07, N 5.91. Found values differ from calculated values due to leave of gaseous decomposition products prior measurement.

LIFDI-MS (m/z): 493.20512 $[M-H]^+$ (19 %).

Synthesis of IDipp·AlH$_2$PH$_2$ (4)

Route 1: A solution of IDipp·AlH_2Cl (50 mg, 0.11 mmol, 1 eq) in 5 mL Et_2O was added to a suspension of $LiPH_2$·DME (29 mg, 0.22 mmol, 2 eq) in 10 mL Et_2O at -30 °C. After stirring the white suspension for 18 hours at -30 °C the solvent was removed *in vacuo*. The white residue was suspended in *n*-hexane and filtered over a celite pad. The clear solution was concentrated and stored at -30 °C to afford **4** as colorless blocks (27 mg, 55 %).

Route 2: A pressure of 6 bar of PH_3 was put on a Fischer- Porter schlenk filled with IDipp·AlH_3 (50 mg, 0.12 mmol) in 10 mL toluene using the construction shown below. The reaction mixture was stirred for 3 days at room temperature. After the reaction the excess of PH_3 got destroyed with $KMnO_4$ and the toluene solution was concentrated and stored at -30 °C. It was only possible to isolate compound **3** as a white powder. (11 mg, 20 %).



^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 0.22 (dt, 2H, $^1J_{P,H}$ = 169.6 Hz, $^3J_{H,H}$ = 3.09 Hz, PH_2), 1.14 (d, 12H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 1.28 (d, 12H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 2.91 (sept, 4H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*), 3.64 (s br, 2H, Al*H*$_2$), 6.57 (s, 2H, NC*H*C*H*N), 7.13 (d, 4H, $^3J_{H,H}$ = 4.45 Hz, aryl-C_{meta}*H*), 7.26 (t, 2H, $^3J_{H,H}$ = 4.45 Hz, aryl-C_{para}*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 23.7 (*i*Pr-*C*H$_3$), 24.6 (*i*Pr-*C*H$_3$), 28.8 (*i*Pr-*C*H(CH$_3$)$_2$), 121.8 (N*C*H*C*HN), 123.7 (aryl-C_{meta}H), 129.2 (aryl-C_{para}H), 138.6 (aryl-C_{ipso}), 146.2 (aryl-C_{ortho}).

^{31}P NMR (161.98 MHz, C_6D_6, 298 K): δ = -285.65 (tt, 2H, $^1J_{P.H}$ = 169.6 Hz, $^2J_{P,H}$ = 18.7 Hz, *P*H$_2$).

$^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, 298 K): δ = -285.65 (s, *P*H_2).

^{27}Al NMR (104.26 MHz, C_6D_6, 298 K): δ = signal overlaid.

$^{27}Al\{^1H\}$ NMR (104.26 MHz, C_6D_6, 298 K): δ = signal overlaid.

CHN: Anal. Calcd. (%) for $C_{27}H_{40}AlN_2P$ (450.60 g/mol): C 71.97, H 8.95, N 6.22; Found: C 80.99, H 9.10, N 6.62. Found values differ from calculated values due to leave of gaseous decomposition products prior measurement and co-crystallization of IDipp·AlH_2I together with **4** (*vide infra)*.

According to reaction NMR spectra compound **3** can be synthesized from the starting material IDipp·GaH_2Cl and IDipp·GaH_2I, respectively. Nonetheless, in our synthesis crystals from compound **3** were obtained using IDipp·GaH_2Cl as starting material. According to the calculations compound **4** should be accessible with IDipp·AlH_2I as starting material as well. Our reactions with IDipp·AlH_2I, which were performed identical to the reactions with IDipp·AlH_2Cl, afforded only IDipp·AlH_3 as product. The analytical data from compound **3** and **4** were all recorded of crystals synthesized via route 1.

5.5.2. NMR data

IDipp·GaH_2Cl

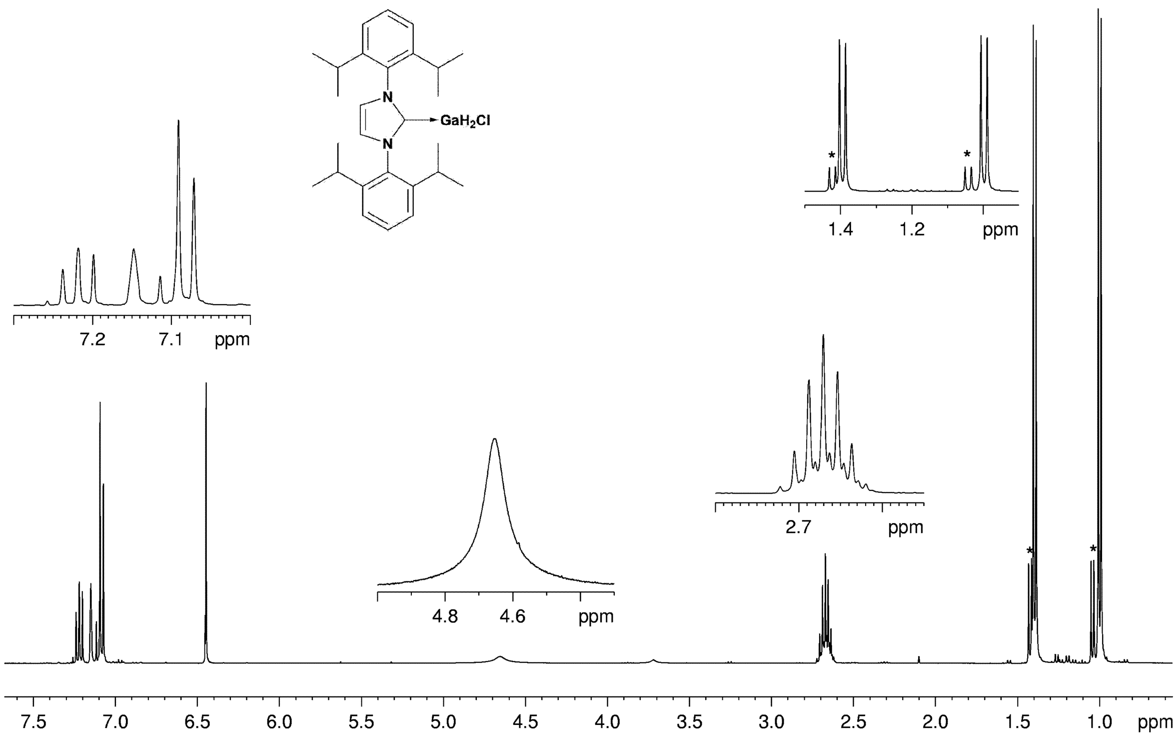


Figure S1: ^1H NMR spectrum of IDipp·GaH_2Cl in C_6D_6 at 298 K. * = IDipp·GaH_3.

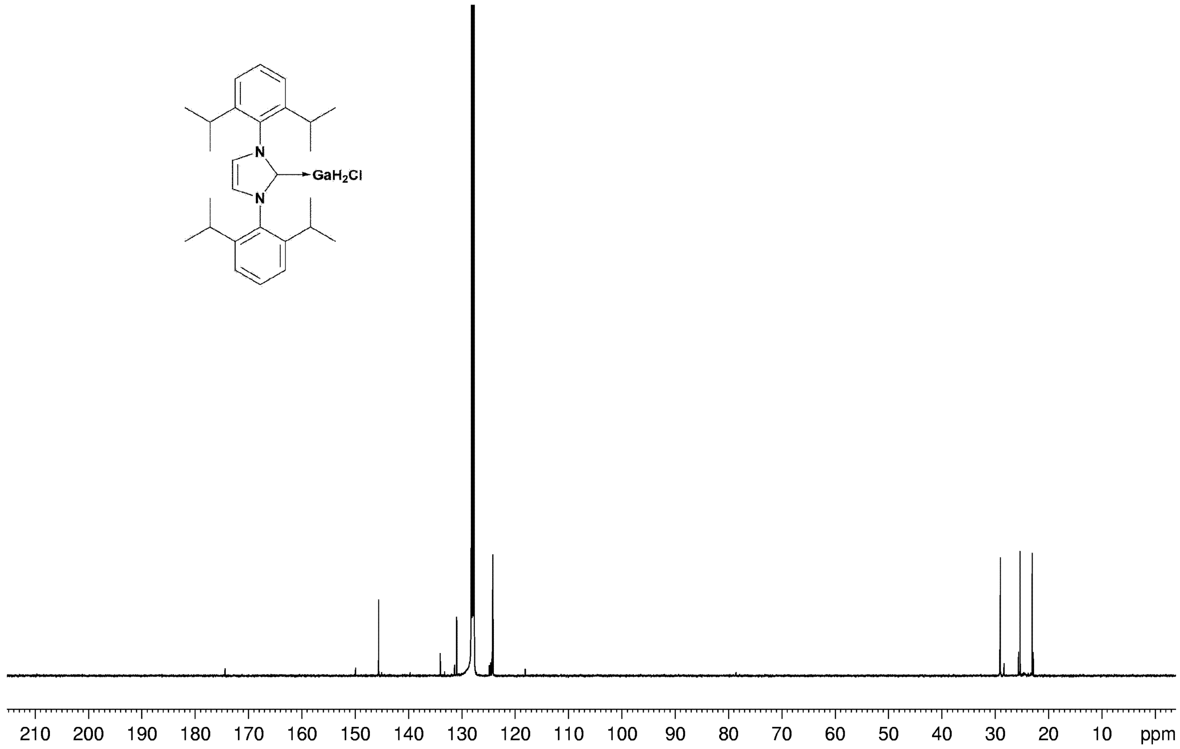


Figure S2: ^{13}C NMR spectrum of IDipp·GaH_2Cl in C_6D_6 at 298 K.

IDipp·AlH_2Cl

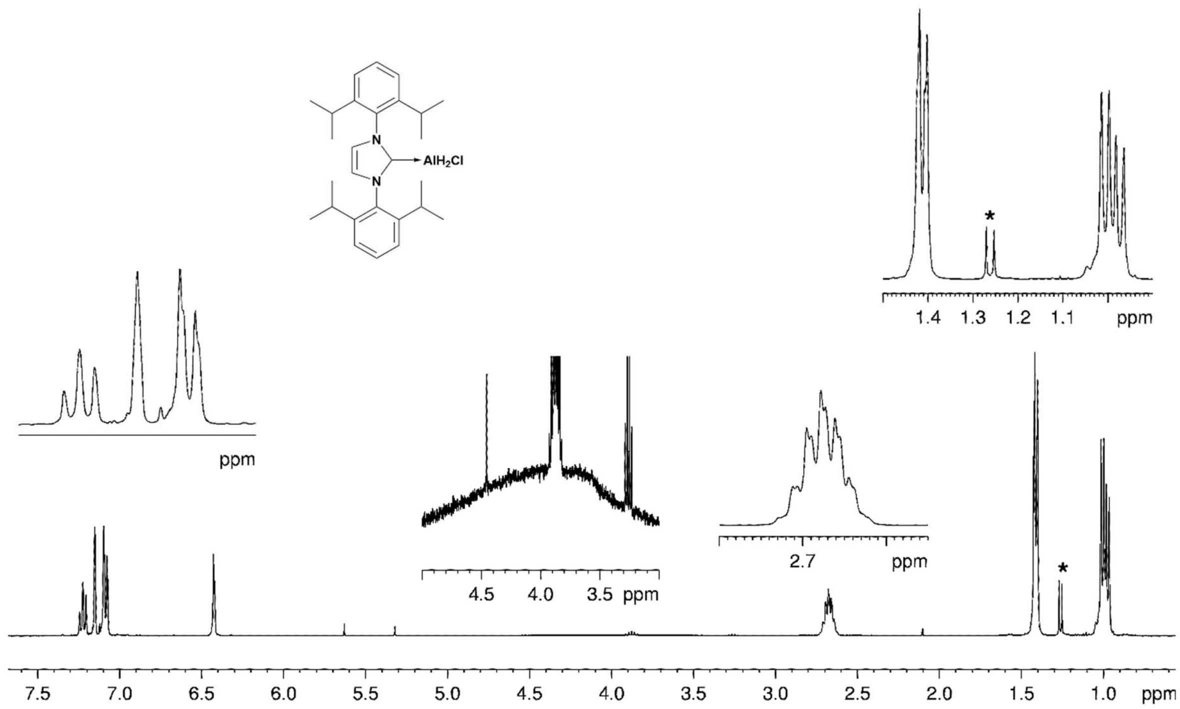


Figure S3: ^{1}H NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K. * = unidentified impurity.

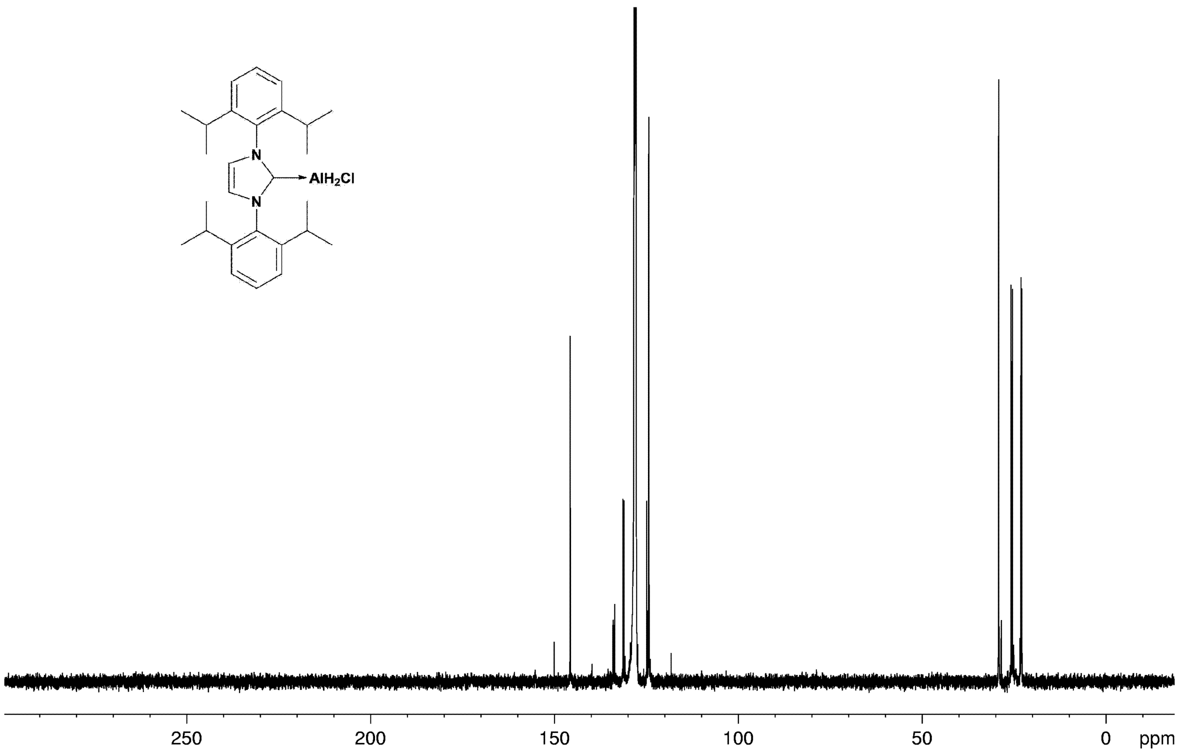


Figure S4: ^{13}C NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K.

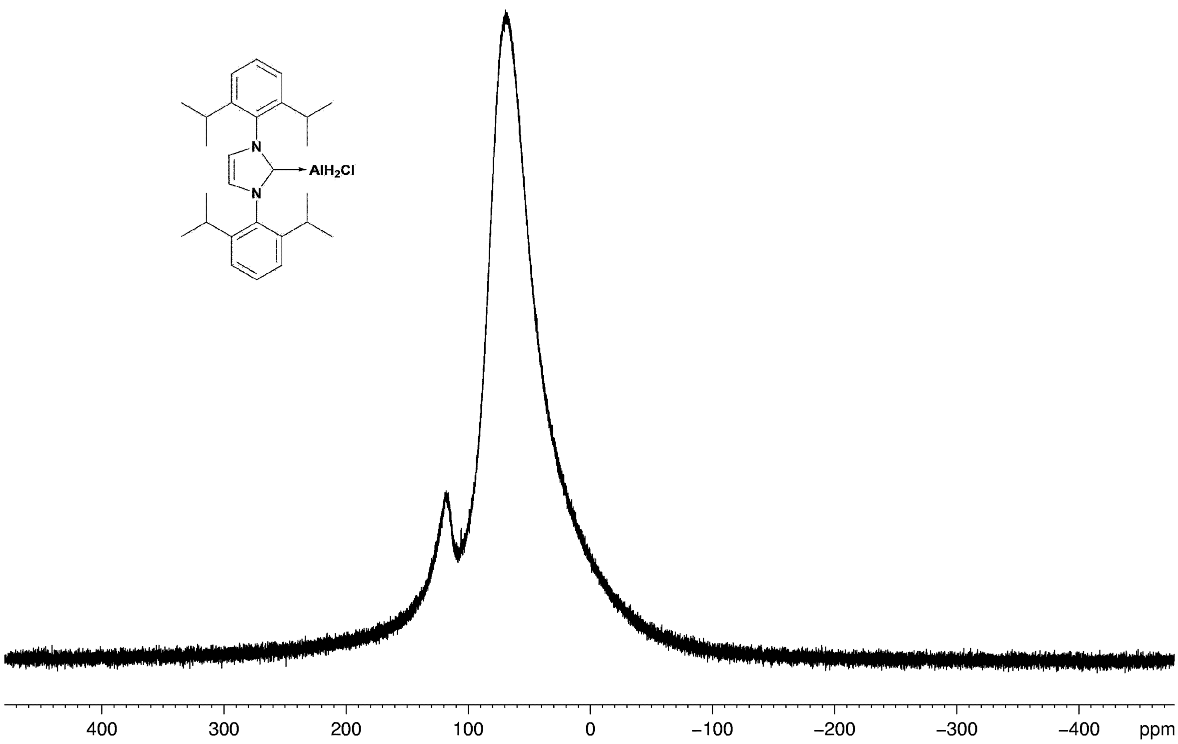


Figure S5: ^{27}Al NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K. * = signal from the NMR tube and the NMR sample head.

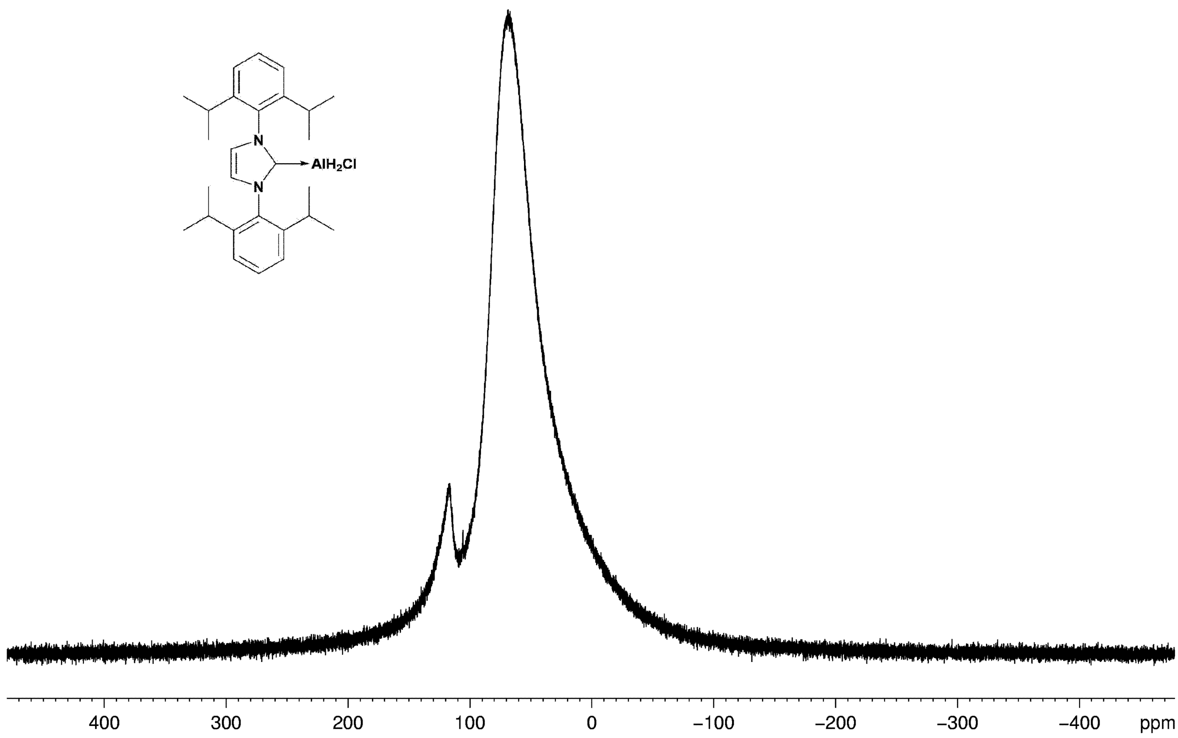


Figure S6: $^{27}Al\{^1H\}$ NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K. * = signal from the NMR tube and the NMR sample head.

IDipp·GaH_2PCy_2 (1)

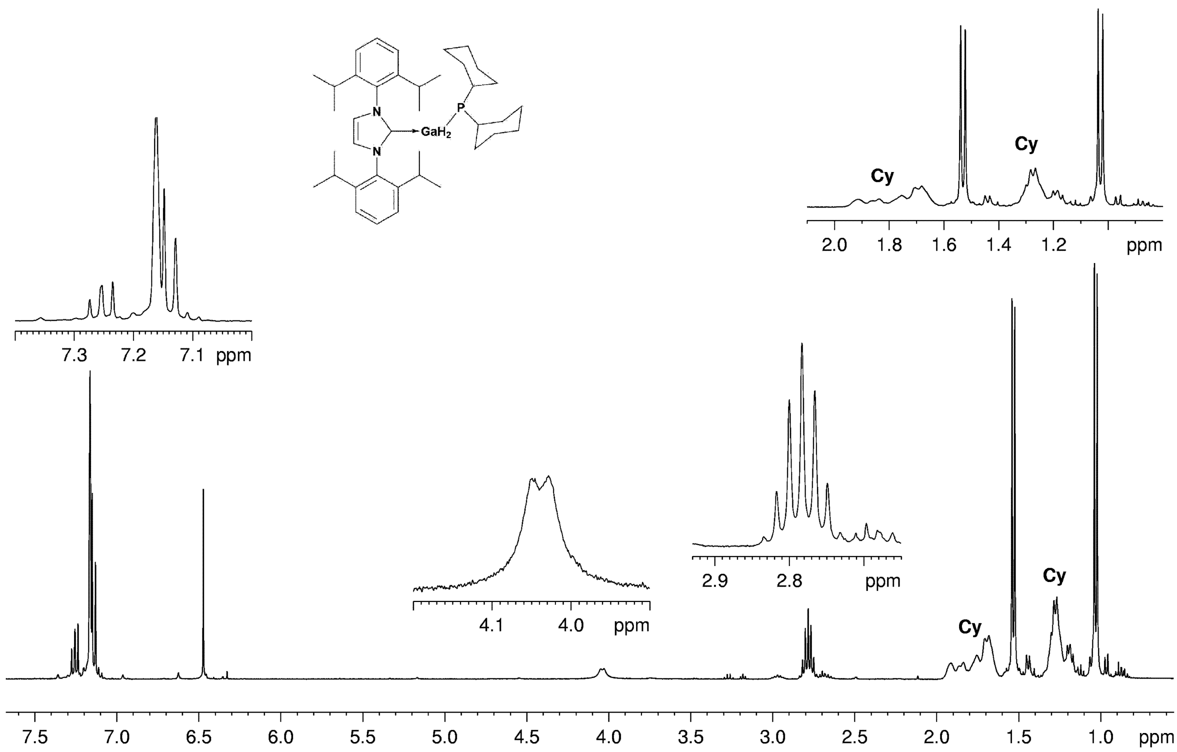


Figure S7: ^1H NMR spectrum of **1** in C_6D_6 at 298 K. Cy = C_6H_{11}.

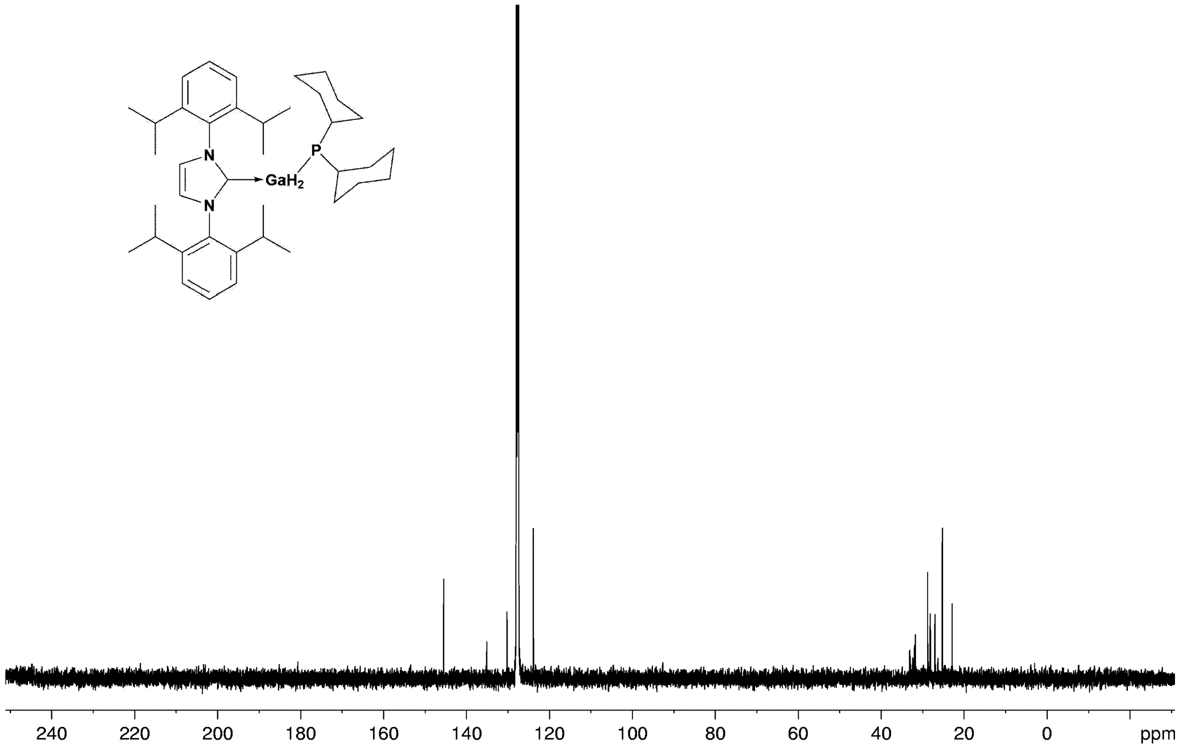


Figure S8: ^{13}C NMR spectrum of **1** in C_6D_6 at 298 K.

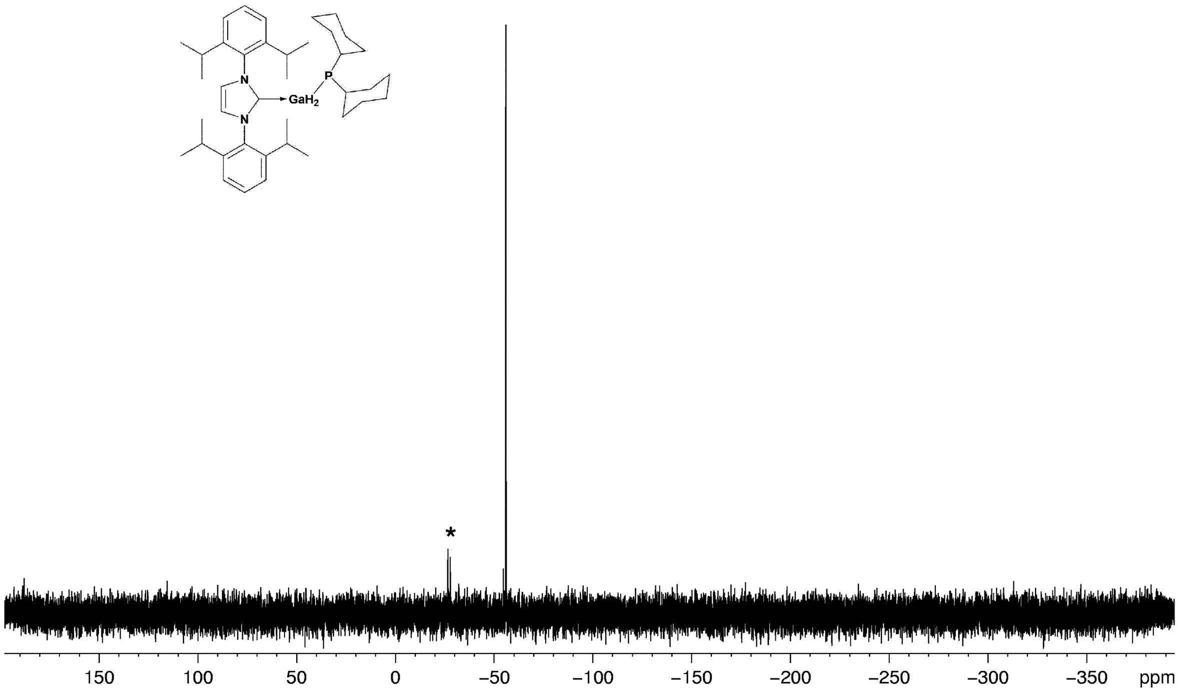


Figure S9: ^{31}P NMR spectrum of **1** in C_6D_6 at 298 K. * = $HPCy_2$.

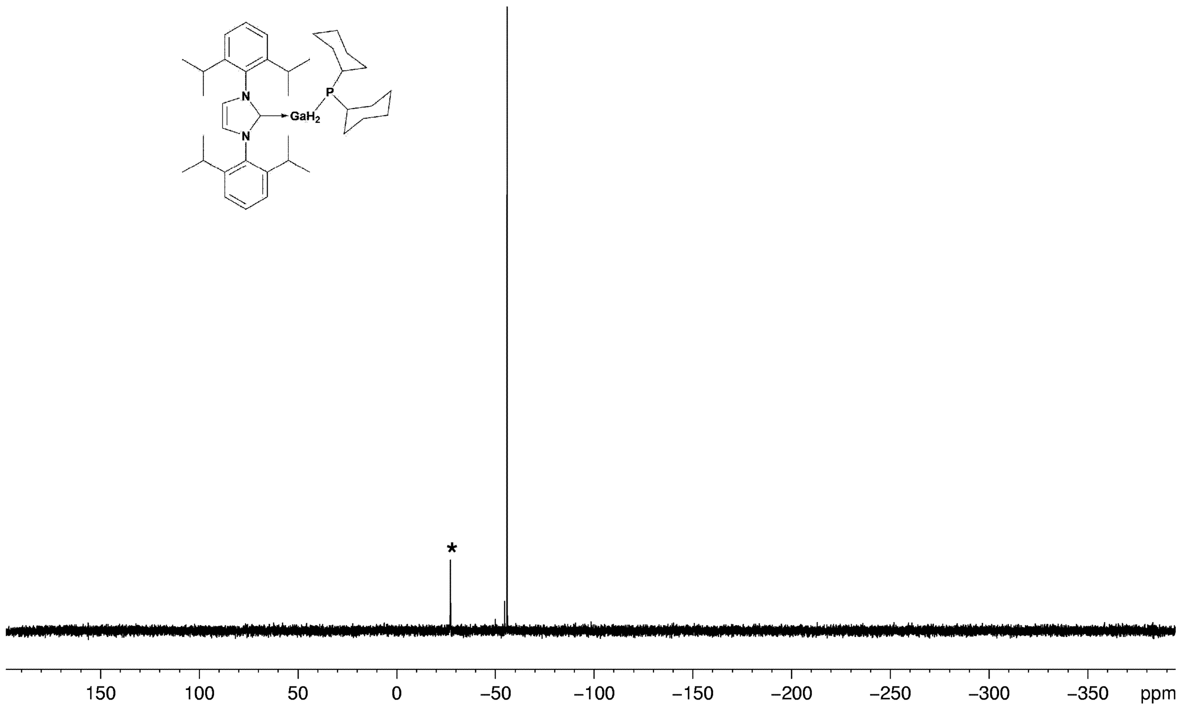


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 298 K. * = $HPCy_2$.

IDipp·AlH_2PCy_2 (2)

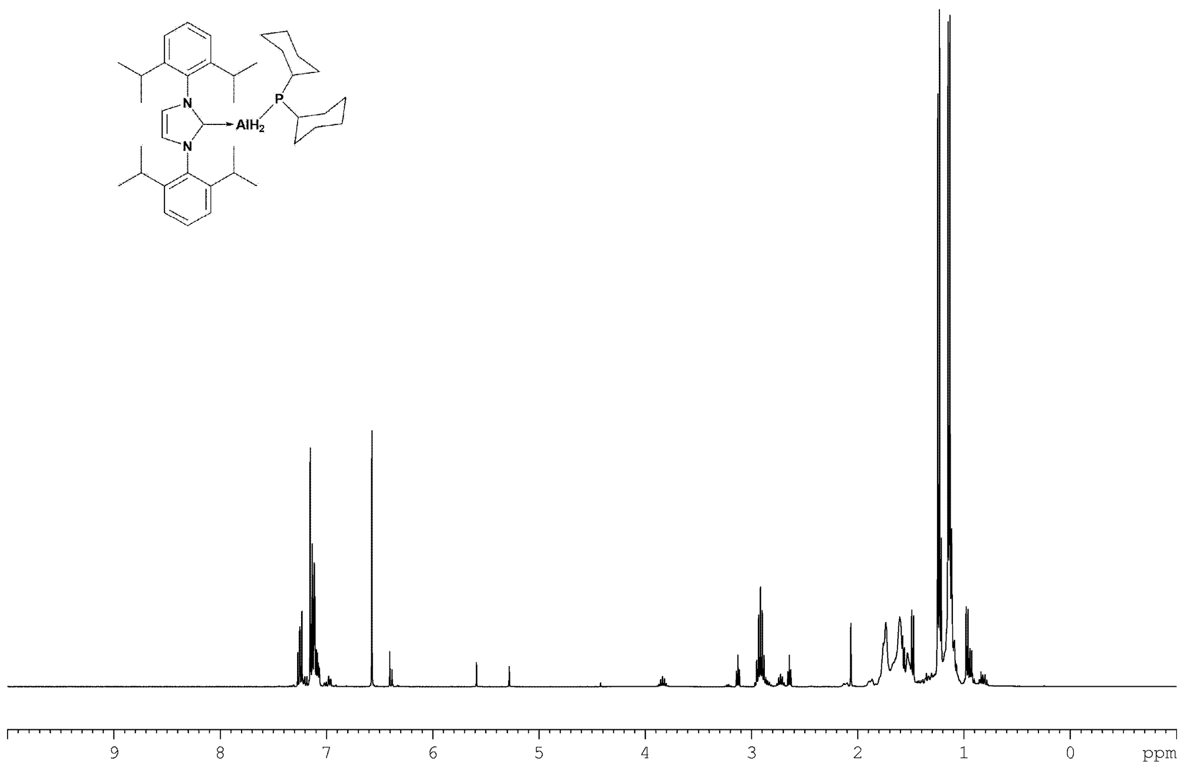


Figure S11: ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K. Impurities could not be separated due to similiarity in solubility.

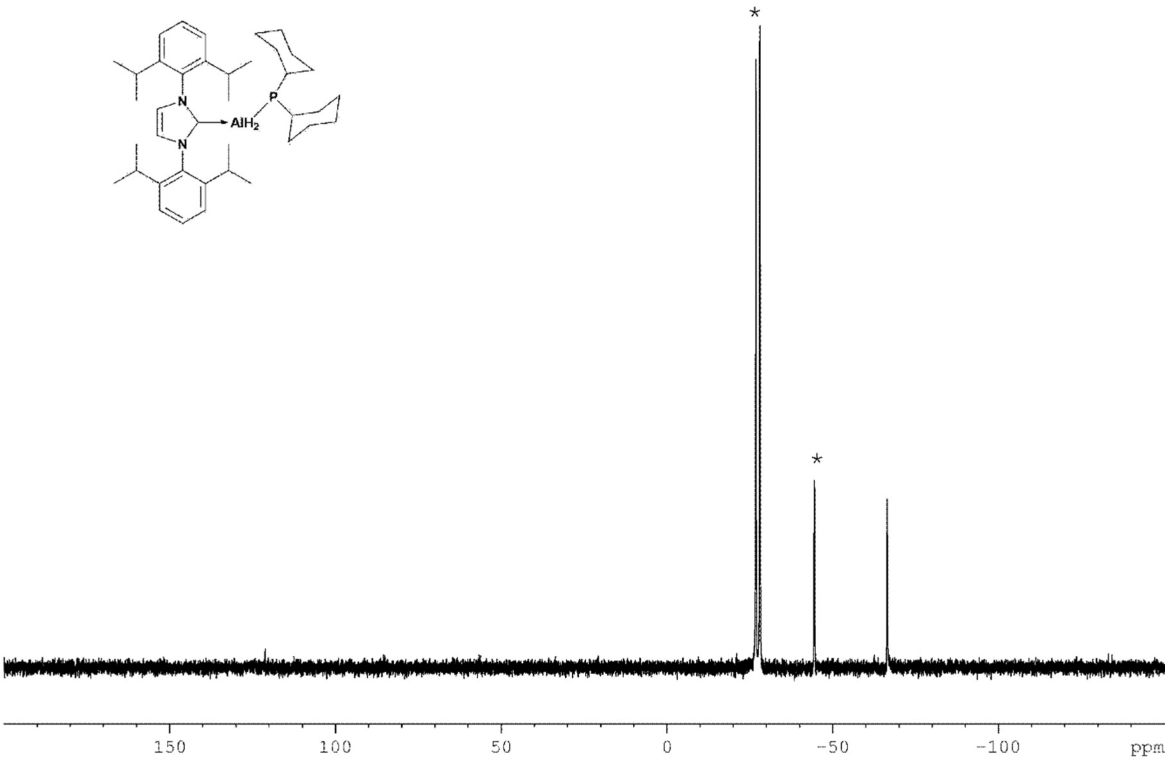


Figure S12: ^{31}P NMR spectrum of **2** in C_6D_6 at 298 K. * = $HPCy_2$ + unidentified impurity.

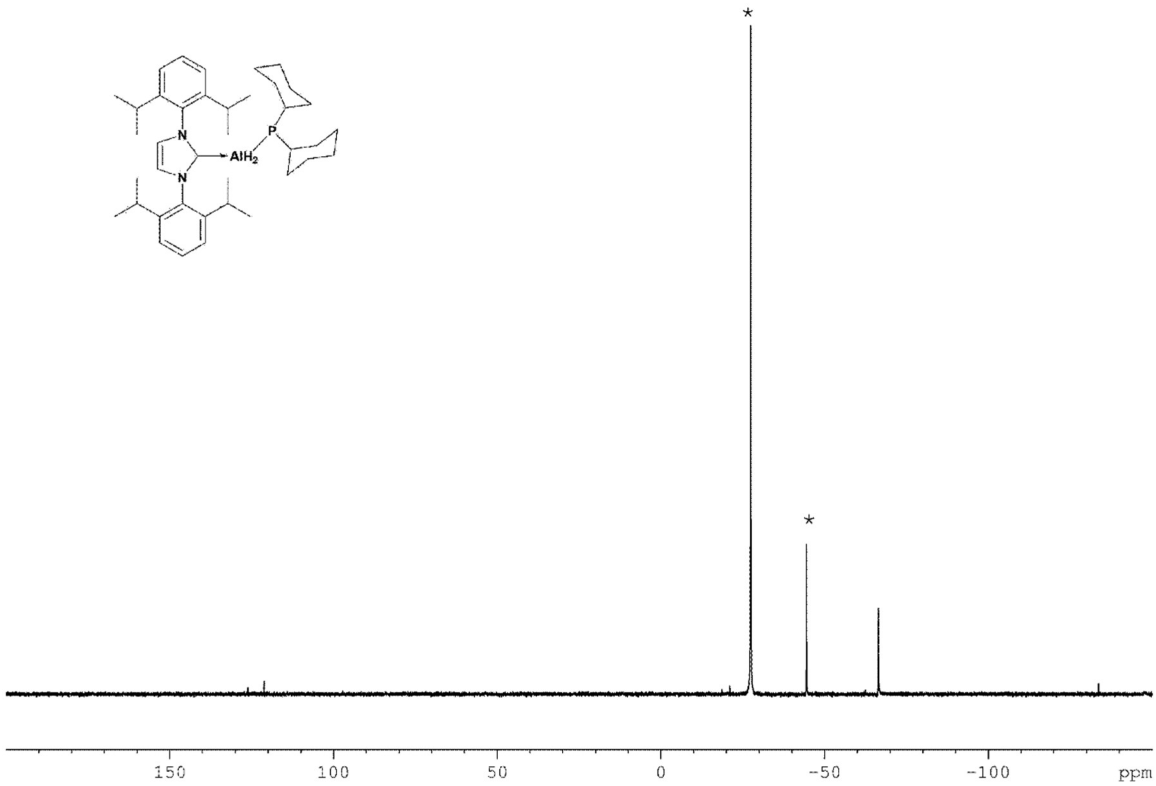


Figure S13: $^{31}P\{^1H\}$ NMR spectrum of **2** in C_6D_6 at 298 K. * = $HPCy_2$ + unidentified impurity.

IDipp·GaH_2PH_2 (3)

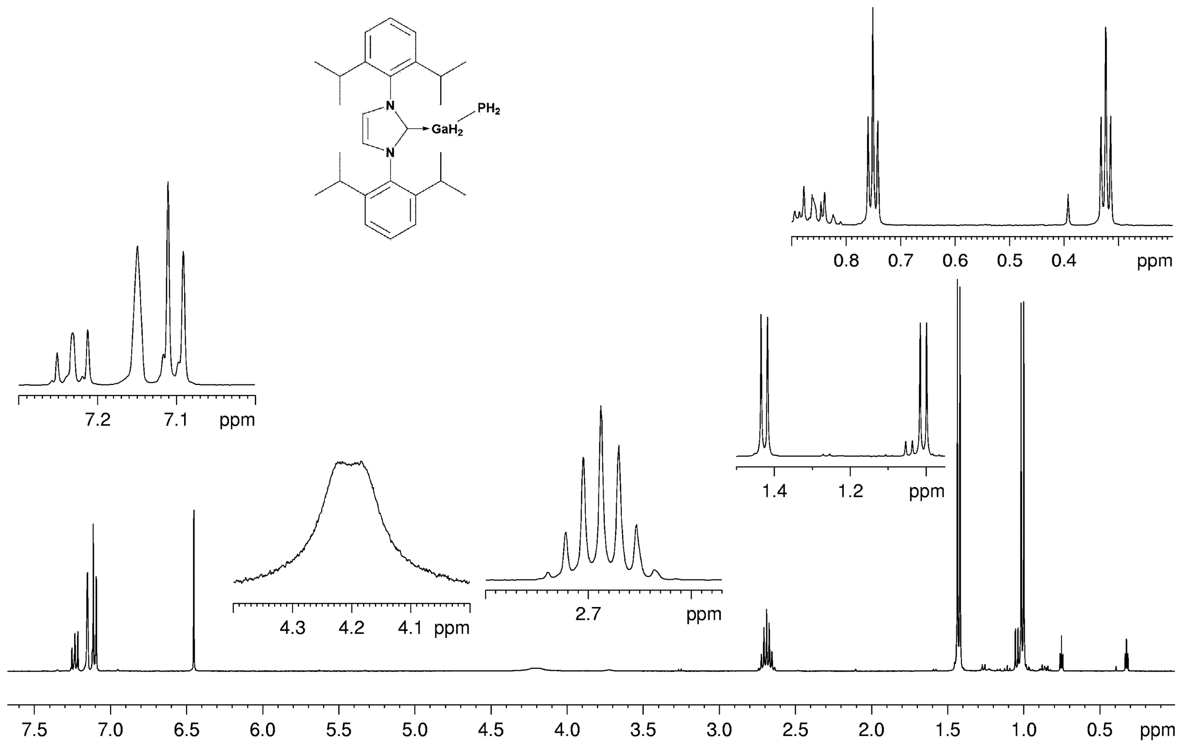


Figure S14: ^{1}H NMR spectrum of **3** in C_6D_6 at 298 K.

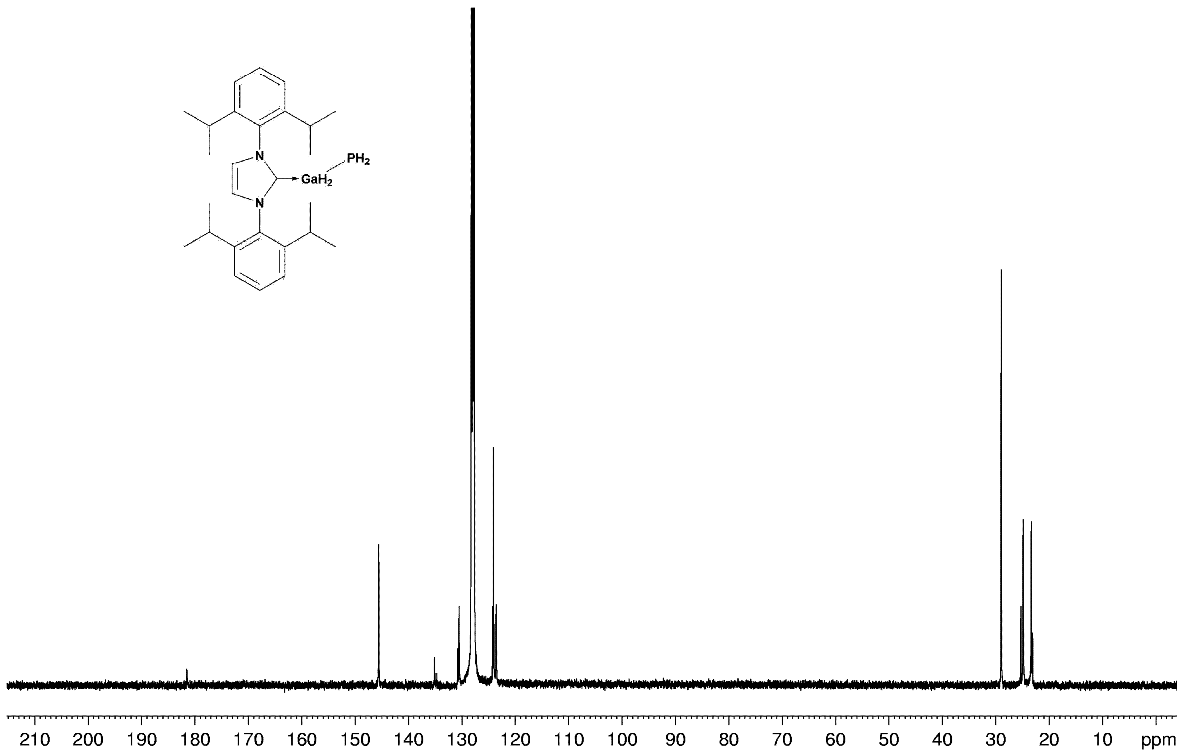


Figure S15: ^{13}C NMR spectrum of **3** in C_6D_6 at 298 K.

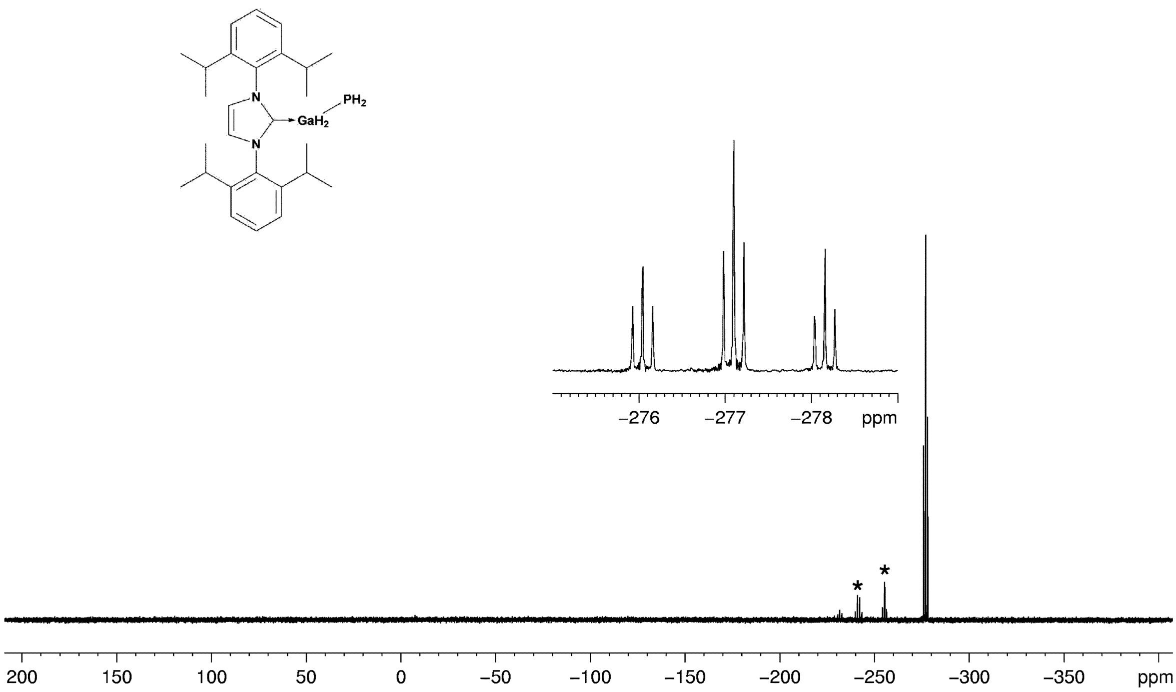


Figure S16: ^{31}P NMR spectrum of **3** in C_6D_6 at 298 K. * = PH_3 and unidentified impurity.

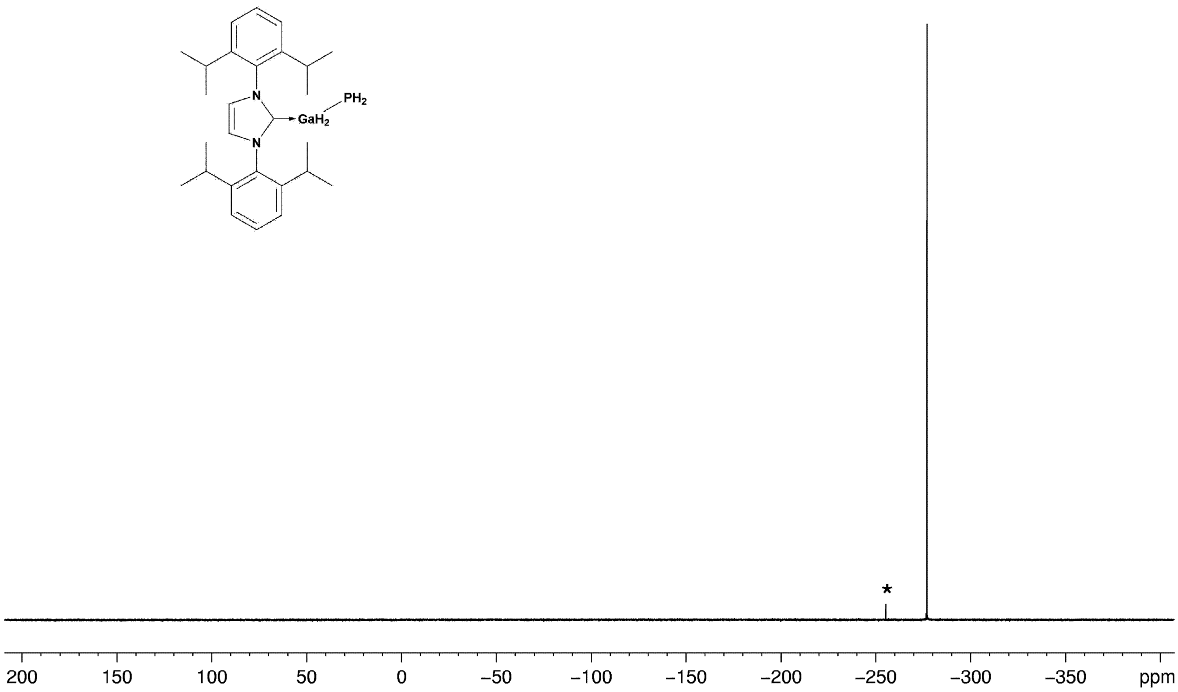


Figure S17: $^{31}P\{^1H\}$ NMR spectrum of **3** in C_6D_6 at 298 K. * = unidentified impurity.

IDipp·AlH_2PH_2 (4)

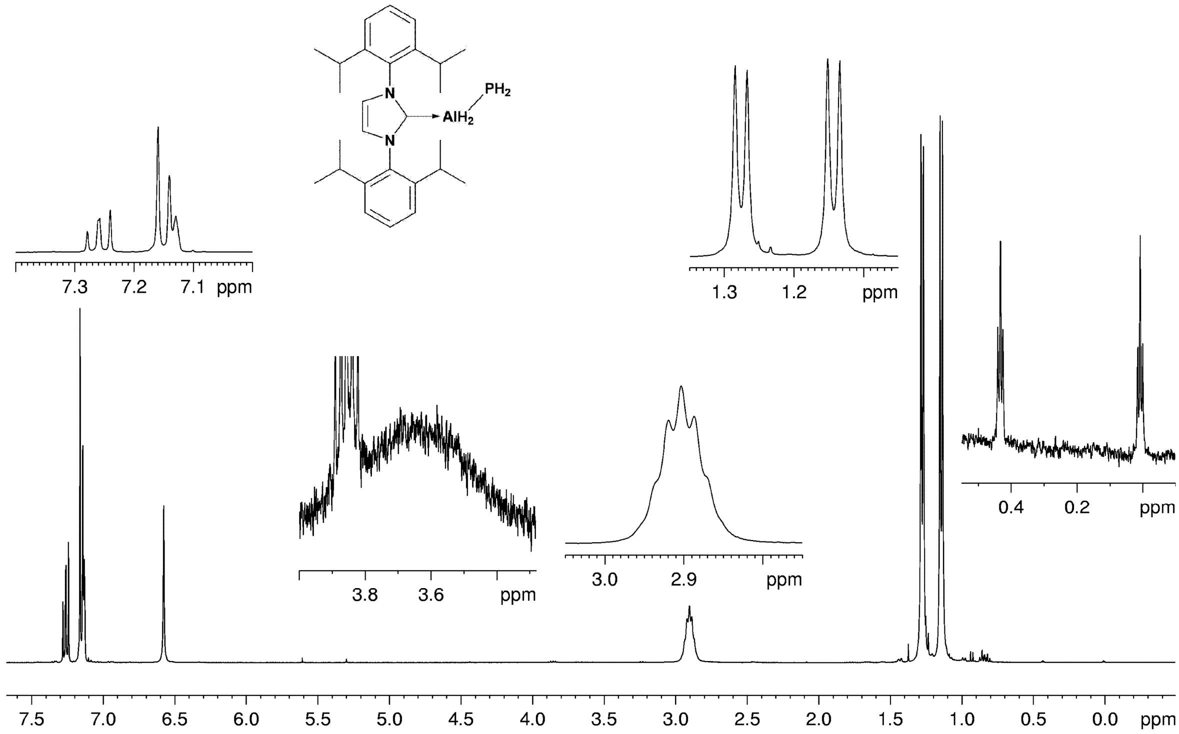


Figure S18: ^{1}H NMR spectrum of **4** in C_6D_6 at 298 K.

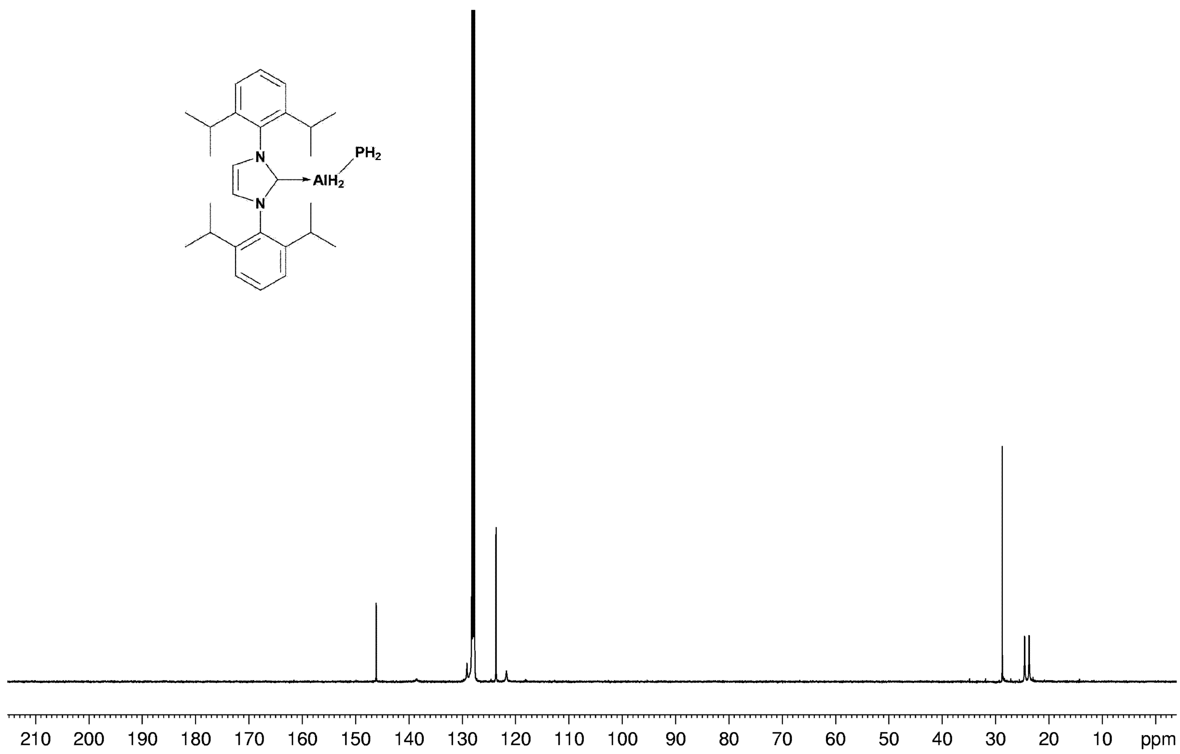


Figure S19: ^{13}C NMR spectrum of **4** in C_6D_6 at 298 K.

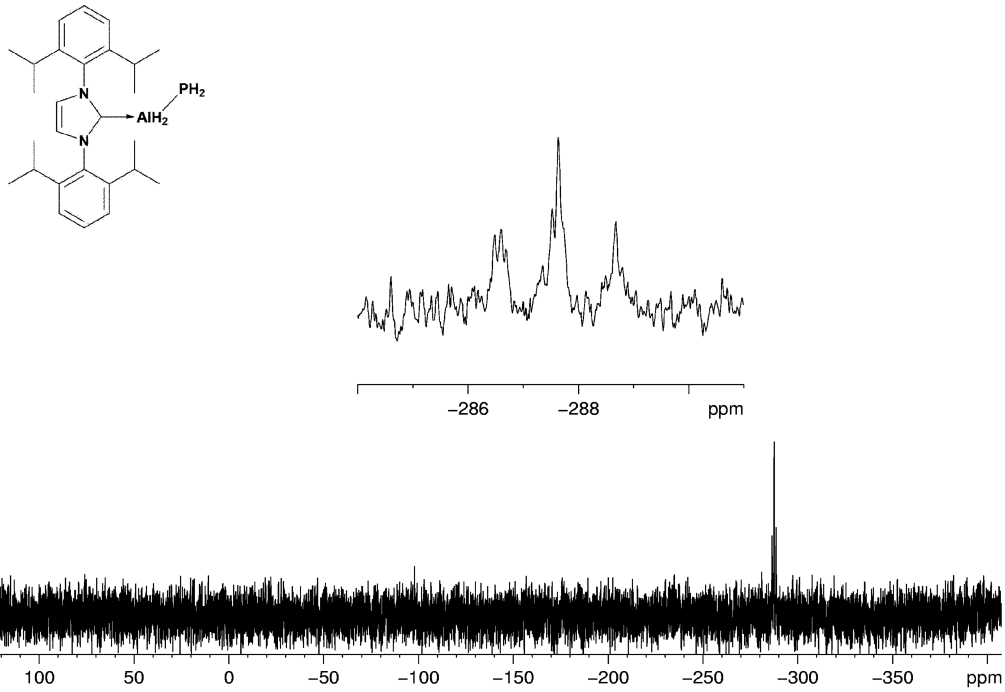


Figure S20: ^{31}P NMR spectrum of **4** in C_6D_6 at 298 K.

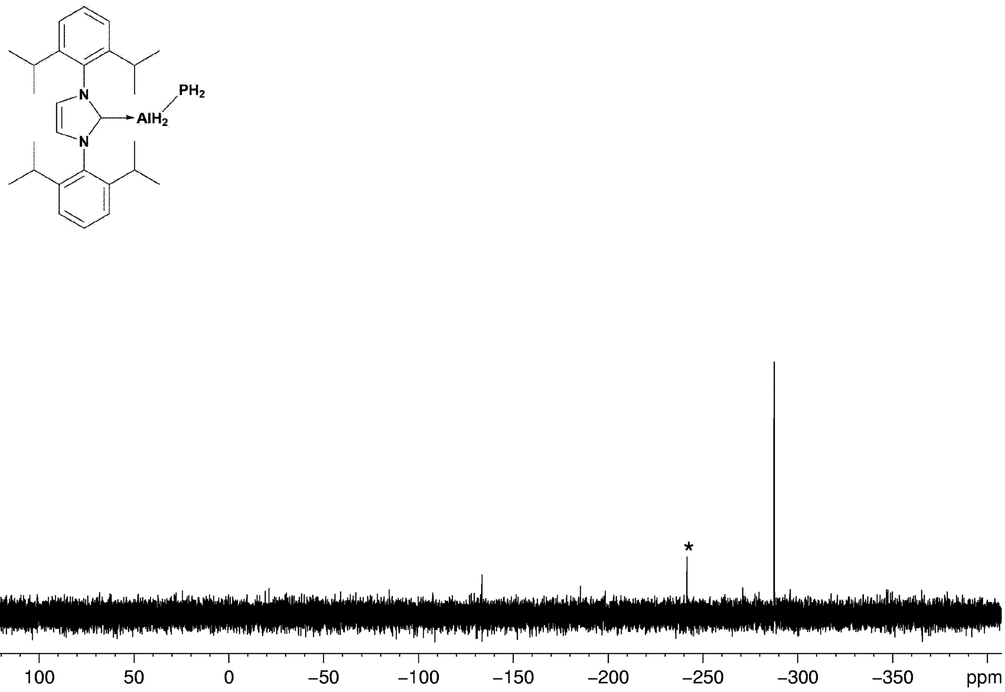


Figure S21: $^{31}P\{^1H\}$ NMR spectrum of **4** in C_6D_6 at 298 K. * = PH_3.

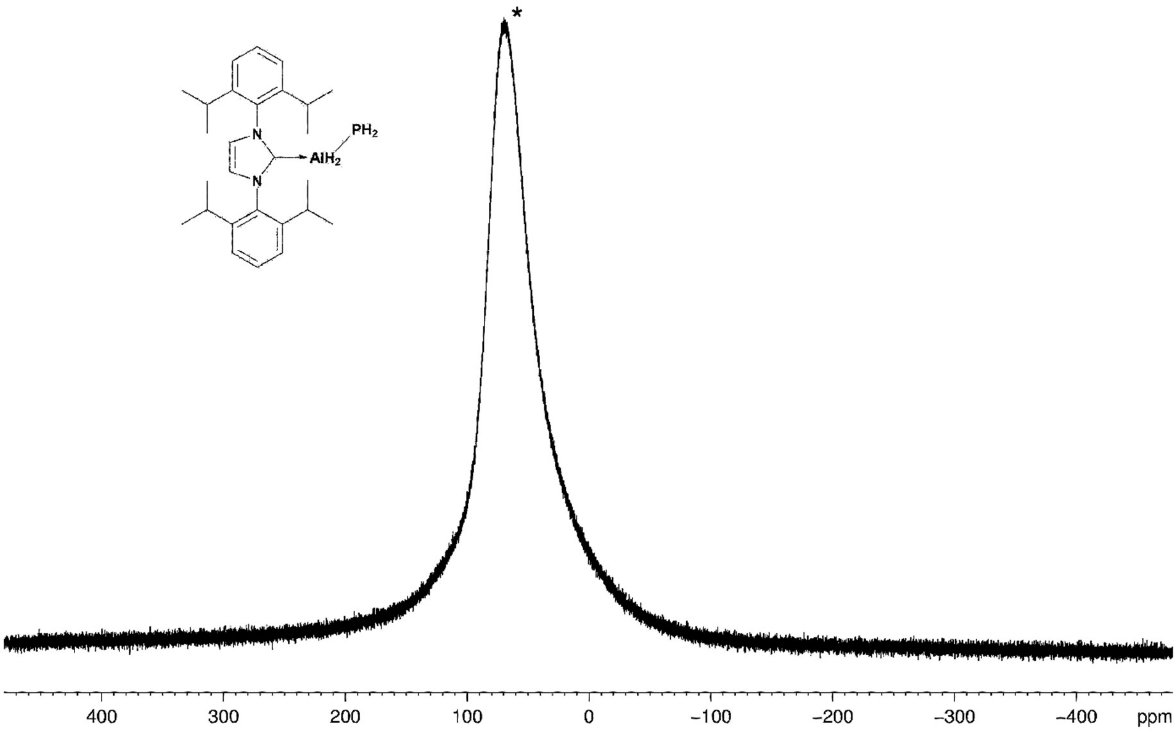


Figure S22: ^{27}Al NMR spectrum of **4** in C_6D_6 at 298 K. * = signal from the NMR tube and the NMR sample head.

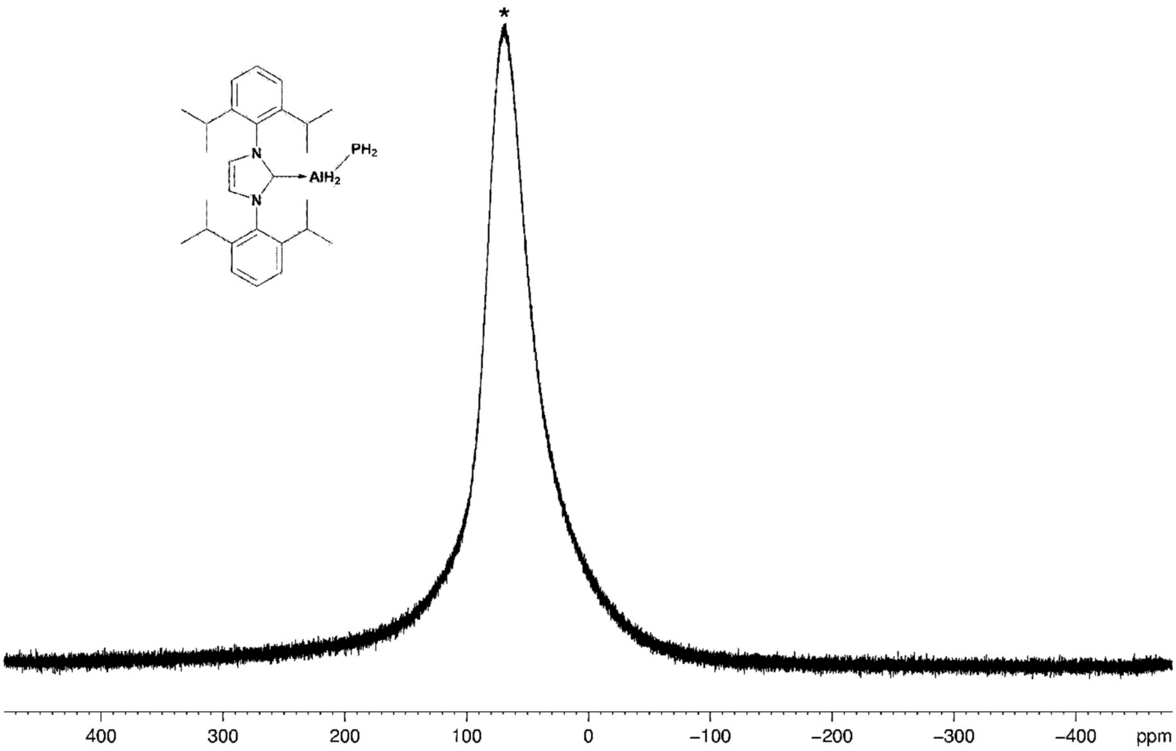


Figure S23: ^{27}Al{^{1}H} NMR spectrum of **4** in C_6D_6 at 298 K. * = signal from the NMR tube and the NMR sample head.

5.5.3. Crystallographic data

Single crystal X-ray structure determination: Single-crystal X-ray diffraction data were collected using Oxford Diffraction diffractometers equipped with a 135 mm Atlas or 165 mm Titan S2 CCD area detector. Crystals were selected under degassed inert oil and mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data were collected using mirror monochromated Cu K_α radiation (λ = 1.5418 Å). Data collected on the Oxford Diffraction Agilent GV1000 or Gemini ultra diffractometer were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro.[3]) Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Absorption correction based on face indexation was applied to the datasets. Structures were subsequently solved using direct methods and refined on F^2 using ShelXL[4] or olex2.refine[5] Hydrogen atoms were included by using a riding model or rigid methyl groups.

Crystallographic data and details of the diffraction experiments are given in Table S1. CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC 1963391-1963393.

Table S1. Crystallographic data and structure refinement of **1**, **3** and **4**.

Compound	**1**	**3**	**4**
Formula	$C_{39}H_{60}GaN_2P$	$C_{27}H_{40}GaN_2P$	$C_{27}H_{39.8}AlN_2P_{0.9}Cl_{0.1}$
$D_{calc.}$ / g · cm^{-3}	1.148	1.180	1.067
μ/mm^{-1}	1.574	2.014	1.302
Formula Weight	657.58	489.27	450.80
Colour	colorless	colorless	colorless
Shape	needle	block	block
Size/mm^3	0.38×0.15×0.13	0.32×0.29×0.19	0.29×0.17×0.16
T/K	123.00	123.00(10)	90.0(3)
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	10.75190(10)	12.3575(2)	19.1703(2)
b/Å	14.75520(10)	15.3905(3)	9.57970(10)
c/Å	23.9953(2)	14.4821(3)	15.3445(2)
α/°	90	90	90
β/°	92.4990(10)	90.479(2)	95.2600(10)
γ/°	90	90	90
V/Å^3	3803.15(5)	2754.23(9)	2806.08(6)
Z	4	4	4
Z'	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	Cu K_α
Θ_{min}/°	3.517	4.192	4.633
Θ_{max}/°	66.367	74.127	74.183
Measured Refl.	26609	13026	15961
Independent Refl.	6680	5290	5500
R_{int}	0.0221	0.0182	0.0262
Parameters	427	305	345
Restraints	0	0	7
Largest Peak	0.474	0.447	0.783
Deepest Hole	-0.409	-0.762	-0.663
GooF	1.040	1.038	1.060
wR_2 (all data)	0.0985	0.0951	0.1780
wR_2	0.0405	0.0942	0.1719
R_1 (all data)	0.0971	0.0351	0.0751
R_1	0.0388	0.0341	0.0684

During the refinement of compound **4** it was possible to show that 10 % of the starting material IDipp·AlH_2Cl crystallized together with IDipp·AlH_2PH_2. Nonetheless it was possible to separate these structures and refine them in different parts. The molecular structure in solid state of the starting material IDipp·AlH_2Cl is shown in Figure S24 and the structure of compound **4** in Figure S25.

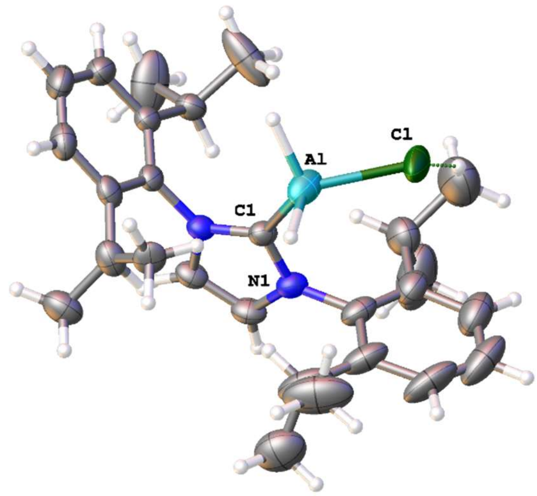


Figure S24: Molecular structure of IDipp·AlH_2Cl in solid state. Chlorine occupation: 10%. Selected bond lenghts [Å]: Al–Cl 2.331(8).

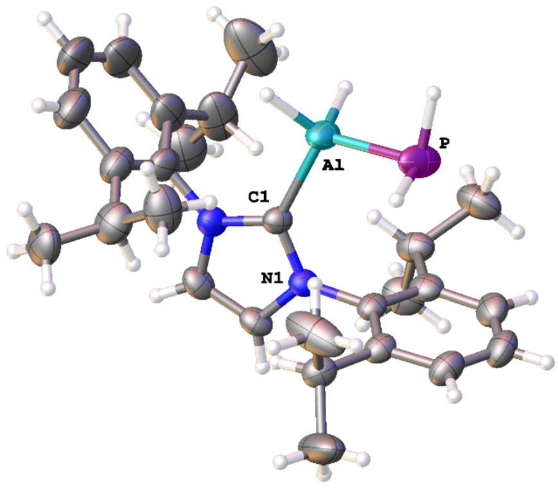


Figure S25: Molecular structure of compound **4** in solid state. Phosphor occupation: 90%. Selected bond lengths [Å]: Al–P 2.3131(10).

5.5.4. Computational data

The geometries of the compounds have been fully optimized with gradient-corrected density functional theory (DFT) in form of Becke's three-parameter hybrid method B3LYP[6] with def2-TZVP all electron basis set (ECP on I).[7] Gaussian 09 program package[8] was used throughout. All structures correspond to minima on their respective potential energy surfaces. Basis sets were obtained from the EMSL basis set exchange database.[9] Data for the standard sublimation enthalpies and entropies of LiCl (215.6 kJ mol^{-1}, 153.6 J mol^{-1} K^{-1}) and LiI (179.1 kJ mol^{-1}, 146.6 J mol^{-1} K^{-1}) were taken from the NIST Chemistry Webbook database.[10]

Thermodynamic characteristic of gas phase reactions

Table S2. Thermodynamic characteristics of gas phase reactions. Standard enthalpies ΔH^o_{298} and standard Gibbs energies ΔG^o_{298} in kJ mol^{-1}, standard entropies ΔS^o_{298} in J mol^{-1} K^{-1}. B3LYP/def2-TZVP level of theory.

	E = Al			E = Ga		
Process	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
$PH_2EH_2 \cdot NMe_3 = PH_2EH_2 + NMe_3$	99.3	157.5	52.3	71.1	154.1	25.2
$PH_2EH_2 \cdot Py = PH_2EH_2 + Py$	103.3	142.8	60.7	71.7	143.0	29.0
$PH_2EH_2 \cdot dmap = PH_2EH_2 + dmap$	121.6	151.0	76.6	86.3	147.6	42.3
$PH_2EH_2 \cdot IDipp = PH_2EH_2 + IDipp$	137.6	195.7	79.2	111.2	185.6	55.9

Table S3. Thermodynamic characteristic of gas phase dissociation reactions IDipp·LA = LA + IDipp. Standard enthalpies ΔH^o_{298} and standard Gibbs energies ΔG^o_{298} in kJ mol^{-1}, standard entropies ΔS^o_{298} in J mol^{-1} K^{-1}. B3LYP/def2-TZVP (ECP on I) level of theory.

LA	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
AlH_2Cl	154.9	182.0	100.6
AlH_2I	153.7	191.3	96.7
AlH_3	148.5	172.6	97.1
AlH_2PH_2	137.6	195.7	79.2
AlH_2PCy_2	118.8	228.6	50.7
GaH_2Cl	134.4	179.0	81.0
GaH_2I	129.2	199.1	69.9
GaH_3	124.7	172.0	73.4
GaH_2PH_2	111.2	191.0	54.3
GaH_2PCy_2	92.2	225.2	25.1

Table S4. Thermodynamic characteristics of reaction of synthesis of $PH_2EH_2{\cdot}IDipp$ (E = Al, Ga). Standard enthalpies ΔH^o_{298} and standard Gibbs energies ΔG^o_{298} in kJ mol^{-1}, standard entropies ΔS^o_{298} in J mol^{-1} K^{-1}. B3LYP/def2-TZVP (ECP on I) level of theory. Data for the sublimation enthalpies and entropies of LiCl and LiI were taken from the NIST Chemistry Webbook database.[10]

Process	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
$IDipp{\cdot}AlH_3 + PH_3 = H_2 + IDipp{\cdot}AlH_2PH_2$	-16.0	-39.0	-4.3
$IDipp{\cdot}GaH_3 + PH_3 = H_2 + IDipp{\cdot}GaH_2PH_2$	-14.6	-36.7	-3.7
$IDipp{\cdot}AlH_3 + PHCy_2 = H_2 + IDipp{\cdot}AlH_2PCy_2$	25.9	-81.1	50.1
$IDipp{\cdot}GaH_3 + PHCy_2 = H_2 + IDipp{\cdot}GaH_2PCy_2$	23.5	-82.3	48.0
$IDipp{\cdot}AlH_2Cl + LiPH_2{\cdot}dme = LiCl(s) + dme + IDipp{\cdot}AlH_2PH_2$	-166.2	-69.0	-145.6
$IDipp{\cdot}GaH_2Cl + LiPH_2{\cdot}dme = LiCl(s) + dme + IDipp{\cdot}GaH_2PH_2$	-197.3	-69.7	-176.5
$IDipp{\cdot}AlH_2I + LiPH_2{\cdot}dme = LiI(s) + dme + IDipp{\cdot}AlH_2PH_2$	-155.6	-53.2	-139.8
$IDipp{\cdot}GaH_2I + LiPH_2{\cdot}dme = LiI(s) + dme + IDipp{\cdot}GaH_2PH_2$	-167.3	-42.7	-154.6
$IDipp{\cdot}AlH_2Cl + LiPCy_2 = LiCl(s) + IDipp{\cdot}AlH_2PCy_2$	-240.2	-219.0	-174.9
$IDipp{\cdot}GaH_2Cl + LiPCy_2 = LiCl(s) + IDipp{\cdot}GaH_2PCy_2$	-275.1	-223.2	-208.5
$IDipp{\cdot}AlH_2I + LiPCy_2 = LiI(s) + IDipp{\cdot}AlH_2PCy_2$	-229.6	-203.2	-169.0
$IDipp{\cdot}GaH_2I + LiPCy_2 = LiI(s) + IDipp{\cdot}GaH_2PCy_2$	-245.1	-196.3	-186.6

Energies $E°_0$, enthalpies $H°_{298}$ and entropies $S°_{298}$

Table S5. Total energies E^o_0, sum of electronic and thermal enthalpies H^o_{298} (Hartree) and standard entropies S^o_{298} (cal mol^{-1}K^{-1}) for studied compounds. B3LYP/def2-TZVP (ECP on I) level of theory.

Compound	E^o_0	H^o_{298}	S^o_{298}
H_2	-1.179649	-1.16627	31.138
LiCl	-467.8319029	-467.826985	50.774
LiI	-305.4051969	-305.40054	55.473
PH_3	-343.176453	-343.148706	52.381
$O(Me)_2$	-155.093713	-155.009066	64.668
$LiPH_2$	-350.10781	-350.087165	59.771
$LiPH_2{\cdot}O(Me)_2$	-505.2330773	-505.124911	98.419
$PHCy_2$	-812.7009479	-812.356831	117.689
$LiPCy_2$	-819.6168422	-819.279853	124.856
IDipp	-1160.453853	-1159.85478	201.948
AlH_3	-244.2325301	-244.2099660	49.526
AlH_2Cl	-703.944988	-703.926017	60.491
AlH_2I	-541.5087228	-541.490169	65.3
GaH_3	-1926.67782	-1926.655147	52.151
GaH_2Cl	-2386.376396	-2386.357529	63.253

GaH_2I	-2223.94912	-2223.93061	68.0
PH_2AlH_2	-586.2384263	-586.2026590	66.957
PCy_2AlH_2	-1055.754512	-1055.401986	130.076
PH_2GaH_2	-2268.684182	-2268.648265	69.163
PCy_2GaH_2	-2738.201612	-2737.849148	131.746
AlH_3·IDipp	-1404.746619	-1404.121324	210.216
AlH_2Cl·IDipp	-1864.461387	-1863.8398	218.93
AlH_2I·IDipp	-1702.024825	-1701.403479	221.527
GaH_3·IDipp	-3087.182738	-3086.557418	212.98
GaH_2Cl·IDipp	-3546.884942	-3546.263502	222.427
GaH_2I·IDipp	-3384.456059	-3383.834604	222.352
PH_2AlH_2·IDipp	-1746.74819	-1746.109847	222.13
PCy_2AlH_2·IDipp	-2216.257003	-2215.302019	277.391
PH_2GaH_2·IDipp	-3429.183794	-3428.545409	225.462
PCy_2GaH_2·IDipp	-3898.693956	-3897.739047	279.866

Optimized xyz coordinates

Table S6. Optimized xyz coordinates (in Angstroms) for studied compounds. B3LYP/def2-TZVP (ECP on I) level of theory.

H_2

1	0.000000000	0.000000000	0.371966000
1	0.000000000	0.000000000	-0.371966000

LiCl

17	0.000000000	0.000000000	0.302587000
3	0.000000000	0.000000000	-1.714658000

LiI

3	0.000000000	0.000000000	-2.265714000
53	0.000000000	0.000000000	0.128248000

PH_3

15	0.000000000	0.128213000	0.000000000
1	0.596216000	-0.641128000	-1.032219000
1	0.596216000	-0.641128000	1.032219000
1	-1.192431000	-0.640945000	0.000000000

$O(Me)_2$

8	-0.000004000	-0.586376000	0.000000000
6	-0.000004000	0.194424000	1.173971000
1	0.000060000	-0.490171000	2.021207000
1	0.890713000	0.834575000	1.231802000
1	-0.890734000	0.834560000	1.231899000
6	-0.000004000	0.194424000	-1.173971000
1	-0.890734000	0.834560000	-1.231899000
1	0.890713000	0.834575000	-1.231802000
1	0.000060000	-0.490171000	-2.021207000

$LiPH_2$

3	0.098141000	1.988924000	0.000000000
15	0.098141000	-0.343354000	0.000000000
1	-0.883269000	-0.408232000	1.033135000
1	-0.883269000	-0.408232000	-1.033135000

$LiPH_2$·$O(Me)_2$

8	-1.361679000	-0.034892000	-0.000023000
6	-2.269241000	-1.136838000	-0.000035000
1	-1.677560000	-2.050310000	-0.000097000

1	-2.899180000	-1.111388000	0.893221000
1	-2.899249000	-1.111313000	-0.893239000
6	-2.017708000	1.234934000	0.000050000
1	-2.638477000	1.341781000	-0.893457000
1	-2.638420000	1.341709000	0.893605000
1	-1.246223000	2.002521000	0.000059000
3	0.518845000	-0.169967000	-0.000077000
15	2.862329000	0.100741000	0.000260000
1	3.061483000	-0.864058000	1.032159000
1	3.061280000	-0.859595000	-1.035827000

$PHCy_2$

15	-0.010020000	-1.376002000	-0.136654000
6	-1.847809000	0.541079000	-1.068820000
1	-2.058471000	-0.184871000	-1.863029000
1	-1.018101000	1.157075000	-1.426190000
6	-1.443247000	-0.217621000	0.205479000
1	-1.150767000	0.512639000	0.966344000
6	1.481251000	-0.247901000	-0.287198000
1	1.296717000	0.343859000	-1.193057000
6	-2.633155000	-1.023309000	0.754346000
1	-2.884707000	-1.821699000	0.046511000
1	-2.352502000	-1.515617000	1.689422000
6	1.727264000	0.717027000	0.880979000
1	1.838146000	0.133753000	1.802622000
1	0.864285000	1.369462000	1.029820000
6	2.730141000	-1.110101000	-0.548724000
1	2.563582000	-1.755131000	-1.414770000
1	2.891176000	-1.776495000	0.307415000
6	-3.866111000	-0.140355000	0.978368000
1	-4.701212000	-0.752780000	1.329524000
1	-3.653019000	0.581048000	1.775645000
6	-3.082973000	1.421654000	-0.846821000
1	-2.832985000	2.224103000	-0.143139000
1	-3.364006000	1.908499000	-1.784775000
6	-4.259682000	0.614923000	-0.293267000
1	-5.110193000	1.272733000	-0.095181000
1	-4.592167000	-0.104096000	-1.050945000
6	4.218604000	0.706974000	0.408249000
1	4.452677000	0.129578000	1.310301000
1	5.088939000	1.338287000	0.209887000
6	2.983938000	1.571849000	0.670308000
1	2.824755000	2.241620000	-0.182816000
1	3.146444000	2.212872000	1.541336000
6	3.984823000	-0.254856000	-0.758633000
1	4.855385000	-0.901878000	-0.897353000
1	3.875199000	0.320786000	-1.685084000
1	0.212870000	-1.769890000	1.211734000

$LiPCy_2$

15	-0.012697000	-1.304196000	-0.377222000
6	-1.824585000	0.834193000	-0.910851000
1	-2.010791000	0.317327000	-1.858969000
1	-0.972814000	1.495998000	-1.086479000
6	-1.465334000	-0.215399000	0.156134000
1	-1.206154000	0.317117000	1.078308000
6	1.471899000	-0.140759000	-0.306798000
1	1.252070000	0.668185000	-1.015629000
6	-2.690538000	-1.092295000	0.455793000
1	-2.915040000	-1.704919000	-0.425851000
1	-2.457412000	-1.791730000	1.267844000
6	1.782720000	0.507127000	1.050763000
1	1.967371000	-0.289845000	1.782998000

1	0.915620000	1.062279000	1.416113000
6	2.716519000	-0.869211000	-0.836211000
1	2.506960000	-1.292232000	-1.821659000
1	2.941938000	-1.719366000	-0.176167000
6	-3.930889000	-0.273924000	0.832541000
1	-4.785580000	-0.939388000	0.988771000
1	-3.751495000	0.231188000	1.789043000
6	-3.055244000	1.665089000	-0.527267000
1	-2.826750000	2.267543000	0.360050000
1	-3.293209000	2.371771000	-1.327968000
6	-4.263475000	0.773894000	-0.232718000
1	-5.117367000	1.379133000	0.085335000
1	-4.568149000	0.265256000	-1.154956000
6	4.236677000	0.704889000	0.448825000
1	4.541768000	-0.065058000	1.168347000
1	5.080118000	1.395622000	0.359680000
6	3.003977000	1.434281000	0.988780000
1	2.776266000	2.287437000	0.339013000
1	3.212909000	1.848536000	1.979919000
6	3.946386000	0.043682000	-0.901037000
1	4.818331000	-0.524529000	-1.239175000
1	3.773413000	0.822018000	-1.653187000
3	0.246595000	-3.022938000	1.165076000

IDipp

6	0.674960000	-0.000061000	1.853488000
6	-0.674915000	0.000151000	1.853504000
7	-1.062430000	0.000181000	0.517812000
6	-0.000003000	-0.000008000	-0.342280000
7	1.062444000	-0.000158000	0.517787000
1	1.379343000	-0.000152000	2.666568000
1	-1.379279000	0.000280000	2.666601000
6	2.435809000	-0.000373000	0.090009000
6	3.085267000	1.227701000	-0.111259000
6	3.084594000	-1.228644000	-0.112192000
6	4.416080000	1.199376000	-0.527433000
6	4.415415000	-1.200728000	-0.528378000
6	5.077373000	-0.000779000	-0.734658000
1	4.940696000	2.131057000	-0.697180000
1	4.939506000	-2.132569000	-0.698867000
6	-2.435805000	0.000376000	0.090067000
6	-3.084599000	1.228638000	-0.112164000
6	-4.415430000	1.200704000	-0.528315000
6	-5.077391000	0.000746000	-0.734534000
1	-4.939527000	2.132537000	-0.698825000
6	-4.416091000	-1.199400000	-0.527282000
1	-4.940708000	-2.131088000	-0.696980000
6	-3.085267000	-1.227707000	-0.111139000
6	-2.379919000	2.563741000	0.074073000
1	-1.393576000	2.364550000	0.491176000
6	-3.116585000	3.476910000	1.064890000
6	-2.165994000	3.265466000	-1.276204000
1	-1.598665000	2.631072000	-1.957893000
1	-3.118903000	3.508866000	-1.751899000
1	-1.614358000	4.198245000	-1.137505000
1	-4.107294000	3.755953000	0.700388000
1	-2.551805000	4.398959000	1.219408000
1	-3.243448000	2.991921000	2.034677000
6	-2.381271000	-2.563037000	0.076099000
1	-1.394748000	-2.364031000	0.492864000
6	-3.118247000	-3.474983000	1.067808000
6	-2.167978000	-3.266026000	-1.273622000

1	-3.121111000	-3.509351000	-1.748906000
1	-1.600472000	-2.632523000	-1.955991000
1	-1.616794000	-4.198969000	-1.134232000
1	-3.244707000	-2.989116000	2.037209000
1	-2.553925000	-4.397197000	1.223016000
1	-4.109161000	-3.753816000	0.703698000
6	2.381278000	2.563038000	0.075947000
1	1.394759000	2.364048000	0.492731000
6	3.118270000	3.475011000	1.067620000
6	2.167970000	3.265989000	-1.273791000
1	3.121097000	3.509298000	-1.749094000
1	1.600454000	2.632467000	-1.956135000
1	1.616789000	4.198937000	-1.134421000
1	3.244740000	2.989172000	2.037034000
1	2.553955000	4.397232000	1.222809000
1	4.109181000	3.753828000	0.703489000
6	2.379915000	-2.563739000	0.074108000
1	1.393589000	-2.364532000	0.491243000
6	2.165939000	-3.265500000	-1.276141000
6	3.116612000	-3.476885000	1.064923000
1	4.107306000	-3.755945000	0.700393000
1	3.243515000	-2.991870000	2.034692000
1	2.551832000	-4.398925000	1.219489000
1	1.598586000	-2.631124000	-1.957827000
1	1.614307000	-4.198275000	-1.137397000
1	3.118831000	-3.508913000	-1.751864000
1	-6.110357000	0.000889000	-1.060192000
1	6.110332000	-0.000936000	-1.060341000

AlH_3

13	0.000000000	0.000000000	0.000000000
1	1.580663248	0.000000000	0.000000000
1	-0.790331624	-1.368894528	0.000000000
1	-0.790331624	1.368894528	0.000000000

AlH_2Cl

13	0.000000000	0.000000000	-1.073844000
17	0.000000000	0.000000000	1.033101000
1	0.000000000	1.390942000	-1.801370000
1	0.000000000	-1.390942000	-1.801370000

AlH_2I

13	0.000000000	0.000000000	-1.918240000
53	0.000000000	0.000000000	0.570668000
1	0.000000000	1.387961000	-2.654137000
1	0.000000000	-1.387961000	-2.654137000

GaH_3

31	0.000000000	0.000000000	0.000000000
1	0.000000000	1.569739000	0.000000000
1	1.359434000	-0.784869000	0.000000000
1	-1.359434000	-0.784869000	0.000000000

GaH_2Cl

31	0.000000000	0.000000000	0.710580000
17	0.000000000	0.000000000	-1.457015000
1	0.000000000	1.410467000	1.370630000
1	0.000000000	-1.410467000	1.370630000

GaH_2I

31	0.000000000	0.000000000	-1.534049000
53	0.000000000	0.000000000	0.980918000
1	0.000000000	1.402381000	-2.216556000
1	0.000000000	-1.402381000	-2.216556000

PH_2AlH_2

15	-0.054631000	-1.134013000	0.000000000
13	-0.054631000	1.198766000	0.000000000
1	-0.125112000	1.976055000	1.374729000
1	-0.125112000	1.976055000	-1.374729000
1	0.889940000	-1.262936000	-1.050026000
1	0.889940000	-1.262936000	1.050026000

PCy_2AlH_2

13	-0.329606000	2.888189000	0.448073000
15	0.041121000	0.896760000	-0.658222000
6	1.769381000	-1.338164000	-0.580495000
1	1.885872000	-1.178096000	-1.658481000
1	0.901329000	-1.989255000	-0.455154000
6	1.528946000	0.019536000	0.100106000
1	1.341434000	-0.162611000	1.162879000
6	-1.431889000	-0.236450000	-0.375762000
1	-1.167787000	-1.158459000	-0.907239000
6	2.780649000	0.904320000	-0.021186000
1	2.939800000	1.151820000	-1.076774000
1	2.629642000	1.852797000	0.499178000
6	-1.735499000	-0.605464000	1.084179000
1	-1.975632000	0.310795000	1.636958000
1	-0.853364000	-1.036226000	1.563546000
6	-2.686281000	0.331566000	-1.061008000
1	-2.471338000	0.550056000	-2.109724000
1	-2.958243000	1.283621000	-0.592739000
6	4.030112000	0.204818000	0.527859000
1	4.902448000	0.849014000	0.388452000
1	3.919039000	0.062810000	1.609057000
6	3.016814000	-2.039290000	-0.029133000
1	2.849913000	-2.299335000	1.022655000
1	3.174401000	-2.982438000	-0.559617000
6	4.258770000	-1.152957000	-0.139001000
1	5.122749000	-1.653341000	0.306507000
1	4.499417000	-0.999204000	-1.197239000
6	-4.163301000	-1.024438000	0.496294000
1	-4.512822000	-0.140310000	1.041804000
1	-4.975621000	-1.755028000	0.536303000
6	-2.915860000	-1.579537000	1.188394000
1	-2.637794000	-2.533517000	0.725691000
1	-3.128138000	-1.795587000	2.239214000
6	-3.870965000	-0.636594000	-0.955608000
1	-4.756702000	-0.187496000	-1.413024000
1	-3.647963000	-1.540943000	-1.533389000
1	0.891317000	3.765661000	0.944976000
1	-1.789156000	3.503314000	0.466700000

PH_2GaH_2

15	0.034728000	1.560946000	0.000000000
31	0.034728000	-0.766591000	0.000000000
1	0.106972000	-1.535194000	1.367744000
1	0.106972000	-1.535194000	-1.367744000
1	-0.905705000	1.710262000	-1.049424000
1	-0.905705000	1.710262000	1.049424000

PCy_2GaH_2

31	0.372917000	2.494831000	-0.248638000
15	-0.073804000	0.489277000	0.801198000
6	-1.850451000	-1.688129000	0.486374000
1	-1.963785000	-1.639886000	1.575541000
1	-0.998997000	-2.343857000	0.291541000
6	-1.577689000	-0.272029000	-0.048437000
1	-1.393812000	-0.344874000	-1.124812000
6	1.360322000	-0.660247000	0.406729000

1	1.053658000	-1.619740000	0.840459000
6	-2.810093000	0.621764000	0.167814000
1	-2.967058000	0.756132000	1.244042000
1	-2.636173000	1.617215000	-0.246178000
6	1.661750000	-0.893312000	-1.081807000
1	1.936765000	0.063611000	-1.541838000
1	0.768666000	-1.244462000	-1.603999000
6	2.628450000	-0.216095000	1.154452000
1	2.411324000	-0.100819000	2.219097000
1	2.941212000	0.768844000	0.791692000
6	-4.072231000	0.014406000	-0.455454000
1	-4.930421000	0.660274000	-0.250938000
1	-3.959104000	-0.015089000	-1.545306000
6	-3.112775000	-2.298198000	-0.134649000
1	-2.947698000	-2.452523000	-1.207256000
1	-3.293094000	-3.287275000	0.295606000
6	-4.335492000	-1.400644000	0.063807000
1	-5.207662000	-1.832342000	-0.434475000
1	-4.578442000	-1.353504000	1.131628000
6	4.067830000	-1.459387000	-0.528124000
1	4.456071000	-0.537505000	-0.976582000
1	4.852857000	-2.212251000	-0.638779000
6	2.807952000	-1.892797000	-1.280800000
1	2.491860000	-2.879347000	-0.922123000
1	3.021551000	-2.005599000	-2.347390000
6	3.775862000	-1.213656000	0.954595000
1	4.673776000	-0.850637000	1.461979000
1	3.511671000	-2.164157000	1.432535000
1	-0.800056000	3.428394000	-0.730437000
1	1.842918000	3.060439000	-0.251215000

AlH_3·IDipp

6	0.675268000	0.032290000	-1.892198000
6	-0.675275000	0.032235000	-1.892194000
7	-1.072351000	0.021606000	-0.566906000
6	0.000006000	0.015139000	0.266599000
7	1.072354000	0.021707000	-0.566920000
1	1.382577000	0.038199000	-2.701403000
1	-1.382586000	0.038109000	-2.701396000
6	2.462893000	0.006893000	-0.168347000
6	3.100877000	-1.231622000	-0.003511000
6	3.127676000	1.231397000	-0.002848000
6	4.452571000	-1.214743000	0.339108000
6	4.478501000	1.186190000	0.336457000
6	5.135837000	-0.021631000	0.506977000
1	4.975801000	-2.151417000	0.479190000
1	5.021392000	2.111465000	0.477749000
6	-2.462895000	0.006876000	-0.168357000
6	-3.100901000	-1.231607000	-0.003291000
6	-4.452598000	-1.214649000	0.339287000
6	-5.135866000	-0.021494000	0.506874000
1	-4.975843000	-2.151290000	0.479546000
6	-4.478523000	1.186281000	0.336103000
1	-5.021407000	2.111595000	0.477174000
6	-3.127674000	1.231411000	-0.003143000
6	-2.392000000	-2.563743000	-0.199905000
1	-1.331939000	-2.364326000	-0.356201000
6	-2.912065000	-3.286912000	-1.453344000
6	-2.495291000	-3.462812000	1.040795000
1	-2.087284000	-2.964871000	1.920214000
1	-3.529238000	-3.744738000	1.249933000
1	-1.929301000	-4.383153000	0.881243000

1	-3.969955000	-3.539468000	-1.354452000
1	-2.360893000	-4.216348000	-1.612087000
1	-2.800547000	-2.670744000	-2.347900000
6	-2.440979000	2.576750000	-0.183990000
1	-1.376797000	2.395624000	-0.336010000
6	-2.964192000	3.305933000	-1.432238000
6	-2.567595000	3.459230000	1.066868000
1	-3.604812000	3.744863000	1.254041000
1	-2.191733000	2.940148000	1.948481000
1	-1.992936000	4.378679000	0.934710000
1	-2.833814000	2.703994000	-2.333889000
1	-2.429981000	4.247928000	-1.574333000
1	-4.027511000	3.536683000	-1.338547000
6	2.391969000	-2.563722000	-0.200356000
1	1.331937000	-2.364256000	-0.356808000
6	2.912191000	-3.286826000	-1.453760000
6	2.495038000	-3.462865000	1.040315000
1	3.528957000	-3.744754000	1.249637000
1	2.086837000	-2.964981000	1.919677000
1	1.929121000	-4.383224000	0.880600000
1	2.800899000	-2.670567000	-2.348282000
1	2.360951000	-4.216189000	-1.612684000
1	3.970033000	-3.539515000	-1.354709000
6	2.440996000	2.576758000	-0.183598000
1	1.376729000	2.395665000	-0.335053000
6	2.568249000	3.459538000	1.066974000
6	2.963698000	3.305598000	-1.432270000
1	4.027116000	3.536134000	-1.339156000
1	2.832741000	2.703510000	-2.333739000
1	2.429603000	4.247672000	-1.574282000
1	2.192826000	2.940664000	1.948894000
1	1.993482000	4.378927000	0.934877000
1	3.605542000	3.745290000	1.253544000
1	-6.184587000	-0.032569000	0.776587000
1	6.184549000	-0.032762000	0.776725000
13	0.000033000	-0.037597000	2.365479000
1	1.350405000	0.722466000	2.772759000
1	0.000673000	-1.617581000	2.670057000
1	-1.350952000	0.721349000	2.772796000

AlH_2Cl·IDipp

6	0.675410000	0.282765000	-2.020492000
6	-0.675381000	0.282765000	-2.020495000
7	-1.073636000	0.174025000	-0.701455000
6	0.000009000	0.107561000	0.127250000
7	1.073657000	0.174022000	-0.701449000
1	1.382486000	0.350022000	-2.826706000
1	-1.382451000	0.350025000	-2.826713000
6	2.468591000	0.155589000	-0.310045000
6	3.142092000	-1.075488000	-0.279121000
6	3.101029000	1.376651000	-0.030389000
6	4.495981000	-1.052941000	0.054087000
6	4.455504000	1.335883000	0.295467000
6	5.146737000	0.136265000	0.339149000
1	5.047406000	-1.982357000	0.094116000
1	4.974696000	2.257511000	0.523203000
6	-2.468572000	0.155610000	-0.310056000
6	-3.142085000	-1.075461000	-0.279111000
6	-4.495976000	-1.052892000	0.054087000
6	-5.146722000	0.136328000	0.339120000
1	-5.047412000	-1.982299000	0.094133000
6	-4.455476000	1.335937000	0.295420000

1	-4.974659000	2.257576000	0.523136000
6	-3.100998000	1.376684000	-0.030428000
6	-2.471306000	-2.395835000	-0.631844000
1	-1.392060000	-2.244106000	-0.603745000
6	-2.846682000	-2.832293000	-2.058903000
6	-2.785613000	-3.510196000	0.375267000
1	-2.521075000	-3.211605000	1.388631000
1	-3.840657000	-3.790897000	0.355354000
1	-2.206863000	-4.402441000	0.128444000
1	-3.920740000	-3.013108000	-2.141390000
1	-2.329403000	-3.757654000	-2.321215000
1	-2.580287000	-2.076035000	-2.799697000
6	-2.382775000	2.716947000	-0.091244000
1	-1.318382000	2.525433000	-0.228607000
6	-2.857218000	3.544523000	-1.297411000
6	-2.528042000	3.512742000	1.214166000
1	-3.562956000	3.813428000	1.389017000
1	-2.194708000	2.924670000	2.069031000
1	-1.927080000	4.423478000	1.165313000
1	-2.714731000	3.006414000	-2.236592000
1	-2.300878000	4.482456000	-1.357516000
1	-3.917947000	3.790222000	-1.213722000
6	2.471310000	-2.395855000	-0.631873000
1	1.392066000	-2.244077000	-0.603976000
6	2.846907000	-2.832434000	-2.058836000
6	2.785396000	-3.510144000	0.375387000
1	3.840449000	-3.790830000	0.355739000
1	2.520622000	-3.211485000	1.388671000
1	2.206713000	-4.402414000	0.128493000
1	2.580696000	-2.076202000	-2.799724000
1	2.329608000	-3.757776000	-2.321177000
1	3.920966000	-3.013333000	-2.141129000
6	2.382821000	2.716923000	-0.091183000
1	1.318427000	2.525423000	-0.228560000
6	2.528087000	3.512686000	1.214246000
6	2.857283000	3.544520000	-1.297328000
1	3.918015000	3.790201000	-1.213629000
1	2.714792000	3.006433000	-2.236522000
1	2.300956000	4.482461000	-1.357417000
1	2.194749000	2.924596000	2.069097000
1	1.927129000	4.423427000	1.165413000
1	3.563002000	3.813362000	1.389107000
1	-6.197674000	0.127561000	0.600032000
1	6.197688000	0.127483000	0.600067000
13	-0.000001000	-0.018375000	2.214670000
1	-1.358041000	0.668302000	2.675125000
1	1.358139000	0.668095000	2.675137000
17	-0.000154000	-2.174145000	2.602416000

AlH_2I·IDipp

6	-0.675641000	1.261641000	2.104903000
6	0.674763000	1.261917000	2.104941000
7	1.074459000	0.766644000	0.878478000
6	-0.000218000	0.459665000	0.105268000
7	-1.075062000	0.766200000	0.878415000
1	-1.382583000	1.568349000	2.853393000
1	1.381534000	1.568908000	2.853475000
6	-2.472852000	0.656578000	0.509054000
6	-3.174025000	-0.508072000	0.861087000
6	-3.081975000	1.748747000	-0.128280000
6	-4.529524000	-0.557365000	0.537274000
6	-4.439623000	1.640984000	-0.424594000

6	-5.156350000	0.501630000	-0.098833000
1	-5.102057000	-1.440682000	0.784103000
1	-4.941377000	2.460412000	-0.921799000
6	2.472303000	0.657565000	0.509161000
6	3.173978000	-0.506705000	0.861457000
6	4.529498000	-0.555492000	0.537652000
6	5.155863000	0.503625000	-0.098701000
1	5.102408000	-1.438510000	0.784679000
6	4.438650000	1.642609000	-0.424696000
1	4.940060000	2.462144000	-0.922069000
6	3.080962000	1.749869000	-0.128387000
6	2.529461000	-1.665625000	1.609980000
1	1.449503000	-1.594412000	1.475214000
6	2.824443000	-1.571507000	3.117989000
6	2.952517000	-3.037863000	1.070189000
1	2.774083000	-3.114556000	-0.001461000
1	4.006280000	-3.245459000	1.266939000
1	2.370448000	-3.820121000	1.560752000
1	3.897210000	-1.649624000	3.308533000
1	2.328120000	-2.384019000	3.652931000
1	2.479544000	-0.628739000	3.545722000
6	2.337829000	3.033307000	-0.470221000
1	1.272355000	2.858962000	-0.319664000
6	2.752420000	4.175164000	0.473290000
6	2.518932000	3.442314000	-1.939002000
1	3.552383000	3.718704000	-2.156724000
1	2.233078000	2.631272000	-2.608268000
1	1.895551000	4.310588000	-2.163197000
1	2.579398000	3.916836000	1.519816000
1	2.182518000	5.079685000	0.249834000
1	3.812681000	4.411400000	0.360911000
6	-2.528993000	-1.666885000	1.609335000
1	-1.449065000	-1.595154000	1.474593000
6	-2.824028000	-1.573251000	3.117361000
6	-2.951406000	-3.039178000	1.069187000
1	-4.005084000	-3.247306000	1.265824000
1	-2.772879000	-3.115523000	-0.002474000
1	-2.369008000	-3.821295000	1.559585000
1	-2.479560000	-0.630419000	3.545301000
1	-2.327336000	-2.385654000	3.652126000
1	-3.896761000	-1.651899000	3.307884000
6	-2.339363000	3.032511000	-0.470020000
1	-1.273845000	2.858700000	-0.319156000
6	-2.520288000	3.441226000	-1.938907000
6	-2.754750000	4.174289000	0.473228000
1	-3.815090000	4.410023000	0.360535000
1	-2.581894000	3.916174000	1.519833000
1	-2.185212000	5.079048000	0.249811000
1	-2.233837000	2.630248000	-2.607998000
1	-1.897320000	4.309809000	-2.163057000
1	-3.553838000	3.717009000	-2.156934000
1	6.208790000	0.439680000	-0.343356000
1	-6.209253000	0.437290000	-0.343487000
13	-0.000081000	-0.197228000	-1.874352000
1	1.361644000	0.334655000	-2.491245000
1	-1.362461000	0.333285000	-2.490982000
53	0.001145000	-2.793697000	-1.780564000

GaH_3·IDipp

6	0.675022000	0.038928000	-2.073300000
6	-0.674998000	0.039008000	-2.073311000
7	-1.072212000	0.021253000	-0.746644000

6	-0.000007000	0.009868000	0.085236000
7	1.072214000	0.021170000	-0.746628000
1	1.382315000	0.049106000	-2.882498000
1	-1.382277000	0.049261000	-2.882520000
6	2.461586000	0.010505000	-0.346579000
6	3.104727000	-1.225509000	-0.183758000
6	3.121327000	1.237022000	-0.176107000
6	4.456173000	-1.204357000	0.159351000
6	4.472173000	1.196584000	0.164342000
6	5.134619000	-0.008946000	0.331121000
1	4.983093000	-2.139322000	0.297180000
1	5.011121000	2.123735000	0.308753000
6	-2.461594000	0.010673000	-0.346626000
6	-3.104888000	-1.225292000	-0.184029000
6	-4.456339000	-1.204033000	0.159053000
6	-5.134640000	-0.008569000	0.331026000
1	-4.983378000	-2.138958000	0.296704000
6	-4.472041000	1.196909000	0.164479000
1	-5.010872000	2.124100000	0.309064000
6	-3.121187000	1.237238000	-0.175950000
6	-2.400052000	-2.559114000	-0.382478000
1	-1.339135000	-2.362126000	-0.535663000
6	-2.919384000	-3.278099000	-1.638533000
6	-2.509155000	-3.460441000	0.856083000
1	-2.107083000	-2.963204000	1.738632000
1	-3.543962000	-3.743464000	1.059482000
1	-1.941745000	-4.380203000	0.698248000
1	-3.978562000	-3.526654000	-1.543040000
1	-2.371411000	-4.209394000	-1.797614000
1	-2.802904000	-2.660653000	-2.531546000
6	-2.428577000	2.580276000	-0.351755000
1	-1.366263000	2.394665000	-0.510591000
6	-2.954666000	3.320906000	-1.591983000
6	-2.544005000	3.455160000	0.905516000
1	-3.579149000	3.741695000	1.102510000
1	-2.162490000	2.930551000	1.781428000
1	-1.968204000	4.374138000	0.775120000
1	-2.832373000	2.724365000	-2.498286000
1	-2.415952000	4.260851000	-1.730612000
1	-4.016157000	3.556983000	-1.491067000
6	2.399721000	-2.559273000	-0.381993000
1	1.338816000	-2.362172000	-0.535122000
6	2.918884000	-3.278463000	-1.638001000
6	2.508792000	-3.460469000	0.856665000
1	3.543569000	-3.743638000	1.060011000
1	2.106876000	-2.963054000	1.739185000
1	1.941220000	-4.380158000	0.698991000
1	2.802412000	-2.661106000	-2.531079000
1	2.370797000	-4.209715000	-1.796940000
1	3.978041000	-3.527121000	-1.542550000
6	2.428915000	2.580116000	-0.352268000
1	1.366544000	2.394628000	-0.510862000
6	2.544693000	3.455454000	0.904652000
6	2.954936000	3.320197000	-1.592855000
1	4.016489000	3.556110000	-1.492193000
1	2.832385000	2.723349000	-2.498921000
1	2.416375000	4.260191000	-1.731739000
1	2.163231000	2.931237000	1.780821000
1	1.969014000	4.374472000	0.774000000
1	3.579912000	3.741910000	1.101369000
1	-6.183322000	-0.016123000	0.601048000
1	6.183296000	-0.016581000	0.601160000

31	-0.000015000	-0.053894000	2.209373000
1	1.342005000	0.694987000	2.605931000
1	0.000374000	-1.620940000	2.501682000
1	-1.342416000	0.694325000	2.605877000

GaH_2Cl·IDipp

6	0.666456000	0.289306000	-2.175401000
6	-0.683960000	0.286763000	-2.173738000
7	-1.080498000	0.178441000	-0.852892000
6	-0.005538000	0.115786000	-0.028813000
7	1.067325000	0.181921000	-0.855792000
1	1.372290000	0.358719000	-2.982411000
1	-1.392364000	0.351791000	-2.978952000
6	2.461643000	0.176112000	-0.462582000
6	3.147420000	-1.048688000	-0.426926000
6	3.080883000	1.403992000	-0.184019000
6	4.500762000	-1.009977000	-0.093489000
6	4.435585000	1.378902000	0.143650000
6	5.139163000	0.186856000	0.189169000
1	5.061817000	-1.933102000	-0.049146000
1	4.944638000	2.306602000	0.370038000
6	-2.473271000	0.159604000	-0.456135000
6	-3.148198000	-1.070720000	-0.428063000
6	-4.500525000	-1.047393000	-0.088624000
6	-5.148048000	0.141184000	0.206838000
1	-5.053109000	-1.976202000	-0.051001000
6	-4.454895000	1.339851000	0.167912000
1	-4.971414000	2.261063000	0.403820000
6	-3.101979000	1.379762000	-0.165102000
6	-2.479826000	-2.390273000	-0.787943000
1	-1.400338000	-2.239991000	-0.762364000
6	-2.861633000	-2.821170000	-2.214998000
6	-2.790782000	-3.507442000	0.216977000
1	-2.515406000	-3.214297000	1.229003000
1	-3.846827000	-3.785198000	0.203476000
1	-2.215630000	-4.399721000	-0.037661000
1	-3.936117000	-3.001503000	-2.293726000
1	-2.345712000	-3.745736000	-2.482509000
1	-2.598141000	-2.062569000	-2.954517000
6	-2.380665000	2.718790000	-0.217280000
1	-1.320371000	2.527086000	-0.382620000
6	-2.878050000	3.571858000	-1.395834000
6	-2.495098000	3.488463000	1.106957000
1	-3.525476000	3.786455000	1.310589000
1	-2.146498000	2.883960000	1.944356000
1	-1.893194000	4.398848000	1.064706000
1	-2.756512000	3.051709000	-2.347931000
1	-2.320253000	4.509349000	-1.449178000
1	-3.935996000	3.818715000	-1.285500000
6	2.486580000	-2.375817000	-0.774215000
1	1.407916000	-2.248845000	-0.678894000
6	2.792620000	-2.771260000	-2.229755000
6	2.879037000	-3.508710000	0.182966000
1	3.933077000	-3.777953000	0.086600000
1	2.675239000	-3.238067000	1.217748000
1	2.293634000	-4.400717000	-0.047580000
1	2.464869000	-2.009284000	-2.939040000
1	2.286419000	-3.705243000	-2.482983000
1	3.865137000	-2.920279000	-2.374309000
6	2.348487000	2.736595000	-0.246120000
1	1.288467000	2.534369000	-0.400244000
6	2.466963000	3.524110000	1.067173000

6	2.829898000	3.578916000	-1.439051000
1	3.886185000	3.837050000	-1.338896000
1	2.707159000	3.045505000	-2.383616000
1	2.262946000	4.510392000	-1.500670000
1	2.127518000	2.928043000	1.914265000
1	1.858602000	4.429834000	1.016964000
1	3.496522000	3.831980000	1.259923000
1	-6.197819000	0.132508000	0.472481000
1	6.190027000	0.189280000	0.450618000
31	-0.003179000	-0.041873000	2.078635000
1	-1.399050000	0.494546000	2.572111000
1	1.340009000	0.614214000	2.574100000
17	0.088256000	-2.289422000	2.345572000

GaH_2I·IDipp

6	-0.675138000	1.276274000	2.217038000
6	0.674951000	1.276336000	2.217047000
7	1.074884000	0.782838000	0.988456000
6	-0.000043000	0.479434000	0.217230000
7	-1.075008000	0.782749000	0.988437000
1	-1.381847000	1.582344000	2.966034000
1	1.381623000	1.582474000	2.966051000
6	-2.470642000	0.680434000	0.610872000
6	-3.178898000	-0.484067000	0.949873000
6	-3.070342000	1.777857000	-0.026003000
6	-4.531472000	-0.526586000	0.613337000
6	-4.425758000	1.676597000	-0.335675000
6	-5.149085000	0.538025000	-0.022753000
1	-5.109195000	-1.409499000	0.848947000
1	-4.920265000	2.500496000	-0.832864000
6	2.470531000	0.680653000	0.610902000
6	3.178902000	-0.483773000	0.949925000
6	4.531479000	-0.526167000	0.613387000
6	5.148987000	0.538492000	-0.022724000
1	5.109287000	-1.409020000	0.849011000
6	4.425549000	1.676989000	-0.335666000
1	4.919977000	2.500926000	-0.832871000
6	3.070124000	1.778123000	-0.025993000
6	2.542811000	-1.648223000	1.696809000
1	1.463715000	-1.593131000	1.548049000
6	2.819100000	-1.542130000	3.207606000
6	2.992209000	-3.017106000	1.170650000
1	2.830684000	-3.101999000	0.096873000
1	4.045219000	-3.210280000	1.386132000
1	2.411876000	-3.803911000	1.655824000
1	3.891124000	-1.598075000	3.410074000
1	2.332886000	-2.362415000	3.739941000
1	2.450316000	-0.605155000	3.627869000
6	2.320176000	3.060422000	-0.356799000
1	1.259064000	2.890780000	-0.173461000
6	2.764070000	4.210256000	0.563186000
6	2.460500000	3.455116000	-1.834256000
1	3.488841000	3.723749000	-2.083634000
1	2.153780000	2.639948000	-2.489428000
1	1.834975000	4.324073000	-2.049592000
1	2.624179000	3.959796000	1.616484000
1	2.186930000	5.112877000	0.350813000
1	3.820050000	4.446196000	0.415842000
6	-2.542693000	-1.648470000	1.696732000
1	-1.463600000	-1.593249000	1.548005000
6	-2.819033000	-1.542459000	3.207525000
6	-2.991922000	-3.017384000	1.170509000

1	-4.044920000	-3.210678000	1.385943000
1	-2.830347000	-3.102225000	0.096735000
1	-2.411524000	-3.804144000	1.655679000
1	-2.450363000	-0.605455000	3.627825000
1	-2.332740000	-2.362706000	3.739847000
1	-3.891055000	-1.598529000	3.409967000
6	-2.320518000	3.060232000	-0.356796000
1	-1.259392000	2.890699000	-0.173436000
6	-2.460854000	3.454902000	-1.834259000
6	-2.764547000	4.210026000	0.563173000
1	-3.820547000	4.445862000	0.415804000
1	-2.624656000	3.959584000	1.616476000
1	-2.187491000	5.112703000	0.350809000
1	-2.154035000	2.639763000	-2.489420000
1	-1.835417000	4.323925000	-2.049588000
1	-3.489219000	3.723422000	-2.083659000
1	6.199726000	0.478862000	-0.277696000
1	-6.199819000	0.478298000	-0.277722000
31	-0.000014000	-0.196398000	-1.780175000
1	1.370907000	0.265353000	-2.396370000
1	-1.371049000	0.265080000	-2.396316000
53	0.000244000	-2.824723000	-1.587190000

PH_2AlH_2·IDipp

6	-0.155241000	-0.160330000	-0.475656000
7	0.763938000	-1.105469000	-0.175683000
7	0.500693000	1.011665000	-0.322648000
6	1.816675000	0.811121000	0.077109000
6	1.985224000	-0.536260000	0.169360000
6	2.765642000	1.930861000	0.321944000
1	3.724319000	1.545756000	0.664496000
1	2.948478000	2.514130000	-0.584236000
1	2.391805000	2.617851000	1.084996000
6	3.175490000	-1.347189000	0.543376000
1	3.505540000	-1.988135000	-0.278297000
1	4.007360000	-0.697285000	0.808564000
1	2.972268000	-1.992570000	1.401468000
6	-0.109355000	2.321556000	-0.511756000
1	-0.303755000	2.796143000	0.450493000
1	0.551050000	2.955988000	-1.101670000
1	-1.047335000	2.192417000	-1.044713000
6	0.508733000	-2.539738000	-0.190819000
1	-0.491835000	-2.706137000	-0.580647000
1	1.232406000	-3.043440000	-0.831855000
1	0.580064000	-2.949098000	0.817651000
13	-2.168820000	-0.389729000	-0.957564000
1	-2.434997000	0.723545000	-2.081582000
1	-2.314879000	-1.915574000	-1.424431000
15	-3.219325000	0.254475000	1.106832000
1	-3.069334000	-0.999664000	1.760036000
1	-4.542037000	-0.028075000	0.672557000

PCy_2AlH_2·IDipp

13	-0.244767000	0.243580000	-1.068778000
15	-2.113137000	1.138965000	0.157120000
7	0.947686000	-1.786690000	1.020247000
7	2.512750000	-0.644591000	0.095011000
6	1.156255000	-0.747243000	0.166982000
6	-0.328492000	-2.322892000	1.447402000
6	-0.916362000	-1.804946000	2.613643000
6	3.286365000	0.313133000	-0.668517000
6	3.785156000	1.446286000	-0.006495000
6	2.144734000	-2.322441000	1.458304000

1	2.183154000	-3.155206000	2.135789000
6	3.128103000	-1.607386000	0.874911000
1	4.197148000	-1.691167000	0.939028000
6	-2.112895000	-2.381963000	3.035022000
1	-2.601873000	-2.003159000	3.921693000
6	4.578633000	2.323263000	-0.744905000
1	4.975854000	3.209884000	-0.269222000
6	-3.182774000	3.774857000	0.318284000
1	-3.357156000	3.545661000	1.376183000
1	-4.072534000	3.440256000	-0.219447000
6	3.525303000	1.724152000	1.468038000
1	2.709482000	1.078201000	1.794582000
6	-0.267329000	-0.704244000	3.441497000
1	0.421975000	-0.163398000	2.791978000
6	-1.943524000	2.999125000	-0.158394000
1	-1.821371000	3.177610000	-1.232432000
6	-3.602107000	0.688041000	-0.924755000
1	-4.427418000	1.275963000	-0.504038000
6	-0.881674000	-3.393047000	0.726121000
6	-0.686414000	3.534067000	0.541593000
1	-0.741725000	3.295964000	1.610926000
1	0.194579000	3.022831000	0.146705000
6	4.865675000	2.081164000	-2.078266000
1	5.480504000	2.778198000	-2.633951000
6	3.568226000	0.036854000	-2.014614000
6	-3.500060000	1.031713000	-2.418345000
1	-2.656477000	0.485699000	-2.854134000
1	-3.286284000	2.094484000	-2.552509000
6	-3.974097000	-0.791132000	-0.739585000
1	-4.092925000	-1.012651000	0.323844000
1	-3.150987000	-1.417967000	-1.097408000
6	3.084159000	3.170647000	1.730339000
1	3.887994000	3.881727000	1.530725000
1	2.799095000	3.288678000	2.777710000
1	2.229287000	3.444605000	1.113910000
6	-0.522311000	5.048518000	0.368549000
1	0.361239000	5.394614000	0.913845000
1	-0.340927000	5.270521000	-0.689270000
6	-2.691051000	-3.428606000	2.335077000
1	-3.623819000	-3.857630000	2.679613000
6	-3.024079000	5.290400000	0.144178000
1	-2.970594000	5.528095000	-0.924716000
1	-3.909392000	5.803834000	0.531295000
6	4.366929000	0.949367000	-2.701807000
1	4.598600000	0.771801000	-3.743415000
6	-1.763599000	5.810458000	0.837837000
1	-1.643273000	6.882484000	0.656316000
1	-1.873152000	5.688417000	1.922038000
6	-0.199083000	-4.014638000	-0.484609000
1	0.583088000	-3.333068000	-0.818078000
6	-2.080205000	-3.928698000	1.197232000
1	-2.539878000	-4.750751000	0.665166000
6	-1.149485000	-4.209855000	-1.672763000
1	-1.942298000	-4.926302000	-1.448482000
1	-0.594394000	-4.596031000	-2.530240000
1	-1.605126000	-3.265236000	-1.966667000
6	-5.151055000	-0.804613000	-2.988198000
1	-4.383564000	-1.431858000	-3.456464000
1	-6.092181000	-1.030896000	-3.498105000
6	-4.780379000	0.667420000	-3.181518000
1	-5.605269000	1.296455000	-2.825692000
1	-4.657487000	0.890961000	-4.245593000

6	-5.252426000	-1.159910000	-1.502323000
1	-5.463891000	-2.226967000	-1.382448000
1	-6.101762000	-0.624033000	-1.061847000
6	3.072747000	-1.214949000	-2.723751000
1	2.304541000	-1.674911000	-2.102870000
6	4.759984000	1.381077000	2.319852000
1	5.065104000	0.341160000	2.194116000
1	4.550031000	1.544574000	3.379096000
1	5.608810000	2.010728000	2.044437000
6	0.550229000	-1.306753000	4.598935000
1	-0.099837000	-1.851517000	5.287467000
1	1.048782000	-0.515746000	5.163574000
1	1.315522000	-1.999711000	4.245977000
6	0.472291000	-5.345653000	-0.102440000
1	1.186387000	-5.220135000	0.713556000
1	1.008554000	-5.760906000	-0.958534000
1	-0.269919000	-6.080545000	0.217115000
6	4.211416000	-2.236568000	-2.885406000
1	5.011621000	-1.835750000	-3.511518000
1	3.839891000	-3.148107000	-3.358706000
1	4.648027000	-2.509642000	-1.922701000
6	-1.271264000	0.323868000	3.977447000
1	-1.882276000	0.726658000	3.169580000
1	-0.733050000	1.149055000	4.449172000
1	-1.927212000	-0.106260000	4.737204000
6	2.418359000	-0.904557000	-4.076932000
1	1.618694000	-0.172736000	-3.966653000
1	1.988147000	-1.815391000	-4.497645000
1	3.142029000	-0.520172000	-4.798765000
1	0.642457000	1.363202000	-1.790548000
1	-0.639977000	-1.002443000	-2.005743000

PH_2GaH_2·IDipp

6	0.678789000	0.339615000	-2.177551000
6	-0.670550000	0.340795000	-2.179188000
7	-1.070782000	0.195366000	-0.861767000
6	0.001618000	0.107268000	-0.032539000
7	1.076000000	0.193193000	-0.859370000
1	1.386461000	0.429607000	-2.980983000
1	-1.376174000	0.431439000	-2.984362000
6	2.470405000	0.169010000	-0.470690000
6	3.150946000	-1.058968000	-0.477884000
6	3.099903000	1.384038000	-0.159305000
6	4.506273000	-1.040209000	-0.150066000
6	4.456107000	1.340283000	0.159651000
6	5.153121000	0.143357000	0.166243000
1	5.062641000	-1.967456000	-0.140298000
1	4.972461000	2.257615000	0.410008000
6	-2.465556000	0.169345000	-0.475493000
6	-3.141675000	-1.061139000	-0.476120000
6	-4.497944000	-1.045631000	-0.152188000
6	-5.149987000	0.137679000	0.154363000
1	-5.050943000	-1.974865000	-0.137841000
6	-4.457374000	1.337147000	0.141845000
1	-4.977938000	2.254095000	0.384598000
6	-3.100432000	1.384078000	-0.173756000
6	-2.467498000	-2.372673000	-0.855258000
1	-1.389011000	-2.229970000	-0.782425000
6	-2.792111000	-2.752251000	-2.310756000
6	-2.827011000	-3.525816000	0.090943000
1	-2.626253000	-3.268250000	1.130190000
1	-3.877261000	-3.811490000	0.003533000

1	-2.228175000	-4.404659000	-0.153988000
1	-3.864406000	-2.915996000	-2.439394000
1	-2.275419000	-3.673751000	-2.587527000
1	-2.488666000	-1.973087000	-3.011863000
6	-2.381709000	2.725067000	-0.209736000
1	-1.313588000	2.532818000	-0.310339000
6	-2.818445000	3.550103000	-1.432126000
6	-2.569537000	3.524401000	1.087428000
1	-3.609461000	3.824837000	1.230218000
1	-2.258428000	2.940339000	1.953244000
1	-1.968667000	4.435842000	1.053593000
1	-2.646705000	3.010551000	-2.365505000
1	-2.260877000	4.488187000	-1.476915000
1	-3.881568000	3.795132000	-1.381535000
6	2.483727000	-2.370743000	-0.868586000
1	1.404412000	-2.232841000	-0.799376000
6	2.817533000	-2.738773000	-2.325086000
6	2.842254000	-3.528712000	0.071747000
1	3.897223000	-3.800886000	-0.000753000
1	2.616217000	-3.284537000	1.108983000
1	2.258151000	-4.411978000	-0.192586000
1	2.517861000	-1.954716000	-3.022452000
1	2.303519000	-3.658693000	-2.611955000
1	3.890721000	-2.900655000	-2.448642000
6	2.376436000	2.722755000	-0.186151000
1	1.309847000	2.528225000	-0.297936000
6	2.550841000	3.507080000	1.122101000
6	2.819915000	3.563624000	-1.395145000
1	3.881758000	3.811555000	-1.333526000
1	2.657199000	3.034394000	-2.336032000
1	2.259613000	4.500398000	-1.433336000
1	2.236465000	2.911078000	1.978519000
1	1.946274000	4.416292000	1.095129000
1	3.588446000	3.809883000	1.276304000
1	-6.203014000	0.124228000	0.406682000
1	6.205471000	0.132048000	0.421512000
31	0.000421000	-0.025184000	2.091896000
1	-1.325776000	0.741659000	2.494669000
1	1.374764000	0.654482000	2.490487000
15	-0.010902000	-2.375731000	2.598643000
1	-1.228874000	-2.369030000	3.327283000
1	0.787425000	-2.239448000	3.763977000

PCy_2GaH_2·IDipp

31	-0.238660000	0.213752000	-0.998858000
15	-2.277741000	0.776666000	0.134446000
7	1.163745000	-1.532153000	1.262165000
7	2.591095000	-0.298099000	0.237514000
6	1.257765000	-0.559730000	0.316880000
6	-0.036316000	-2.221614000	1.689218000
6	-0.735472000	-1.737190000	2.806698000
6	3.256439000	0.632826000	-0.650277000
6	3.602107000	1.900725000	-0.157689000
6	2.412004000	-1.871416000	1.755579000
1	2.541609000	-2.627852000	2.507218000
6	3.308606000	-1.097791000	1.111445000
1	4.378967000	-1.043397000	1.186231000
6	-1.848714000	-2.462880000	3.226963000
1	-2.419096000	-2.114267000	4.076544000
6	4.308020000	2.749979000	-1.008394000
1	4.586082000	3.736757000	-0.663541000
6	-3.714643000	3.239544000	0.192576000
1	-3.997303000	2.955432000	1.213436000

1	-4.472118000	2.810950000	-0.466854000
6	3.264238000	2.358015000	1.254511000
1	2.505446000	1.684040000	1.654182000
6	-0.287910000	-0.506381000	3.583086000
1	0.337237000	0.094159000	2.920754000
6	-2.329767000	2.651032000	-0.121723000
1	-2.086367000	2.882000000	-1.164666000
6	-3.603347000	0.173742000	-1.074927000
1	-4.532105000	0.607628000	-0.683529000
6	-0.404419000	-3.395353000	1.012389000
6	-1.266552000	3.320850000	0.760793000
1	-1.445986000	3.046738000	1.807194000
1	-0.278186000	2.936065000	0.500278000
6	4.655770000	2.355996000	-2.290230000
1	5.200795000	3.033897000	-2.935242000
6	3.601557000	0.203591000	-1.940853000
6	-3.466247000	0.612078000	-2.540495000
1	-2.528363000	0.219178000	-2.946439000
1	-3.403588000	1.700276000	-2.611436000
6	-3.759488000	-1.352083000	-0.985295000
1	-3.901922000	-1.650462000	0.056538000
1	-2.833324000	-1.828373000	-1.321858000
6	2.670885000	3.773118000	1.289303000
1	3.410457000	4.529707000	1.020170000
1	2.320653000	4.005346000	2.296952000
1	1.827144000	3.868265000	0.607015000
6	-1.279877000	4.848235000	0.630963000
1	-0.533894000	5.287468000	1.300395000
1	-0.985008000	5.125192000	-0.387773000
6	-2.243994000	-3.617206000	2.570466000
1	-3.116132000	-4.160536000	2.912473000
6	-3.738195000	4.767995000	0.064152000
1	-3.574239000	5.044147000	-0.983997000
1	-4.728303000	5.148290000	0.333000000
6	4.305208000	1.096954000	-2.747534000
1	4.581649000	0.800442000	-3.750583000
6	-2.663984000	5.427897000	0.930782000
1	-2.664367000	6.511173000	0.778841000
1	-2.902398000	5.261672000	1.988107000
6	0.396875000	-3.969043000	-0.148634000
1	1.095033000	-3.204564000	-0.488205000
6	-1.527981000	-4.077399000	1.478060000
1	-1.844699000	-4.982459000	0.977347000
6	-0.478571000	-4.334477000	-1.354433000
1	-1.181108000	-5.136244000	-1.119373000
1	0.150589000	-4.682722000	-2.176321000
1	-1.041774000	-3.470750000	-1.705375000
6	-4.793803000	-1.408439000	-3.302015000
1	-3.917170000	-1.890298000	-3.750459000
1	-5.661284000	-1.738752000	-3.880991000
6	-4.634130000	0.110070000	-3.399976000
1	-5.561253000	0.592440000	-3.067354000
1	-4.486537000	0.409188000	-4.442119000
6	-4.924122000	-1.859433000	-1.844556000
1	-4.980134000	-2.951010000	-1.790220000
1	-5.867284000	-1.479774000	-1.433659000
6	3.273431000	-1.184746000	-2.471746000
1	2.583144000	-1.660690000	-1.776209000
6	4.495036000	2.272306000	2.173771000
1	4.900474000	1.260364000	2.217786000
1	4.233148000	2.574143000	3.190269000
1	5.289895000	2.933370000	1.821134000

6	0.565290000	-0.909710000	4.799453000
1	-0.020772000	-1.510518000	5.498701000
1	0.913112000	-0.020784000	5.330525000
1	1.441435000	-1.493205000	4.512633000
6	1.223532000	-5.183248000	0.309829000
1	1.892972000	-4.929308000	1.133720000
1	1.832367000	-5.562098000	-0.514048000
1	0.574528000	-5.994062000	0.647864000
6	4.537147000	-2.058718000	-2.540390000
1	5.266025000	-1.642711000	-3.239392000
1	4.284668000	-3.065419000	-2.880427000
1	5.022267000	-2.143651000	-1.566006000
6	-1.456183000	0.384068000	4.025646000
1	-2.096668000	0.633516000	3.179532000
1	-1.069180000	1.311173000	4.454124000
1	-2.063013000	-0.096686000	4.796055000
6	2.565010000	-1.137980000	-3.832909000
1	1.663690000	-0.527866000	-3.785140000
1	2.273692000	-2.146251000	-4.134073000
1	3.214294000	-0.737222000	-4.613968000
1	0.498617000	1.466120000	-1.644251000
1	-0.376928000	-1.046818000	-1.968244000

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5.6. Author contributions

The syntheses and characterization of compounds **1**, **2**, **3** and **4** were performed by Michael Weinhart.

X-ray structural analyses of **1**, **2**, **3** and **4** were performed by Michael Weinhart.

Structure refinements of the X-ray structural analyses of **1**, **2**, **3** and **4** were performed by Michael Seidl.

Computational analyses were performed by Alexey Y. Timoshkin.

The manuscript was written by Michael Weinhart.

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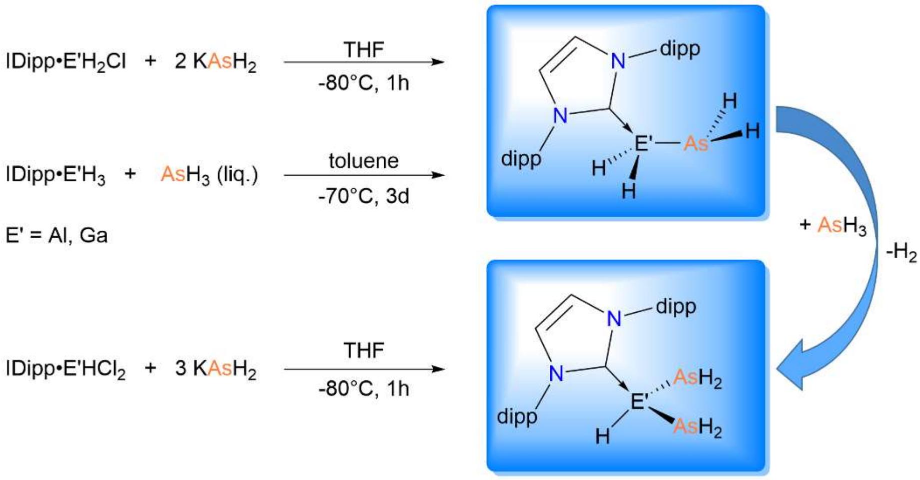
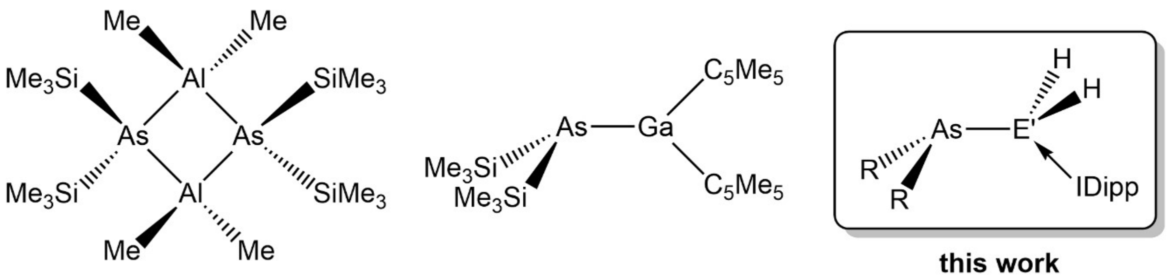
6. NHC-stabilized Parent Arsanylalanes and –gallanes



Abstract: The synthesis and characterization of the unprecedented compounds IDipp·E'H_2AsH_2 (E' = Al, Ga; IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene) are reported, the first monomeric, only by a LB (LB = Lewis Base) stabilized parent representatives of an arsanylalane and arsanylgallane, respectively. They are prepared via a salt metathesis reaction of KAsH_2 with IDipp·E'H_2Cl (E' = Al, Ga). The H_2-elimination pathway by the reaction of AsH_3 with IDipp·E'H_3 (E' = Al, Ga) was found to be a possible synthetic route with some disadvantages compared to the salt metathesis reaction. The corresponding organo-substituted compounds IDipp·GaH_2AsPh_2 (**1**) and IDipp·AlH_2AsPh_2 (**2**) were obtained by the reaction of KAsPh_2 with IDipp·E'H_2Cl (E' = Al, Ga). The novel branched parent compounds IDipp·E'H(EH_2)$_2$ (E' = Al, Ga; E = P, As) were synthesized via salt metathesis reactions starting from IDipp·E'HCl_2 (E' = Al, Ga). Supporting DFT computations give insight into the different synthetic pathways and the stability of the products.

6.1. Introduction

The chemistry of group 13/15 compounds is an active research field and has influenced many areas of chemistry. For instance, unsaturated compounds of the type $H_2E'EH_2$ (E' = Group 13 element, E = Group 15 element) are isoelectronic to alkenes. They are of interest as starting materials for semiconducting applications[1] or as precursor for composite 13/15 materials.[2] In comparison to aminoboranes $LB{\cdot}BR_2NR_2{\cdot}LA$ (LB = Lewis base, LA = Lewis acid) the chemistry of the heavier group 13/15 element analogues is rarely investigated. The few known compounds of arsanylalanes and –gallanes $LB{\cdot}[E'R_2AsR_2]_n{\cdot}LA$ (E' = Al, Ga) exist as dimers (**A**, *n* = 2),[3] trimers (*n* = 3)[4] or as LB/LA-stabilized monomers depending on the steric demands of the organic substituents[5] (**B**, Figure 1) as well as the LA/LB. Since these compounds are precursors for the synthesis of binary GaAs or AlAs materials *via* MOCVD processes (metal-organic chemical vapor deposition),[6] especially the parent compounds of these precursors are of interest to improve the current MOCVD-process which involves the reaction of trimethylgallium with the toxic gas AsH_3 at elevated temperatures. In contrast to the phosphorus analogue $E'H_2PH_2$ (E' = Al, Ga), for which we recently succeeded in the synthesis of the first only LB-stabilized parent compounds $IDipp{\cdot}E'H_2PH_2$ (E' = Al, Ga; IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene),[7] the heavier arsenic analogues exhibit a higher lability of the Ga–As/Al–As bond, which is why they have so far only been studied by theoretical methods.[8]



A **B** **C**

IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene
E' = Al, Ga
R = H, Ph

Figure 1: Examples of dimeric (**A**) and monomeric arsanyltrielanes (**B** and **C**).

In fact, because of their toxicity, light sensitivity and tendency to decompose, as well as the unsuitable NMR activity of the As nucleus, the handling and characterization of such compounds inheres numerous difficulties. Moreover, only a few examples of stable primary arsines, like $(2,6\text{-}Tipp_2C_6H_3)AsH_2$ (Tipp = $2,4,6\text{-}i Pr_3C_6H_2$), $TriptAsH_2$ (Tript = tribenzobarellene)[9] or $NMe_3{\cdot}BH_2AsH_2$,[10a] have so far been reported containing bulky or special substituents. Therefore, the question arises whether compounds containing AsH_2 bound on alanes and gallanes can be synthesized. In any case, a stabilization via a LB and a LA or at least via a LB alone would be needed if one avoided organic substitution at the As and the Al and Ga atoms, respectively. Even under this view, it is astonishing that only parent arsanylboranes exist as LA/LB[10b] or LB[10a] stabilized molecules. No LA/LB stabilized arsanylalanes or -galanes have been reported yet, only their phosphanyl analogues,[10c] which reflects the specific lability of the corresponding E'-As bonds (E' = Al, Ga). Herein, we report the synthesis and characterization of the first only by a LB stabilized monomeric parent compound of an arsanylgallane, IDipp·GaH_2AsH_2 (**3**), and an arsanylalane, IDipp·AlH_2AsH_2 (**4**), as well as their organo-substituted analogues IDipp·$E'H_2AsPh_2$ (**1**: E' = Ga, **2**: E' = Al; **C**). The initially formed unprecedented side products IDipp·$E'H(EH_2)_2$ (E' = Al, Ga; E = As, P; **5** – **8**) could be synthesized and characterized on a selective route.

6.2. Results and Discussion

The organo-substituted compounds IDipp·GaH_2AsPh_2 (**1**) and IDipp·AlH_2AsPh_2 (**2**) can be synthesized by the reaction of IDipp·$E'H_2Cl$ (E' = Ga, Al) with $KAsPh_2$·dioxane in Et_2O at –80 °C (Eq. 1). Compound **1** was isolated at –30 °C as colorless crystals in a yield of 63% and **2** as pale yellow blocks in a yield of 52 %.

$$\text{IDipp•E'H}_2\text{Cl} + 2\ \text{KAsPh}_2\text{•dioxane} \xrightarrow[-80^\circ\text{C} \rightarrow \text{RT}]{\text{Et}_2\text{O}} \text{IDipp•E'H}_2\text{AsPh}_2 \quad \text{E' = Ga (\textbf{1}), Al (\textbf{2})} \qquad (1)$$

$$\text{route 1: IDipp•E'H}_2\text{Cl} + 2\ \text{KAsH}_2 \xrightarrow[-80^\circ\text{C, 1h}]{\text{THF}} \text{IDipp•E'H}_2\text{AsH}_2$$

$$\text{route 2: IDipp•E'H}_3 + \text{AsH}_3 \xrightarrow[-70^\circ\text{C, 3d}]{\text{toluene}} \text{IDipp•E'H}_2\text{AsH}_2 \quad \text{E' = Ga (\textbf{3}), Al (\textbf{4})} \qquad (2)$$

In the solid state, **1** and **2** can be stored at ambient temperatures in an inert atmosphere for more than two months without decomposition. The molecular ion peak of **1** is detected at *m/z* 688.2142 in the mass spectrum (LIFDI-MS). The LIFDI-MS spectrum of **2** shows a fragment peak of IDipp due to decomposition of **2** during the ionization process. The ^{1}H NMR spectra of **1** and **2** show a broad singlet at δ = 4.28 ppm for the GaH_2 moiety in **1** and a broad singlet at δ = 3.95 ppm for the AlH_2 moiety in **2**, respectively. The ^{27}Al NMR spectrum of **2** reveals a broad singlet at δ = 126.5 ppm which partially overlays with the signal of the NMR sample head and the NMR tube material. The structures of **1** and **2**, determined by single-crystal X-ray analysis, are depicted in Figure 2 and Figure S35 (cf. SI), respectively.

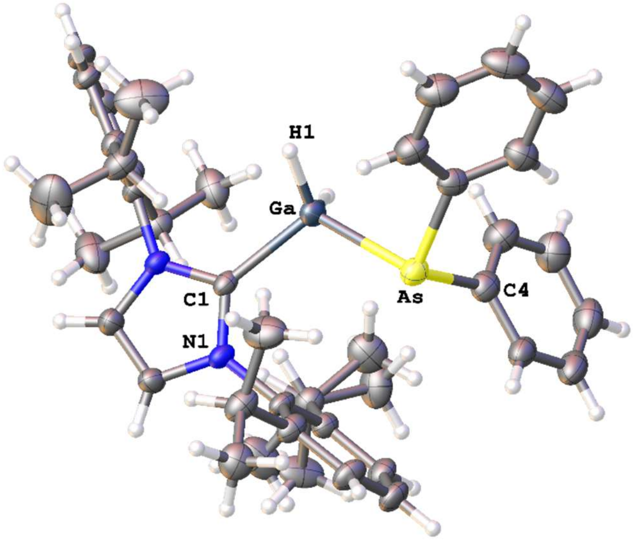


Figure 2: Molecular structure of **1** in the solid state. Selected bond lengths [Å] and angles [°]: Ga–As 2.4659(5), Ga–C1 2.068(3), C1–Ga–As 109.33(8), H1–Ga–As–C4 134.4.

The Al–As bond in **2** shows a length of 2.4929(4) Å which is slightly longer than the Al–As bond length (2.485(2) Å) in $tmp_2AlAsPh_2$[11] (tmp = 2,2,6,6-tetramethylpiperidine). Compound **1** reveals a Ga–As bond length of 2.4659(5) Å which is in good agreement with the sum of the covalent radii (2.46 Å) of Ga and As.[12] Comparing to the few other known examples of monomeric arsanylgallanes, the Ga–As bond in **1** is slightly longer than in $(C_5Me_5)_2GaAs(SiMe_3)_2$ (2.433 Å)[5a] and similar to $(Mes_2As)_3Ga$ (2.433–2.508 Å)[13] and (*t*-Bu)$_2$GaAs(*t*-Bu)$_2$ (2.466 Å).[5b] In contrast, dimeric structures of the type $[R_2GaAsR'_2]_2$ feature larger Ga–As bond distances of 2.558, 2.550 and 2.524 Å in [*n*-Bu_2GaAs(*t*-Bu)$_2$]$_2$,[14] [Me_2GaAs(*t*-Bu)$_2$]$_2$[14] and $[Ph_2GaAs(CH_2SiMe_3)_2]_2$,[4] respectively. These larger Ga–As distances are not the result of the tetracoordination of the Ga atom or the ring formation, since the trimer $[Br_2GaAs(CH_2SiMe_2)_2]_3$ exhibits shorter Ga–As bond lengths of 2.432(2)–2.464(1) Å. A more plausible explanation is the steric repulsion and the ring strain due to endocyclic bond angles of 83–96° in the dimers in contrast to 103–121° in the trimer $[Br_2GaAs(CH_2SiMe_2)_2]_3$. Compounds **1** and **2** reveal an eclipsed conformation with a torsion angle of H1–Ga–As–C4 = 134.4° and H1–Al–As–C4 = 138.1°, respectively. The E'–C1 bond distances in **1** (2.068(3) Å, E' = Ga) and **2** (2.0634(12) Å, E' = Al) are in the range of usual E'–C single bonds and are similar to the Ga–C1 bond length in IDipp·GaH_2PCy_2 (2.090(2) Å,[7] Cy = cyclohexyl) and to the Al-C1 (2.056(2) Å) bond distance in IDipp·AlH_2PH_2,[7] respectively. The C1–Ga–As angle of **1** (109.33(8)°) is in good agreement with the C1–Al–As angle in **2** (109.53(3)°).

To synthesize the parent compounds IDipp·GaH_2AsH_2 (**3**) and IDipp·AlH_2AsH_2 (**4**) two different routes were used (Eq. 2). Similarly to the substituted analogues, compounds **3** and **4** are accessible *via* a salt metathesis reaction between IDipp·E'H_2Cl (E' = Al, Ga) and $KAsH_2$ at –80 °C in THF (route 1). Furthermore, **3** and **4** can be synthesized *via* H_2-

elimination reactions of IDipp·E'H_3 (E' = Al, Ga) and AsH_3 (route 2). For this purpose, an excess of AsH_3 is condensed onto a solution of IDipp·E'H_3 in toluene at –70 °C and stirred for 3 days at this temperature. Unfortunately, **3** and **4** were formed only in minor amounts *via* route 2 according to ^{1}H NMR spectroscopic monitoring (Figure S1 and S2). The low yield of these H_2-elimination reactions is obviously caused by the applied temperature of –70 °C, which significantly slows down the exergonic reaction between IDipp·E'H_3 and AsH_3 but was needed throughout the reaction to keep AsH_3 condensed (vide infra Table 1, process 1). Compound **3** can be isolated at –30 °C in a crystalline yield of 39% *via* route 1. In the mass spectrum (LIFDI-MS) the molecular ion peak of **3** is detected at *m/z* 535.1239 $[M-H]^+$. The ^{1}H NMR spectrum of **3** in C_6D_6 shows a triplet at δ = – 0.18 ppm ($^3J_{H,H}$ = 3.68 Hz) for the AsH_2 moiety and a broad singlet at δ = 4.31 ppm for the GaH_2 moiety. Compound **3** co-crystallizes with the starting material IDipp·GaH_2Cl (for more information see SI). The structure of **3** in solid state is shown in Figure 3. With a distance of 2.4503(12) Å the Ga–As bond length in **3** is between the Ga–As bond lengths in **1** (2.4659(5) Å), $(C_5Me_5)_2GaAs(SiMe_3)_2$ (2.433 Å)[5a] and (*t*-Bu)$_2$GaAs(*t*-Bu)$_2$ (2.466 Å).[5b] The Ga–C1 bond length in **3** (2.0476(17) Å) is shorter compared to the Ga–C1 distance in **1** (2.068(3) Å) which reveals the repulsion between the NHC and the phenyl groups in **1**. Since the H substituents at the As atom had to be restrained no statement about the conformation of **3** can be made. The C1–Ga–As angle in **3** (107.99(6)°) is slightly smaller compared to the substituted analogue **1** (109.35(3)°) and to the phosphorus derivative IDipp·GaH_2PH_2 (109.19(5)°).[7]

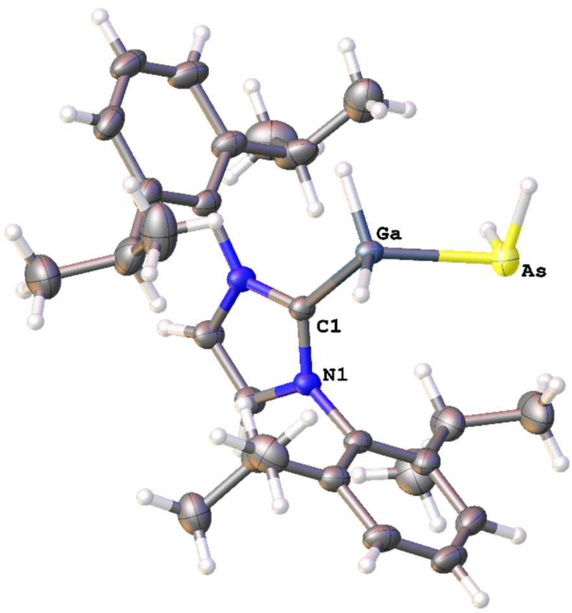


Figure 3: Molecular structure of **3** in the solid state. Selected bond lengths [Å] and angles [°]: Ga–As 2.4503(12), Ga–C1 2.0476(17), C1–Ga–As 107.99(6).

IDipp·AlH_2AsH_2 (**4**) can be isolated at –30 °C as colorless plates in a yield of 40% *via* route 1. The LIFDI-MS spectrum of **4** only shows the fragment ion peak of IDipp due to the decomposition of **4** during the ionization process. The ^{1}H NMR spectrum of **4** in C_6D_6 reveals a triplet at δ = –0.47 ppm ($^3J_{H,H}$ = 3.23 Hz) for the AsH_2 moiety and a broad singlet at δ = 4.1 ppm for the AlH_2 moiety. In the ^{1}H NMR spectrum, besides **4** a side product IDipp·AlH$(AsH_2)_2$ (**5**) can be detected as two doublets of doublets at δ = –0.15 ppm and δ = –0.04 ppm, respectively, for the AsH_2 moieties ($^2J_{H,H}$ = 12.59 Hz, $^3J_{H,H}$ = 2.80 Hz). The signals for these two AsH_2 moieties split in two separated signals because of the prochirality of the entities. The ^{27}Al NMR spectrum of **4** shows a broad signal at δ = 133.5 ppm which is partly superimposed with the signal of the NMR sample head and the NMR tube material. Compound **4** (Figure 4) crystallizes in the monoclinic space group *I*2/*a* and it co-crystallizes with IDipp·AlH$(AsH_2)_2$ (**5**) (for more information see SI). The Al–As distance in **4** is in the range of 2.399(6)–2.473 Å. The Al–C1 bond length (2.060(2) Å) is very similar to the bond length in **1** (2.0634(12) Å) and IDipp·AlH_2PH_2 (2.056(2) Å).[7] The C1–Al–As angle varies between 107.83(17)° and 114.3(2)° because of the disorder of the AsH_2 moiety.

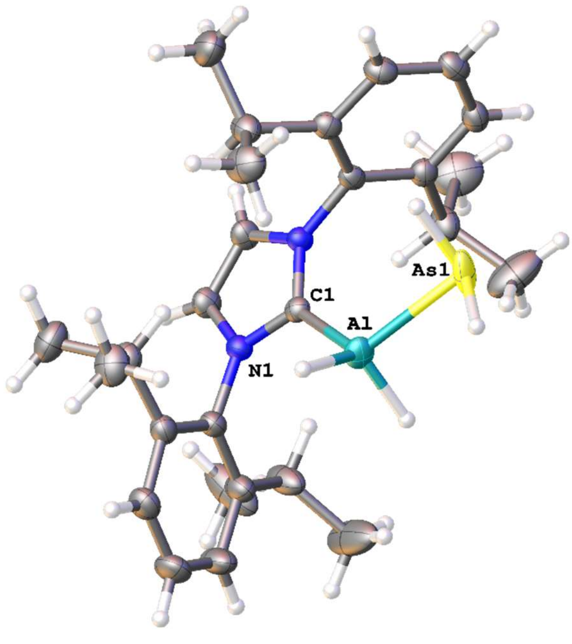
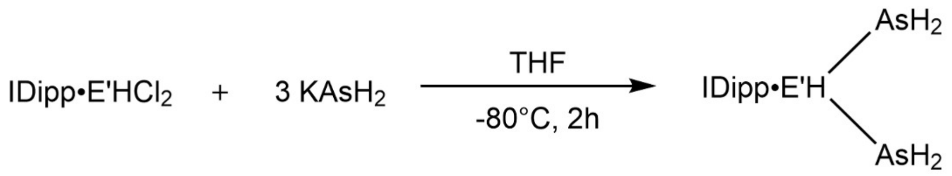


Figure 4: Molecular structure of **4** in solid state (part 1). Selected bond lengths [Å] and angles [°]: Al–As 2.399(6), C1–Al 2.060(2), C1–Al–As 107.83(17)-114.3(2).

The formation of IDipp·AlH$(AsH_2)_2$ (**5**) as a side product led us to the question if the selective synthesis of compounds of such type IDipp·E'H$(AsH_2)_2$ (E' = Al, Ga) is possible and indeed we were able to synthesize **5** and IDipp·GaH$(AsH_2)_2$ (**6**) *via* the corresponding salt metathesis route (Eq. 3) which was supported by DFT computations (see Table 1, process 10). In fact, such branched alkane-like parent compounds are so far unknown and only additional donor stabilized compounds of the type $(Dipp_2Nacnac)E'(EH_2)_2$ ($Dipp_2Nacnac$ = HC[C(Me)N(Ar)]$_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) exist for E = N,[15a] P, As.[15b]



(3)

E' = Al (**5**), Ga (**6**)

Compound **5** and **6** crystallize as colorless thin needles at –30 °C in a yield of 42% and 36%, respectively. The LIFDI-MS spectrum of **5** shows a fragment ion peak of IDipp due to decomposition of **5** during the ionization process. In the mass spectrum of **6** (LIFDI-MS) the molecular ion peak is detected at *m/z* 611.0607 $[M\text{-}H]^+$. Solutions of **5** show a strong tendency towards decomposition. The ^1H NMR spectrum of **5** in toluene-d_8 at –80 °C reveals two doublet of doublets at δ = -0.09 ppm and δ = 0.14 ppm ($^2J_{H,H}$ = 12.40 Hz, $^3J_{H,H}$ = 2.71 Hz) for the two AsH_2 moieties, a broad singlet at δ = 4.82 ppm for the AlH moiety, as well as the formation of $IDippH_2$ and free IDipp as decomposition products. In the ^1H NMR spectrum of **6** in C_6D_6 the signals for the AsH_2 moieties and the GaH moiety are downfield shifted compared to **5** to δ = 0.20 ppm, 0.38 ppm ($^2J_{H,H}$ = 12.77 Hz, $^3J_{H,H}$ = 3.46 Hz) and δ = 5.09 ppm. Compound **5** and **6** crystallize from concentrated *n*-hexane solutions as very thin colorless plates. Because of the thinness of the crystals the single-crystal X-ray analysis of **6** was only possible to a theta range of 47°. Nevertheless, it was possible to solve the structure and prove the framework of the heavy atoms of **6** (see Figure S42). Compound **5** co-crystallizes with 6% of the starting material IDipp·$AlHCl_2$ (see Figure S41). Compound **5** and **6** crystallize in the monoclinic space group *I*2/*a*. The molecular structure of **5** in solid state is depicted in Figure 5.

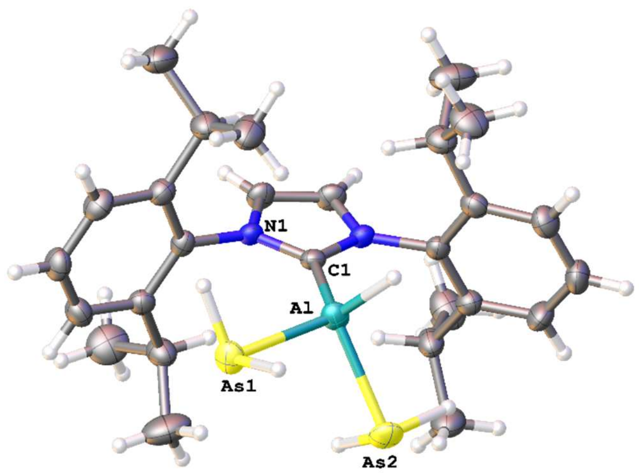


Figure 5: Molecular structure of **5** in solid state. Selected bond lengths [Å] and angles [°]: Al–As1 2.451(4), Al–As2 2.474(3), Al–C1 2.066(3), As1–Al–C1 114.38(10), As2–Al–C1 114.24(9).

The E'–As distances in **5** and **6** are in the range of 2.451(4) – 2.511(6) Å (**5**) and 2.4412(19) – 2.446(2) Å (**6**), respectively, and with this similar to the Al–As bonds in $(Dipp_2Nacnac)Al(AsH_2)_2$ ($Dipp_2Nacnac$ = $HC[C(Me)N(Ar)]_2$, Ar = 2,6-$i$$Pr_2C_6H_3$).[14] The E'–C1 bond lengths (Al–C1 = 2.066(3) Å, Ga–C1 = 2.064(9) Å) are not heavily affected by the presence of a second AsH_2 moiety compared to **3** (2.0476(17) Å) and **4** (2.060(2) Å), respectively. The C1–E'–As angles are 114.24(9)° and 114.38(10)° for **5** as well as 111.7(2)° and 113.3(2)° for **6**.

Interestingly, during the synthesis of the phosphorus analogue IDipp·E'H_2PH_2 (E' = Al, Ga) *via* the reaction of IDipp·E'H_2Cl with $NaPH_2$ we did not find any sign for the formation of IDipp·E'H$(PH_2)_2$ (E' = Al, Ga) as a side product.[7] A possible pathway for the formation of **5** as a side product in the arsenic case is the reaction of the formed product IDipp·E'H_2AsH_2 with *in situ* formed AsH_3 in an H_2-elimination reaction. Computations confirm that this route is possible in the arsenic case (Table 1, process 7) while it is more unlikely for phosphorus (Table 1, process 8), which agrees with our experimental observations.

Likewise to **5** and **6**, we were able to synthesize the parent branched compounds IDipp·GaH$(PH_2)_2$ (**7**) and IDipp·AlH$(PH_2)_2$ (**8**) selectively *via* the salt metathesis reaction of IDipp·E'HCl_2 and $NaPH_2$ in Et_2O (Table 1, process 9). Compounds **7** and **8** can be isolated at –30 °C in a yield of 57% and 48%, respectively. The ^{1}H NMR spectrum of **7** in C_6D_6 shows a doublet which splits into multipletts at δ = 0.54 ppm ($^1J_{P,H}$ = 175 Hz) for the PH_2 moieties and a broad singlet at δ = 4.81 ppm for the GaH moiety. In the ^{1}H NMR spectrum of **8** in toluene-d_8 at –80 °C the PH_2 moieties can be detected at δ = 0.42 ppm ($^1J_{P,H}$ = 175.4 Hz) as a doublet of multiplets. The AlH moiety can be detected as a broad singlet at δ = 4.56 ppm. The ^{31}P NMR spectra of **7** and **8** show a triplet of multiplets at δ = -255.4 ppm (**7**, $^1J_{P,H}$ = 175 Hz, $^2J_{P,H}$ = 18.17 Hz) and at δ = -270.8 ppm (**8**, $^1J_{P,H}$ = 175.4 Hz, $^2J_{P,H}$ = 15.48 Hz), respectively. Due to the prochirality of the PH_2 groups in **7** and **8** the signals in the ^{1}H and ^{31}P NMR spectra reveal a fine splitting which could not be resolved. Like **5**, solutions of **8** show a strong tendency towards decomposition. Compound **7** and **8** crystallize in the monoclinic space group *I2/a*. The molecular structures of **7** and **8** in solid state are shown in Figure 6 and Figure S44, respectively. The E'–P bond distances are shorter compared to the arsenic analogues with 2.3437(10) – 2.3574(9) Å (**7**) and 2.3075(10) – 2.3418(9) Å (**8**). The E'–C1 bond lengths are again not affected by the change from arsenic substituents to phosphorus substituents on the E' atom. The Ga–C1 bond length is 2.075(3) Å and the Al–C1 bond length is 2.066(2) Å. The C1–E'–P angles (112.38(7)° and 113.68(7)° for **7**; 112.04(6)° and 113.91(6)° for **8**) are comparable to the C1–E'–As angles in the arsenic analogues **5** and **6**.

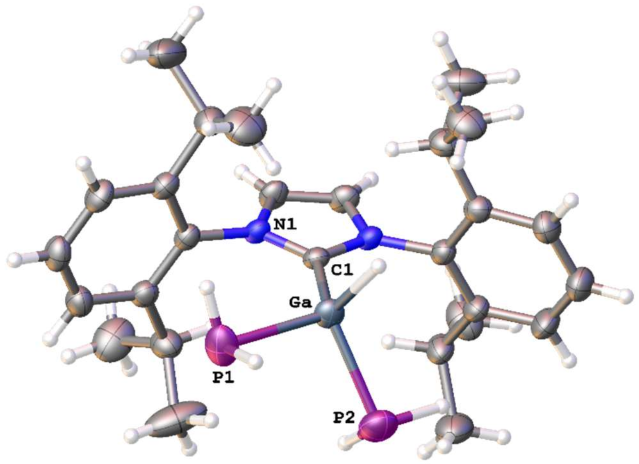


Figure 6: Molecular structure of **7** in solid state. Selected bond lengths [Å] and angles [°]: Ga–P1 2.3574(9), Ga–P2 2.3437(10), Ga–C1 2.075(3), P1–Ga–C1 113.68(7), P2–Ga–C1 112.38(7).

Computational studies indicate that the salt elimination route *via* solid potassium chloride formation is highly exothermic and exergonic both for the parent and the substituted compounds which could be experimentally verified by the synthesis of **1** – **4**. (Table 1, process 3 and 4). The hydrogen elimination route *via* the reaction of IDipp·E'H_3 with AsH_3 (Table 1, process 1) is exothermic and at 298 K exergonic by about 20 kJ mol^{-1}, but slightly endergonic (2-7 kJ mol^{-1}) for the reaction with diphenylarsine (Table 1, process 2), which reflects that via route 2 compounds **1** and **2** couldn't be accessed. Compounds **1** – **4** are predicted to be stable with respect to IDipp dissociation with formation of $(E'H_2AsH_2)_n$ polymers, which were modeled by the formation of the trimer[15] (Table 1, process 5 and 6). The interaction of IDipp·E'H_2AsH_2 with an *in situ* formed arsine (Table 1, process 7) is also exergonic (Al: -10.1 kJ mol^{-1}, Ga: -13.8 kJ mol^{-1}) and may explain the formation of **5** as a side product during the synthesis of IDipp·AlH_2AsH_2 *via* route 1. In contrast, a similar reaction for the phosphorus analogues (Table 1, process 8) is energetically less favored and has Gibbs energies close to zero at 298 K. Nevertheless, computations show that route 1 is an even more exergonic reaction for the synthesis of branched pnictogenylalanes and –gallanes as for the synthesis of the linear compounds (Table 1, process 9 and 10). This is confirmed by the synthesis of the unique molecules IDipp·E'H$(AsH_2)_2$ (**5**: Al, **6**: Ga) and IDipp·E'H$(PH_2)_2$ (**7**: Ga, **8**: Al) *via* route 1.

Table 1. Thermodynamic characteristics of studied reactions (gas phase compounds if not noted otherwise). Standard enthalpies ΔH^o_{298} and standard Gibbs energies ΔG^o_{298} in kJ mol^{-1}, standard entropies ΔS^o_{298} in J mol^{-1} K^{-1}. B3LYP/def2-TZVP level of theory.

N	Process	E = Al			E = Ga		
		ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}	ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
1	IDipp·E'H_3 + AsH_3 = H_2 + IDipp·E'H_2AsH_2	-27.6	-26.3	-19.7	-29.2	-26.3	-21.4
2	IDipp·E'H_3 + $AsHPh_2$ = H_2 + IDipp·E'H_2AsPh_2	-11.2	-61.8	7.2	-15.7	-60.6	2.3
3	IDipp·E'H_2Cl + $KAsH_2$ = $KCl_{(s)}$ + IDipp·E'H_2AsH_2	-227.7	-179.8	-174.1	-261.9	-182.8	-207.4
4	IDipp·E'H_2Cl + $KAsPh_2$·dioxane = $KCl_{(s)}$ + dioxane + IDipp·E'H_2AsPh_2	-97.2	98.6	-126.6	-134.2	96.7	-163.1
5	IDipp·E'H_2AsH_2 = $^1/_3$(E'H_2AsH_2)$_3$ + IDipp	65.4	76.5	42.6	52.9	75.4	30.4
6	IDipp·E'H_2AsPh_2 = $^1/_3$(E'Ph_2AsH_2)$_3$ + IDipp	44.5	70.3	23.6	33.8	75.1	11.4
7	IDipp·E'H_2AsH_2 + AsH_3 = H_2 + IDipp·E'H(AsH_2)$_2$	-23.0	-43.3	-10.1	-25.4	-39.0	-13.8
8	IDipp·E'H_2AsH_2 + PH_3 = H_2 + IDipp·E'H(PH_2)$_2$	-13.0	-38.5	-1.6	-11.9	-40.6	0.2
9	IDipp·E'HCl_2 + 2$NaPH_2$ = 2$NaCl_{(s)}$ + IDipp·E'(PH_2)$_2$	-468.6	-354.8	-362.8	-536.0	-343.8	-433.5
10	IDipp·E'HCl_2 + 2$KAsH_2$ = 2$KCl_{(s)}$ + IDipp·E'(AsH_2)$_2$	-461.8	-367.9	-352.1	-535.9	-352.9	-430.7

6.3. Conclusion

The results show that regardless of the rather low E'-As bond stability (E' = Al, Ga) we succeeded in the synthesis of the first monomeric parent arsanylalanes and –gallanes stabilized only by a LB. Besides the synthesis of the organo-substituted arsenic derivatives *via* salt metathesis, it was shown that the monomeric parent compounds can be obtained *via* salt metathesis and H_2-eliminations, respectively. The latter method is however incomplete, so that the first one is the preferred one. Furthermore, in contrast to the synthesis of the corresponding phosphanylalanes and -gallanes, the As derivatives exhibit a different reactivity to form the branched side products IDipp·E'H(AsH_2)$_2$ (E' = Al, Ga) obviously by AsH_3-caused substitution reactions. This kind of alkane-like branched parent derivatives had been unknown before and subsequently the double substituted parent compounds IDipp·E'H(EH_2)$_2$ (E' = Al, Ga; E = As, P) could be selectively synthesized *via* salt metathesis reactions. They may serve as potential chelating ligands in coordination chemistry, which is currently investigated. The monomeric compounds IDipp·E'H_2AsH_2 (E' = Al, Ga) represent unprecedented parent arsanylalanes and –gallanes without any primarily sterical stabilization by a substituent but by a LB. In further studies their reaction behavior towards catenation and as precursor for CVD-processes to obtain Group 13/15 materials will be focused on.

6.4. References

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6.5. Supporting Information

6.5.1. Experimental section

General procedure

All reactions and subsequent manipulations were performed under an argon atmosphere in a Braun glovebox or using standard Schlenk techniques. NMR spectra were recorded on a Bruker Avance 400 and a Bruker Avance 300. Deuterated solvents (C_6D_6, toluene-d_8) were distilled, and oxygen removed via freeze-pump-thaw procedure prior use. Chemical shifts are listed in parts per million (ppm) and were referenced to external standards (^{1}H and ^{13}C: $Si(CH_3)_3$, ^{27}Al: $Al(NO_3)_3$, ^{31}P: 85% H_3PO_4). Coupling constants are quoted in Hertz. Elemental analysis (CHN) were determined using in-house facility. LIFDI-MS spectra were recorded with a Jeol AccuTOF GCX.

IDipp (1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene)[1], $LiGaH_4$[2], $(NMe_3)_2{\cdot}AlH_2Cl$[3], $KAsPh_2{\cdot}$dioxane[4], $KAsH_2$[5], IDipp·GaH_3, IDipp·AlH_3[6] IDipp·GaH_2Cl, IDipp·AlH_2Cl, IDipp·$GaHCl_2$ and IDipp·$AlHCl_2$[7] were prepared according to published procedures. $GaCl_3$ was purchased from Sigma Aldrich and sublimated prior use. $LiAlH_4$ was purchased from Sigma Aldrich and used as received. All solvents were purified with a MBRAUN SPS-800 and oxygen removed via freeze-pump-thaw procedure before use.

Synthesis of IDipp·GaH_2Cl

A slurry of IDipp·$GaCl_3$ (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene) (180 mg, 0.300 mmol, 1 eq) in 10 mL toluene was added slowly to a solution of IDipp·GaH_3 (280 mg, 0.610 mmol, 2 eq) in 10 mL toluene. The slightly gray suspension was warmed to 55 °C and stirred for 6 hours. After filtration over a celite pad the solution was concentrated and stored at –30 °C to afford IDipp·GaH_2Cl as colorless crystals (280 mg, 62%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 1.00 (d, 12H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-C*H*$_3$), 1.39 (d, 12H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-C*H*$_3$), 2.67 (sept, 4H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-C*H*), 4.66 (s, 2H, Ga*H*$_2$), 6.44 (s, 2H, NC*H*C*H*N), 7.08 (d, 4H, $^3J_{H,H}$ = 7.73 Hz, aryl-C$_{meta}$*H*), 7.22 (t, 2H, $^3J_{H,H}$ = 7.73 Hz, aryl-C$_{para}$*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 23.1 (*i*Pr-*C*H$_3$), 25.4 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H(CH$_3$)$_2$), 124.2 (N*C*H*C*HN), 124.4 (aryl-*C*$_{meta}$H), 131.0 (aryl-*C*$_{para}$H), 134.1 (aryl-*C*$_{ipso}$), 145.7 (aryl-*C*$_{ortho}$), 174.4 (N*C*N).

CHN: Anal. Calcd. (%) for $C_{27}H_{38}N_2GaCl$ (495.79 g/mol): C 65.41, H 7.73, N 5.65; Found: C 67.27, H 7.41, N 5.67 (found values differ because of co-crystallization of IDipp·GaH_3).

Synthesis of IDipp·AlH_2Cl

A solution of IDipp (1.06 g, 2.74 mmol, 1 eq) in 10 mL Et_2O was added dropwise to a suspension of $(NMe_3)_2{\cdot}AlH_2Cl$ (500 mg, 2.74 mmol, 1 eq) in 10 mL Et_2O at –60 °C. The suspension was stirred for 3 hours at room temperature. After removing the solvent *in vacuo* the off-white residue was suspended in toluene and filtered over a celite pad. The solution was concentrated and stored at –30 °C to afford IDipp·AlH_2Cl as colorless crystals (700 mg, 56%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 0.97 (d, 6H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 1.00 (d, 6H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 1.41 (d, 12H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*$_3$), 2.68 (sept, 4H, $^3J_{H,H}$ = 7.01 Hz, *i*Pr-C*H*), 3.86 (s br, 2H, Al*H*$_2$Cl), 6.43 (s, 2H, NC*H*C*H*N), 7.08 (d, 4H, $^3J_{H,H}$ = 7.83 Hz, aryl-C$_{meta}$*H*), 7.22 (t, 2H, $^3J_{H,H}$ = 7.83 Hz, aryl-C$_{para}$*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 22.9 (*i*Pr-*C*H$_3$), 25.5 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H(CH$_3$)$_2$), 124.2 (N*C*H*C*HN), 124.3 (aryl-*C*$_{meta}$H), 131.2 (aryl-*C*$_{para}$H), 133.7 (aryl-*C*$_{ipso}$), 145.6 (aryl-*C*$_{ortho}$), 150.0 (N*C*N).

^{27}Al NMR (104.26 MHz, C_6D_6, 298 K): δ = 118.0 (s, *Al*H$_2$Cl).

^{27}Al{^{1}H} NMR (104.26 MHz, C_6D_6, 298 K): δ = 118.0 (s, *Al*H$_2$Cl).

CHN: Anal. Calcd. (%) for $C_{27}H_{38}N_2AlCl$ (453.05 g/mol): C 71.58, H 8.45, N 6.18; Found: C 69.65, H 7.67, N 5.97 (found values differ because of decomposition).

Synthesis of IDipp·GaHCl$_2$

A solution of IDipp·GaH$_3$ (120 mg, 0.270 mmol, 1 eq) in 10 mL toluene was added slowly to a suspension of IDipp·GaCl$_3$ (300 mg, 0.530 mmol, 2 eq) in 10 mL toluene. The white suspension was stirred for 16 hours at 55 °C. After filtration over a celite pad the solution was concentrated and stored at –30 °C to afford IDipp·GaHCl$_2$ as colorless crystals (210 mg, 49%).

^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ = 0.97 (d, 6H, $^{3}J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.00 (d, 6H, $^{3}J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.40 (d, 6H, $^{3}J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.42 (d, 6H, $^{3}J_{H,H}$ = 6.88, *i*Pr-C*H*$_3$), 2.68 (sept, 4H,$^{3}J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*), 4.66 (s, 1H, Ga*H*), 6.46 (s, 2H, NC*H*C*H*N), 7.08 (d, 4H, $^{3}J_{H,H}$ = 7.92 Hz, aryl-C$_{meta}$*H*), 7.22 (t, 2H, $^{3}J_{H,H}$ = 7.92 Hz, aryl-C$_{para}$*H*).

CHN: Anal. Calcd. (%) for $C_{27}H_{37}N_2GaCl_2$ (530.23 g/mol): C 61.16, H 7.03, N 5.28; Found: C 62.08, H 6.88, N 5.21.

Synthesis of IDipp·AlHCl$_2$

A solution of IDipp·AlH$_3$ (120 mg, 0.290 mmol, 1 eq) in 5 mL toluene was added slowly to a suspension of IDipp·AlCl$_3$ (300 mg, 0.570 mmol, 2 eq) in 5 mL toluene. The white suspension was stirred for 3 days at room temperature. After centrifugation for 10 min at 2000 rpm the clear supernatant was decanted off the white residue, concentrated and stored –30 °C to afford IDipp·AlHCl$_2$ as colorless crystals. (200 mg, 48%).

^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ = 0.98 (d, 12H, $^{3}J_{H,H}$ = 6.92 Hz, *i*Pr-C*H*$_3$), 1.42 (d, 12H, $^{3}J_{H,H}$ = 6.92 Hz, *i*Pr-C*H*$_3$), 2.69 (sept, 4H, $^{3}J_{H,H}$ = 6.92 Hz, *i*Pr-C*H*), 6.41 (s, 2H, NC*H*C*H*N), 7.08 (d, 4H, $^{3}J_{H,H}$ = 7.90 Hz, aryl-C$_{meta}$*H*), 7.23 (t, 2H, $^{3}J_{H,H}$ = 7.90 Hz, aryl-C$_{para}$*H*).

CHN: Anal. Calcd. (%) for $C_{27}H_{37}N_2AlCl_2$ (487.49 g/mol): C 66.52, H 7.65, N 5.75; Found: C 66.08, H 7.57, N 5.56.

Synthesis of IDipp·GaH_2AsPh_2 (1)

A solution of IDipp·GaH_2Cl (50 mg, 0.10 mmol, 1 eq) in 5 mL Et_2O was added to a solution of $KAsPh_2$·dioxane (Ph = C_6H_5) (70 mg, 0.20 mmol, 2 eq) in 10 mL Et_2O at –80 °C. The yellow suspension was warmed up to room temperature overnight whereby the color changed to white. The solvent was removed *in vacuo* and the white residue suspended in *n*-hexane. After filtration over a celite pad the solution was concentrated and stored at –30 °C to afford **1** as colorless plates (43 mg, 63%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 0.99 (d, 12H, $^3J_{H,H}$ = 6.97 Hz, *i*Pr-C*H*$_3$), 1.36 (d, 12H, $^3J_{H,H}$ = 6.97 Hz, *i*Pr-C*H*$_3$), 2.72 (sept, 4H, $^3J_{H,H}$ = 6.97 Hz, *i*Pr-C*H*), 4.28 (s, 2H, Ga*H*$_2$), 6.45 (s, 2H, NC*H*C*H*N), 6.94-7.04 (m, 6H, C_6H_5), 7.07 (d, 4H, $^3J_{H,H}$ = 7.79 Hz, aryl-$C_{meta}H$), 7.21 (t, 2H, $^3J_{H,H}$ = 7.79 Hz, aryl-$C_{para}H$), 7.55-7.58 (m, 4H, C_6H_5).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 22.7 (*i*Pr-*C*H$_3$), 25.0 (*i*Pr-*C*H$_3$), 28.7 (*i*Pr-*C*H(CH_3)$_2$), 123.9 (aryl-C_{meta}), 124.1 (N*C*H*C*HN), 125.2 (C_6H_5), 130.5 (aryl-C_{para}), 134.5 (C_6H_5), 135.6 (aryl-C_{ipso}) 143.6 (C_6H_5), 145.2 (aryl-C_{ortho}), 178.9 (N*C*N).

CHN: Anal. Calcd. (%) for $C_{39}H_{48}N_2GaAs$ (689.47 g/mol): C 67.94, H 7.02, N 4.06; Found: C 68.23, H 6.97, N 3.59.

LIFDI-MS: (m/z): 688.2142 $[M-H]^+$ (100 %).

Synthesis of IDipp·AlH_2AsPh_2 (2)

A solution of IDipp·AlH_2Cl (50 mg, 0.11 mmol, 1 eq) in 10 mL Et_2O was added to a solution of $KAsPh_2$·dioxane (79 mg, 0.22 mmol, 2 eq) in 10 mL Et_2O at –80 °C. The yellow suspension was warmed up to room temperature overnight. The solvent was removed and the yellow residue was suspended in *n*-hexane and filtrated over a celite pad. The yellow solution was concentrated and stored at –30 °C to afford **2** as pale yellow blocks (37 mg, 52%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 0.97 (d, 12H, $^3J_{H,H}$ = 6.93 Hz, *i*Pr-C*H*$_3$), 1.34 (d, 12H, $^3J_{H,H}$ = 6.93 Hz, *i*Pr-C*H*$_3$), 2.69 (sept, 4H, $^3J_{H,H}$ = 6.93 Hz, *i*Pr-C*H*), 3.95 (s br, 2H, Al*H*$_2$), 6.42 (s, 2H, NC*H*C*H*N), 6.91-7.02 (m, 6H, C_6H_5), 7.05 (d, 4H, $^3J_{H,H}$ = 7.87 Hz, aryl-$C_{meta}H$), 7.19 (t, 2H, $^3J_{H,H}$ = 7.87 Hz, aryl-$C_{para}H$), 7.56-7.61 (m, 4H, C_6H_5).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 23.0 (*i*Pr-*C*H$_3$), 25.4 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H(CH_3)$_2$), 124.5 (aryl-C_{meta}), 125.4 (N*C*H*C*HN), 131.0 (aryl-C_{para}), 134.6 (C_6H_5), 136.0 (aryl-C_{ipso}), 142.7 (C_6H_5), 145.7 (aryl-C_{ortho}), 175.8(N*C*N).

^{27}Al NMR (104.26 MHz, C_6D_6, 298 K): δ = 126.5 (s br, *Al*H$_2$).

^{27}Al{^{1}H} NMR (104.26 MHz, C_6D_6, 298 K): δ = 126.5 (s br, *Al*H$_2$).

CHN: Anal. Calcd. (%) for $C_{39}H_{48}N_2AlAs$ (646.73 g/mol): C 72.43, H 7.48, N 4.33; Found: C 72.59, H 7.39, N 4.28.

LIFDI-MS: does not show a molecular ion peak due to decomposition during the ionization process.

Synthesis of IDipp·GaH$_2$AsH$_2$ (3)

Route 1: A solution of IDipp·GaH$_2$Cl (50 mg, 0.10 mmol, 1 eq) in 5 mL THF was added to a suspension of KAsH$_2$ (24 mg, 0.20 mmol, 2 eq) in 5 mL THF at –80 °C. The reaction mixture was stirred for 1 hour at –80 °C. The solvent was removed *in vacuo* and the off-white residue was suspended in *n*-hexane. After centrifuging for 10 minutes with 2000 rpm, the colorless supernatant was concentrated and stored at –30 °C to afford **3** as dull colorless needles (21 mg, 39%).

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): δ = -0.18 (t, 2H, $^3J_{H,H}$ = 3.68 Hz, AsH_2), 1.00 (d, 12H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-CH_3), 1.42 (d, 12H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-CH_3), 2.68 (sept, 4H, $^3J_{H,H}$ = 6.96 Hz, *i*Pr-C*H*), 4.31 (s br, 2H, GaH_2), 6.44 (s, 2H, NC*H*C*H*N), 7.10 (d, 4H, $^3J_{H,H}$ = 7.78 Hz, aryl-C$_{meta}$*H*), 7.23 (t, 2H, $^3J_{H,H}$ = 7.78 Hz, aryl-C$_{para}$*H*).

^{13}C NMR (100.66 MHz, C_6D_6, 298 K): δ = 22.8 (*i*Pr-*C*H$_3$), 25.0 (*i*Pr-*C*H$_3$), 28.7 (*i*Pr-*C*H(CH$_3$)$_2$), 123.7 (aryl-*C*$_{meta}$), 124.1 (N*C*H*C*HN), 130.6 (aryl-*C*$_{para}$), 134.4 (aryl-*C*$_{ipso}$), 145.3 (aryl-*C*$_{ortho}$).

CHN: Anal. Calcd. (%) for $C_{27}H_{40}N_2GaAs$ (537.28 g/mol): C 60.36, H 7.50, N 5.21; Found: C 60.86, H 7.35, N 5.12.

LIFDI-MS (m/z): 535.1239 $[M-H]^+$ (7 %).

Route 2: A solution of IDipp·GaH$_3$ (100 mg, 0.22 mmol) in 10 mL toluene was cooled to –70 °C with a cryostat. Holding this temperature AsH$_3$ was condensed on the solution for 2 minutes using the construction shown below. The dull reaction mixture was stirred at –70 °C for 24 hours. The temperature was slowly increased in 5 °C steps to evaporate the AsH$_3$ which was subsequently destroyed by bubbling through a KMnO$_4$ solution at 0 °C. The resulting dull toluene solution was centrifuged and decanted to afford a clear solution. Any try to crystallize compound **3** via route 2 failed due to insufficient conversion (see reaction NMR; Figure S1).

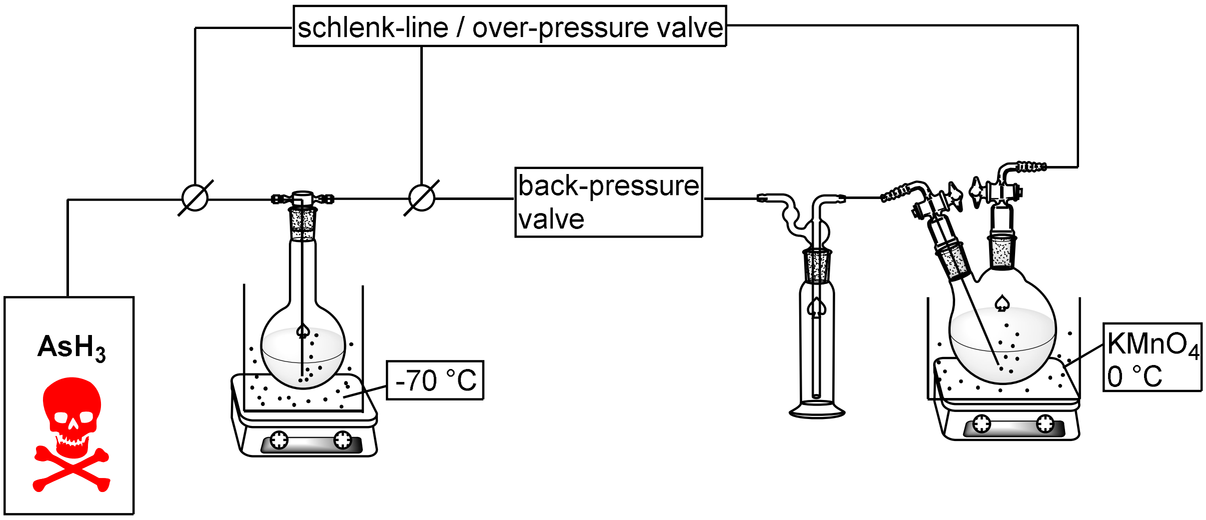
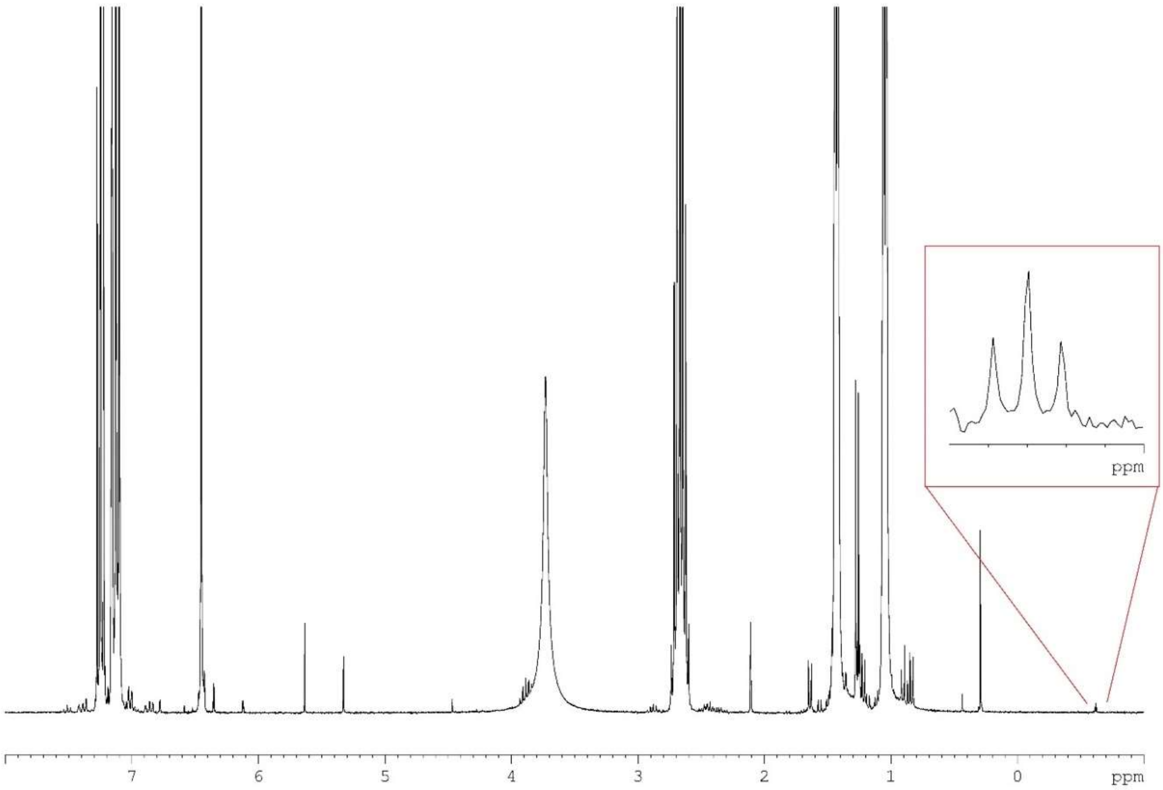


Figure S1: Reaction ^{1}H NMR spectrum of **3** via route 2 in C_6D_6 at 298 K.



Synthesis of IDipp·AlH_2AsH_2 (4)

Route 1: A solution of IDipp·AlH_2Cl (50 mg, 0.11 mmol, 1 eq) in 5 mL THF was added to a suspension of $KAsH_2$ (26 mg, 0.22 mmol, 2 eq) in 5 mL THF at –80 °C. An instant discoloration of the yellow suspension can be seen during the combination of the starting materials. After the addition of IDipp·AlH_2Cl the solvent was removed immediately at below –30 °C. The yellowish residue was suspended in *n*-hexane and centrifuged for 10 minutes with 2000 rpm. The colorless supernatant was concentrated and stored at –30 °C to afford **4** as dull colorless plates (22 mg, 40%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = -0.47 (t, 2H, $^3J_{H,H}$ = 3.23 Hz, As*H*$_2$), 0.95 (d, 12H, $^3J_{H,H}$ = 6.89 Hz, *i*Pr-C*H*$_3$), 1.43 (d, 12H, $^3J_{H,H}$ = 6.89 Hz, *i*Pr-C*H*$_3$), 2.68 (sept, 4H, $^3J_{H,H}$ = 6.89 Hz, *i*Pr-C*H*), 4.10 (s br, 2H, Al*H*$_2$), 6.41 (s, 2H, NC*H*C*H*N), 7.09 (d, 4H, $^3J_{H,H}$ = 7.72 Hz, aryl-C_{meta}*H*), 7.23 (t, 2H, $^3J_{H,H}$ = 7.72 Hz, aryl-C_{para}*H*).

^{13}C NMR (100.61 MHz, C_6D_6, 298 K): δ = 23.0 (*i*Pr-*C*H$_3$), 25.7 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H(CH$_3$)$_2$), 124.7 (aryl-C_{meta}), 127.3 (N*C*H*C*HN), 131.4 (aryl-C_{para}), 134.3 (aryl-C_{ipso}), 145.7 (aryl-C_{ortho}).

^{27}Al NMR (104.26 MHz, C_6D_6, 298 K): δ = 133.5 (s, *Al*H$_2$).

^{27}Al{^{1}H} NMR (104.26 MHz, C_6D_6, 298 K): δ = 133.5 (s, *Al*H$_2$).

CHN: Anal. Calcd. (%) for $C_{27}H_{40}N_2AlAs$ (494.35 g/mol): C 65.58, H 8.15, N 5.66; Found: C 69.06, H 8.07, N 5.77 (found values differ because of co-crystallization of IDippH$_2$ and IDipp·AlH(AsH$_2$)$_2$).

LIFDI-MS: does not show a molecular ion peak due to decomposition during the ionization process.

Route 2: A solution of IDipp·AlH$_3$ (130 mg, 0.31 mmol) in 10 mL toluene was cooled to –70 °C with a cryostat. Holding this temperature AsH_3 was condensed on the solution for 2 minutes using the construction shown above. The dull reaction mixture was stirred at –70 °C for 24 hours. The temperature was slowly increased in 5 °C steps to evaporate the AsH_3 which was subsequently destroyed by bubbling through a $KMnO_4$ solution at 0 °C. The resulting pale beige toluene solution was centrifuged and decanted to afford a clear solution. Any try to crystallize compound **4** via route 2 failed due to insufficient conversion and decomposition of the starting material (see reaction NMR; Figure S2).

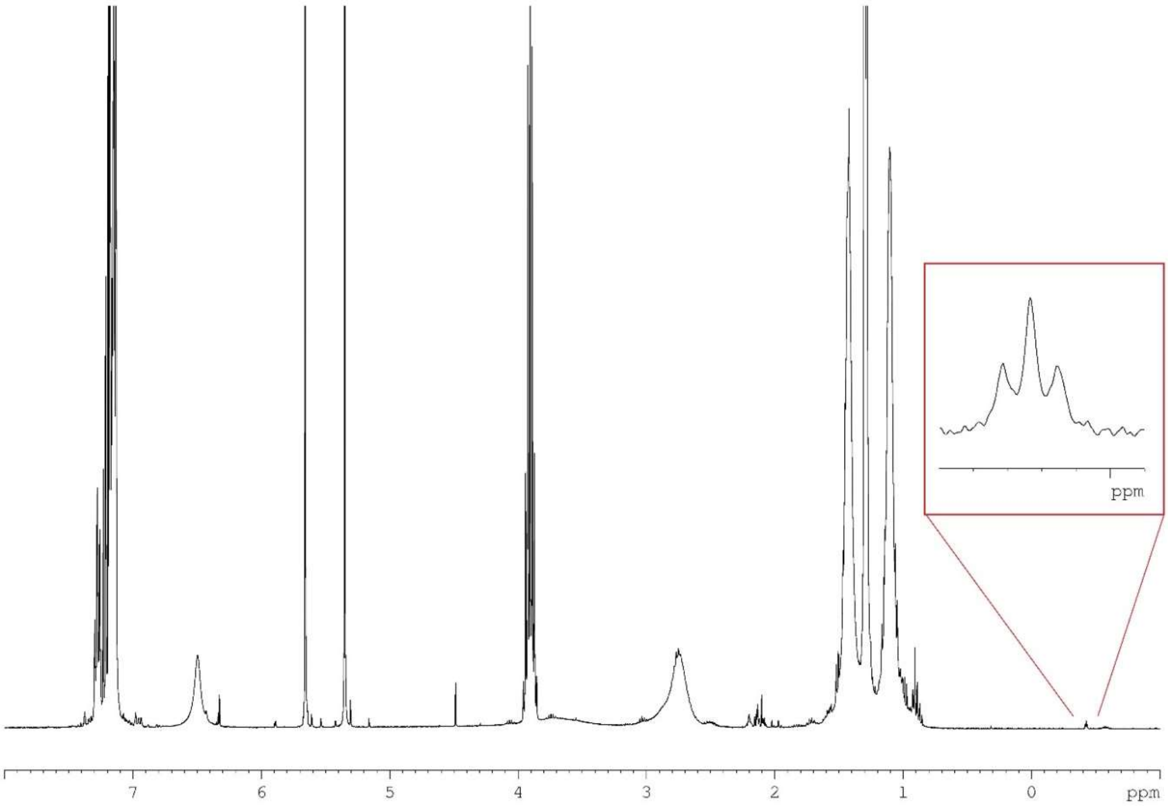


Figure S2: Reaction ^{1}H NMR spectrum of **4** in C_6D_6 at 298 K.

Synthesis of IDipp·AlH(AsH$_2$)$_2$ (5)

A solution of IDipp·AlHCl$_2$ (50 mg, 0.10 mmol, 1 eq) in 5 mL THF was added to a suspension of $KAsH_2$ (36 mg, 0.30 mmol, 3 eq) in 10 mL THF at –80 °C. The off-white suspension was stirred for 3 hours at –40 °C. The solvent was removed *in vacuo* and the off-white solid was suspended in *n*-hexane and centrifuged for 10 minutes at 2000 rpm. The colorless supernatant was concentrated and stored at –30 °C to afford **6** as colorless thin needles (24 mg, 42%).

^{1}H NMR (400.13 MHz, toluene-d$_8$, 213 K): δ = -0.09 (dd, 2H, $^{2}J_{H,H}$ = 12.40 Hz, $^{3}J_{H,H}$ = 2.71 Hz, AsH_2), 0.14 (dd, 2H, $^{2}J_{H,H}$ = 12.40 Hz, $^{3}J_{H,H}$ = 2.71 Hz, AsH_2), 0.96 (d, 12H, $^{3}J_{H,H}$ = 6.88 Hz, *i*Pr-CH_3), 1.47 (d, 12H, $^{3}J_{H,H}$ = 6.88 Hz, *i*Pr-CH_3), 2.68 (sept, 4H, $^{3}J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*), 4.82 (s br, 1H, Al*H*), 6.24 (s, 2H, NC*H*C*H*N), 7.12 (d, 4H, $^{3}J_{H,H}$ = 7.80 Hz, aryl-C$_{meta}$*H*), 7.29 (t, 2H, $^{3}J_{H,H}$ = 7.80 Hz, aryl-C$_{para}$*H*).

LIFDI-MS: does not show a molecular ion peak due to decomposition during the ionization process.

Synthesis of IDipp·GaH(AsH$_2$)$_2$ (6)

A solution of IDipp·GaHCl$_2$ (50 mg, 0.090 mmol, 1 eq) in 5 mL THF was added to a suspension of KAsH$_2$ (33 mg, 0.28 mmol, 3 eq) in 10 mL THF at –80 °C. The white suspension was stirred for 2 hours at –40 °C. The solvent was removed *in vacuo* to afford an off-white powder which was suspended in *n*-hexane and centrifuged for 10 minutes at 2000 rpm. The colorless supernatant was concentrated and stored at –30 °C to afford **5** as colorless thin plates (20 mg, 36%).

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): δ = 0.20 (dd, 2H, $^{2}J_{H,H}$ = 12.77 Hz, $^{3}J_{H,H}$ = 3.46 Hz, As*H*$_2$), 0.38 (dd, 2H, $^{2}J_{H,H}$ = 12.77 Hz, $^{3}J_{H,H}$ = 3.46 Hz, As*H*$_2$), 1.00 (d, 12H, $^{3}J_{H,H}$ = 7.15 Hz, *i*Pr-C*H*$_3$), 1.48 (d, 12H, $^{3}J_{H,H}$ = 7.15 Hz, *i*Pr-C*H*$_3$), 2.74 (sept, 4H, $^{3}J_{H,H}$ = 7.15 Hz, *i*Pr-C*H*), 5.09 (s br, 1H, Ga*H*), 6.47 (s, 2H, NC*H*C*H*N), 7.14 (d, 4H, $^{3}J_{H,H}$ = 7.88 Hz, aryl-C$_{meta}$*H*), 7.27 (t, 2H, $^{3}J_{H,H}$ = 7.88 Hz, aryl-C$_{para}$*H*).

^{13}C NMR (100.66 MHz, C_6D_6, 298 K): δ = 22.7 (*i*Pr-*C*H$_3$), 25.3 (*i*Pr-*C*H$_3$), 28.8 (*i*Pr-*C*H(CH$_3$)$_2$), 124.4 (aryl-*C*$_{meta}$), 125.7 (N*C*H*C*HN), 130.9 (aryl-*C*$_{para}$), 134.2 (aryl-*C*$_{ipso}$), 145.4 (aryl-*C*$_{ortho}$).

CHN: Anal. Calcd. (%) for $C_{27}H_{41}N_2GaAs_2$ (612.10 g/mol): C 52.89, H 6.74, N 4.57; Found: C 54.04, H 6.78, N 4.57.

LIFDI-MS (m/z): 611.0607 [M-H]$^+$ (47 %).

Synthesis of IDipp·GaH(PH$_2$)$_2$ (7)

A solution of IDipp·GaHCl$_2$ (50 mg, 0.090 mmol, 1 eq) in 10 mL Et$_2$O was added to a suspension of NaPH$_2$ (16 mg, 0.28 mmol, 3 eq) in 10 mL Et$_2$O at –80 °C. The white suspension was stirred at room temperature for 24 hours. The solvent was removed *in vacuo*. The off-white residue was suspended in *n*-hexane and centrifuged for 10 minutes at 2000 rpm. The colorless supernatant was stored at –30 °C to afford **7** as colorless needles (27 mg, 57%).

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): δ = 0.54 (dm, 4H, $^{1}J_{P,H}$ = 175 Hz, (P*H*$_2$)$_2$), 1.01 (d, 12H, $^{3}J_{H,H}$ = 7.43 Hz, *i*Pr-C*H*$_3$), 1.49 (d, 12H, $^{3}J_{H,H}$ = 7.43 Hz, *i*Pr-C*H*$_3$), 2.75 (sept, 4H, $^{3}J_{H,H}$ = 7.43 Hz, *i*Pr-C*H*), 4.81 (s br, 1H, Ga*H*), 6.48 (s, 2H, NC*H*C*H*N), 7.14 (d, 4H, $^{3}J_{H,H}$ = 7.70 Hz, aryl-C$_{meta}$*H*), 7.27 (t, 2H, $^{3}J_{H,H}$ = 7.70 Hz, aryl-C$_{para}$*H*).

^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ = -255.4 (s, (*P*H$_2$)$_2$).

^{31}P NMR (162.04 MHz, C_6D_6, 298 K): δ = -255.4 (tm, $^{1}J_{P,H}$ = 175 Hz, $^{2}J_{P,H}$ = 18.17 Hz, (*P*H$_2$)$_2$).

Synthesis of IDipp·AlH(PH$_2$)$_2$ (8)

A solution of IDipp·AlHCl$_2$ (50 mg, 0.10 mmol, 1 eq) in 10 mL Et$_2$O was added to a suspension of NaPH$_2$ (0.017 mg, 0.30 mmol, 3 eq) in 10 mL Et$_2$O at –80 °C. The white suspension was stirred for 24 hours at room temperature. The solvent was removed *in vacuo*. The white solid was suspended in *n*-hexane and centrifuged for 10 minutes at 2000 rpm. The colorless supernatant was stored at –30 °C to afford **8** as colorless needles (23 mg, 48%).

^{1}H NMR (400.13 MHz, toluene-d$_8$, 213 K): δ = 0.42 (dm, 4H, $^1J_{P,H}$ = 175.4 Hz, (P*H*$_2$)$_2$), 0.98 (d, 12H, $^3J_{H,H}$ = 6.91 Hz, *i*Pr-C*H*$_3$), 1.49 (d, 12H, $^3J_{H,H}$ = 6.91 Hz, *i*Pr-C*H*$_3$), 2.70 (sept, 4H, $^3J_{H,H}$ = 6.91 Hz, *i*Pr-C*H*), 4.56 (s br, 1H, Al*H*), 6.27 (s, 2H, NC*H*C*H*N), 7.00 (d, 4H, $^3J_{H,H}$ = 7.62 Hz, aryl-C$_{meta}$*H*), 7.19 (t, 2H, $^3J_{H,H}$ = 7.62 Hz, aryl-C$_{para}$*H*).

^{31}P{^{1}H} NMR (161.98 MHz, toluene-d$_8$, 213 K): δ = -270.8 (s, (*P*H$_2$)$_2$).

^{31}P NMR (161.98 MHz, toluene-d$_8$, 213 K): δ = -270.8 (tm, $^1J_{P,H}$ = 175.4 Hz, $^2J_{P,H}$ = 15.48 Hz, (*P*H$_2$)$_2$).

6.5.2. NMR data

IDipp·GaH$_2$Cl:

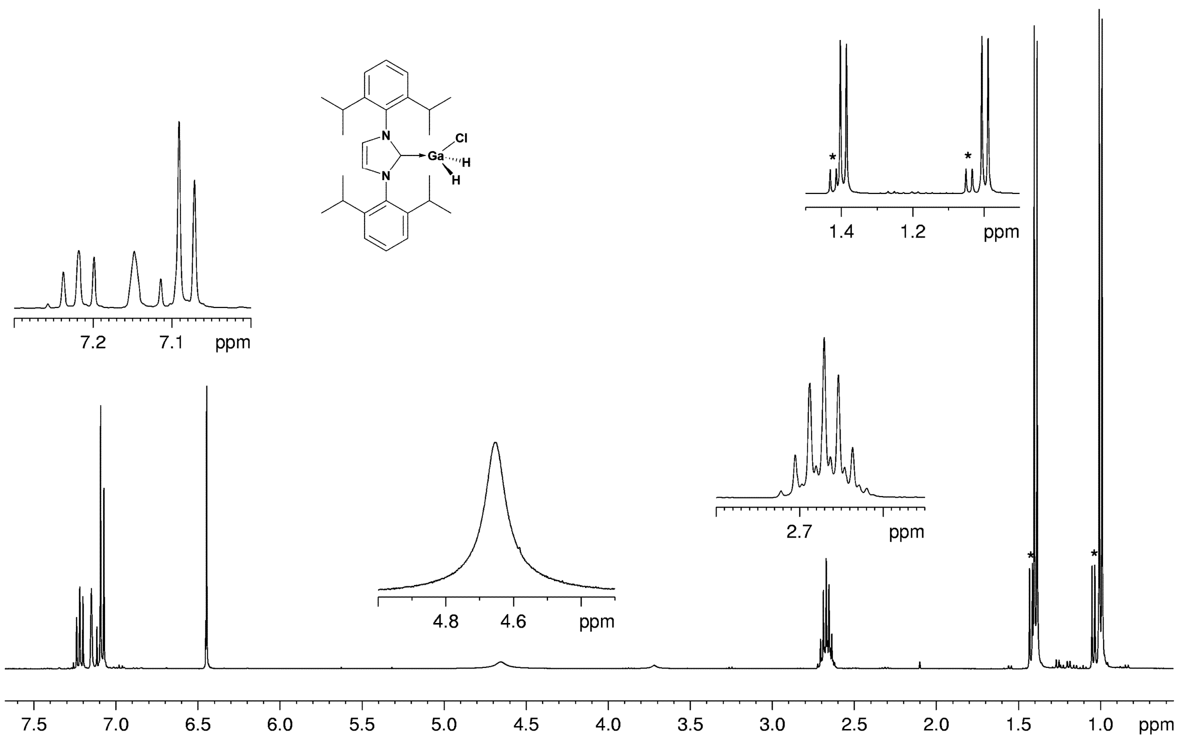


Figure S3: ^{1}H NMR spectrum of IDipp·GaH$_2$Cl in C$_6$D$_6$ at 298 K. * = IDipp·GaH$_3$, formed due to a possible disproportion of IDipp·GaH$_2$Cl.

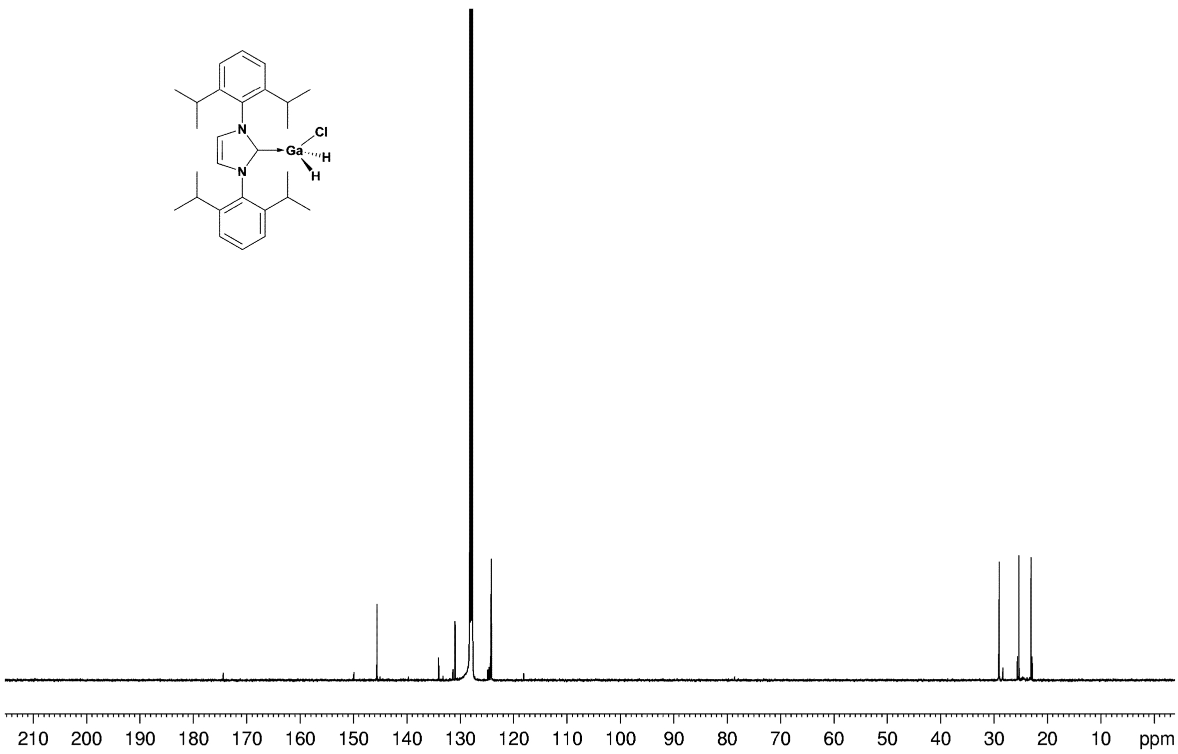


Figure S4: ^{13}C NMR spectrum of IDipp·GaH_2Cl in C_6D_6 at 298 K.

IDipp·AlH_2Cl:

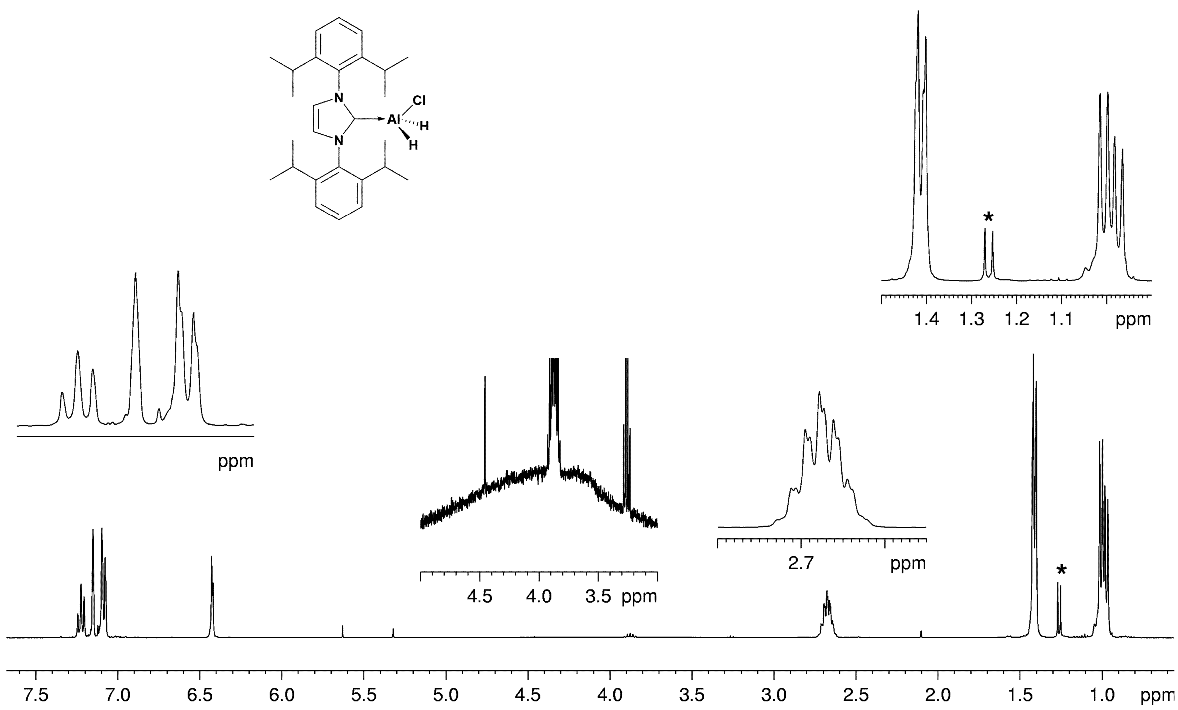


Figure S5: ^{1}H NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K. * = $IDippH_2$, formed due to partial hydrolysis of IDipp·AlH_2Cl.

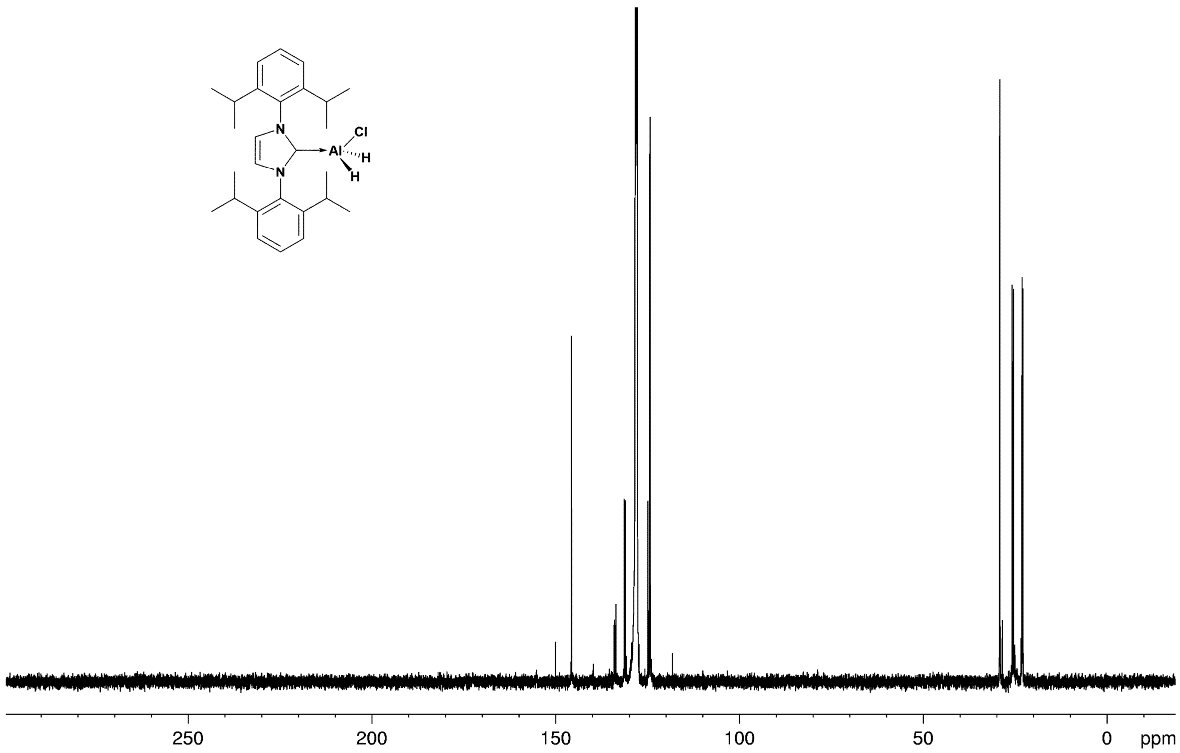


Figure S6: ^{13}C NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K.

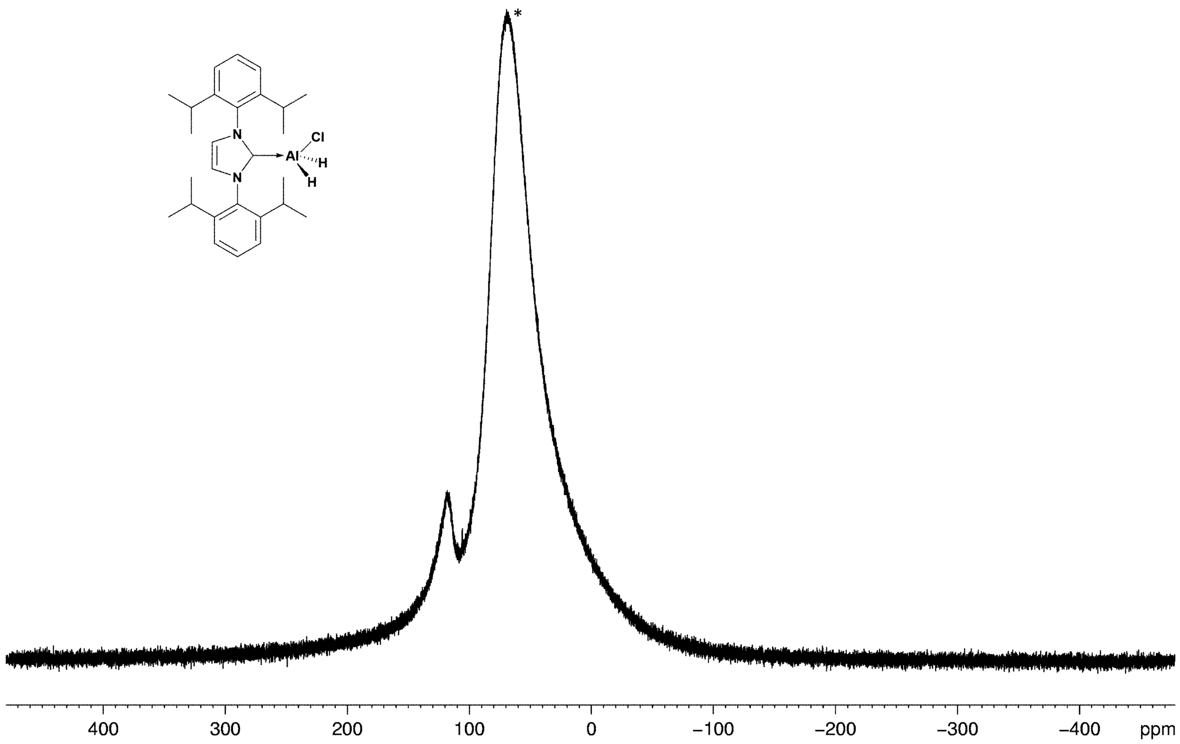


Figure S7: ^{27}Al NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K. * = signal from the NMR tube and the NMR sample head.

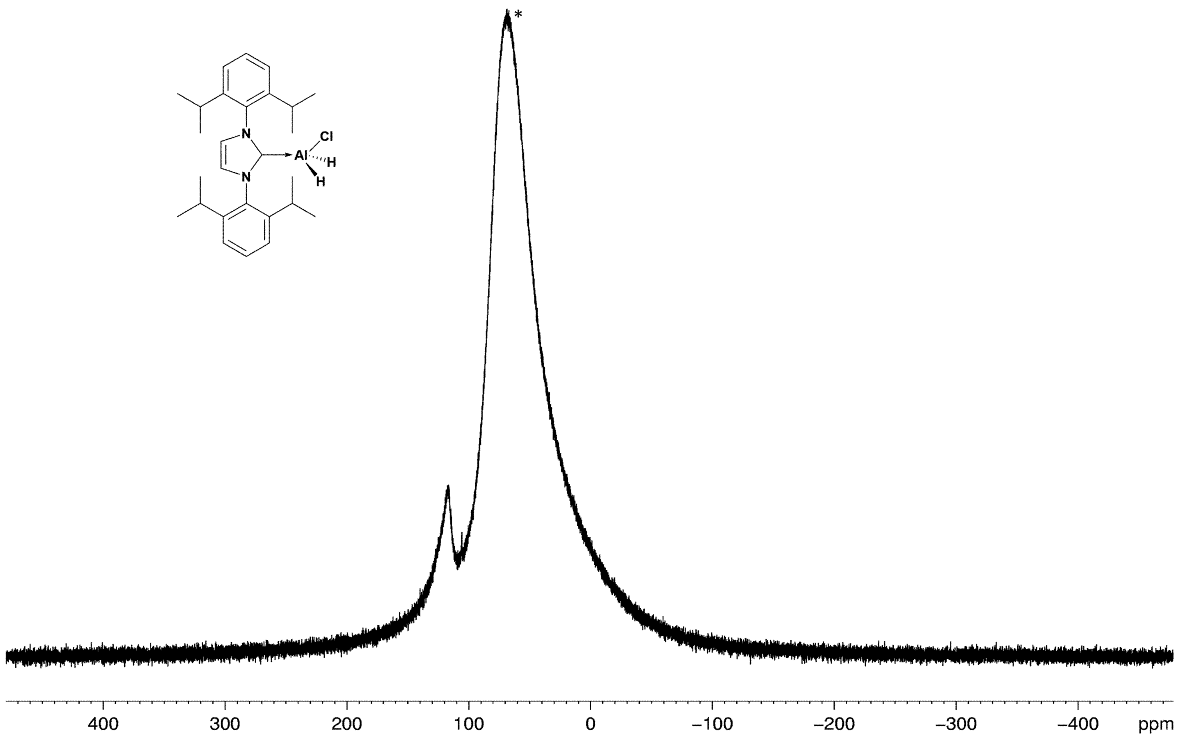


Figure S8: $^{27}Al\{^{1}H\}$ NMR spectrum of IDipp·AlH_2Cl in C_6D_6 at 298 K. * = signal from the NMR tube and the NMR sample head.

IDipp·$GaHCl_2$:

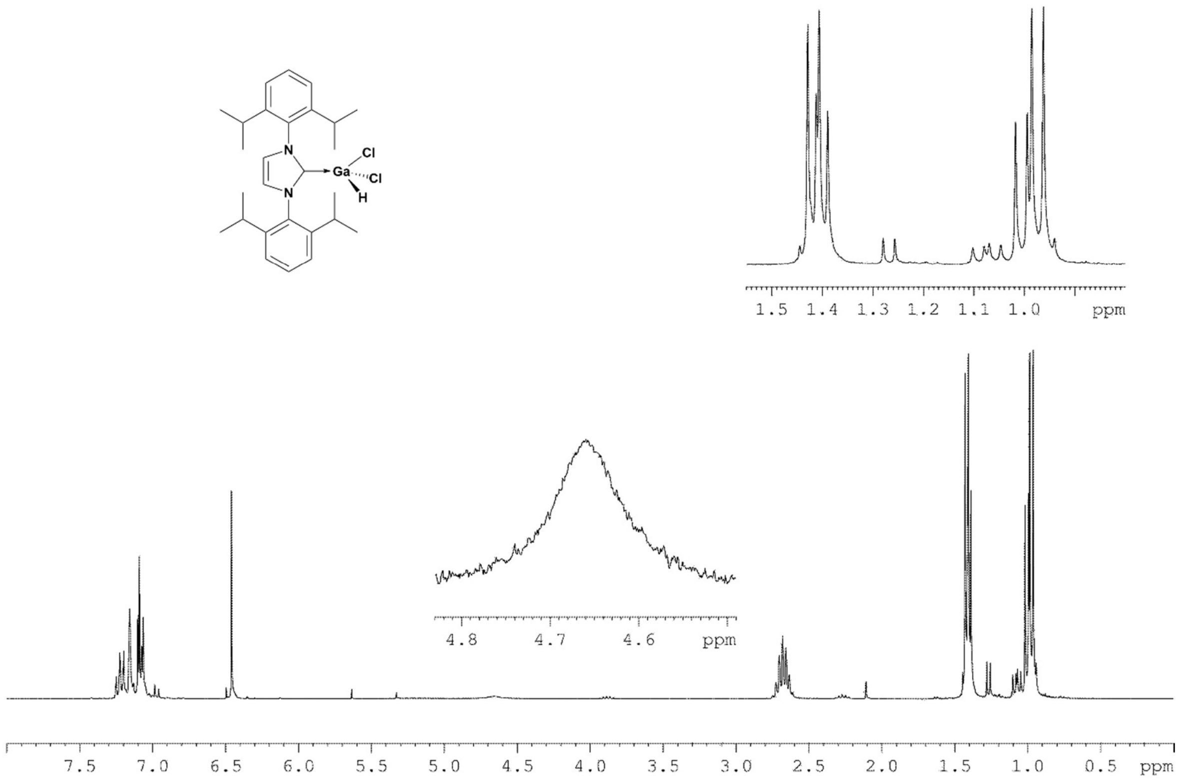


Figure S9: ^{1}H NMR spectrum of IDipp·$GaHCl_2$ in C_6D_6 at 298 K.

IDipp·AlHCl$_2$:

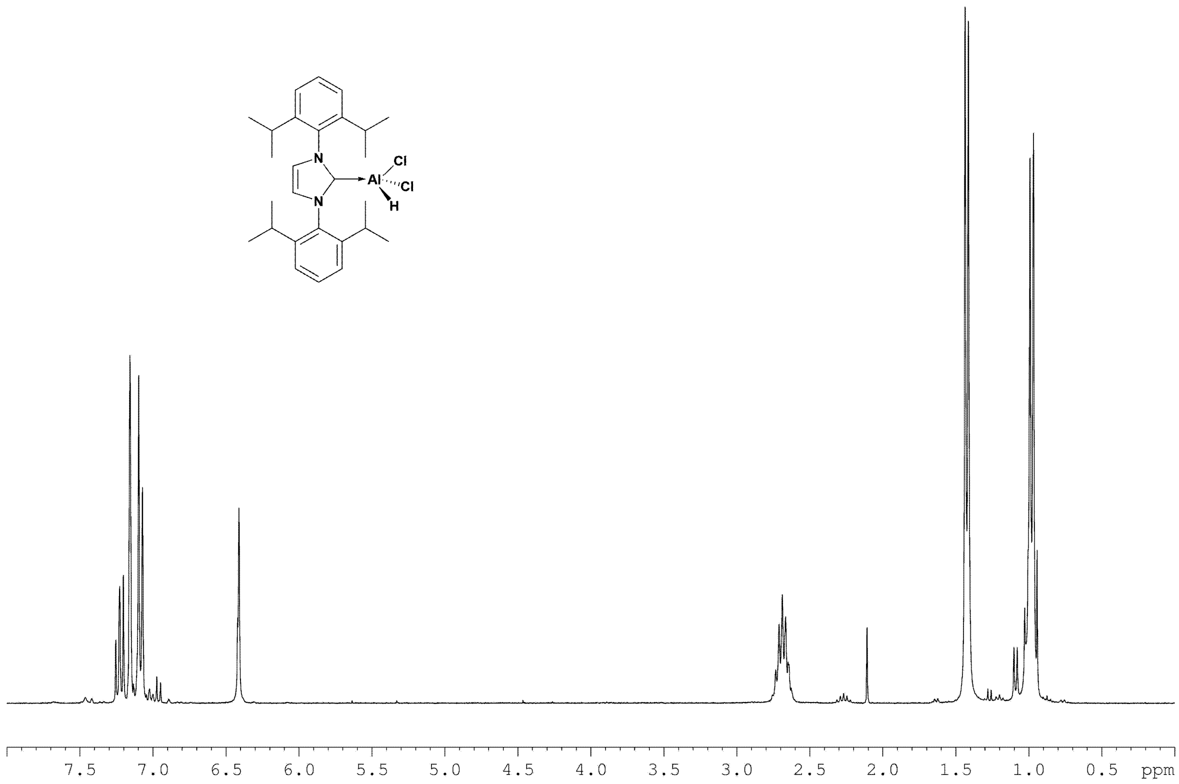


Figure S10: ^{1}H NMR spectrum of IDipp·AlHCl$_2$ in C_6D_6 at 298 K.

IDipp·GaH$_2$AsPh$_2$ (1):

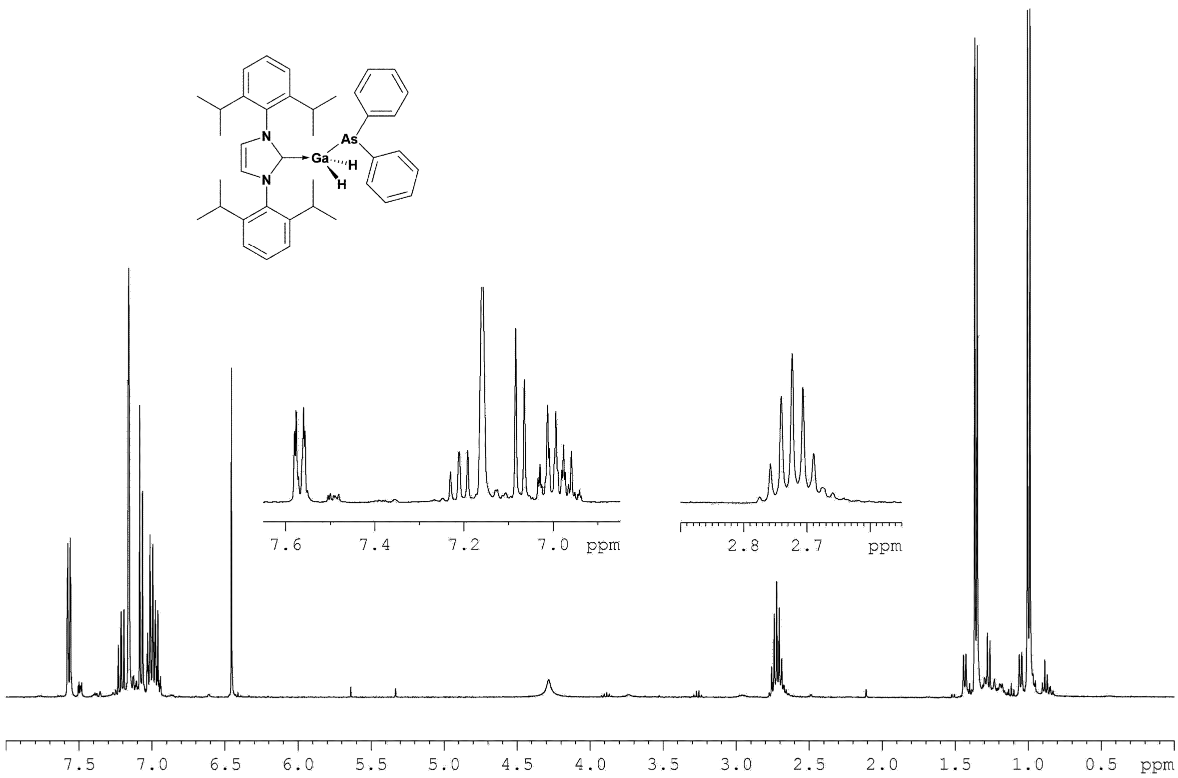


Figure S11: ^{1}H NMR spectrum of **1** in C_6D_6 at 298 K.

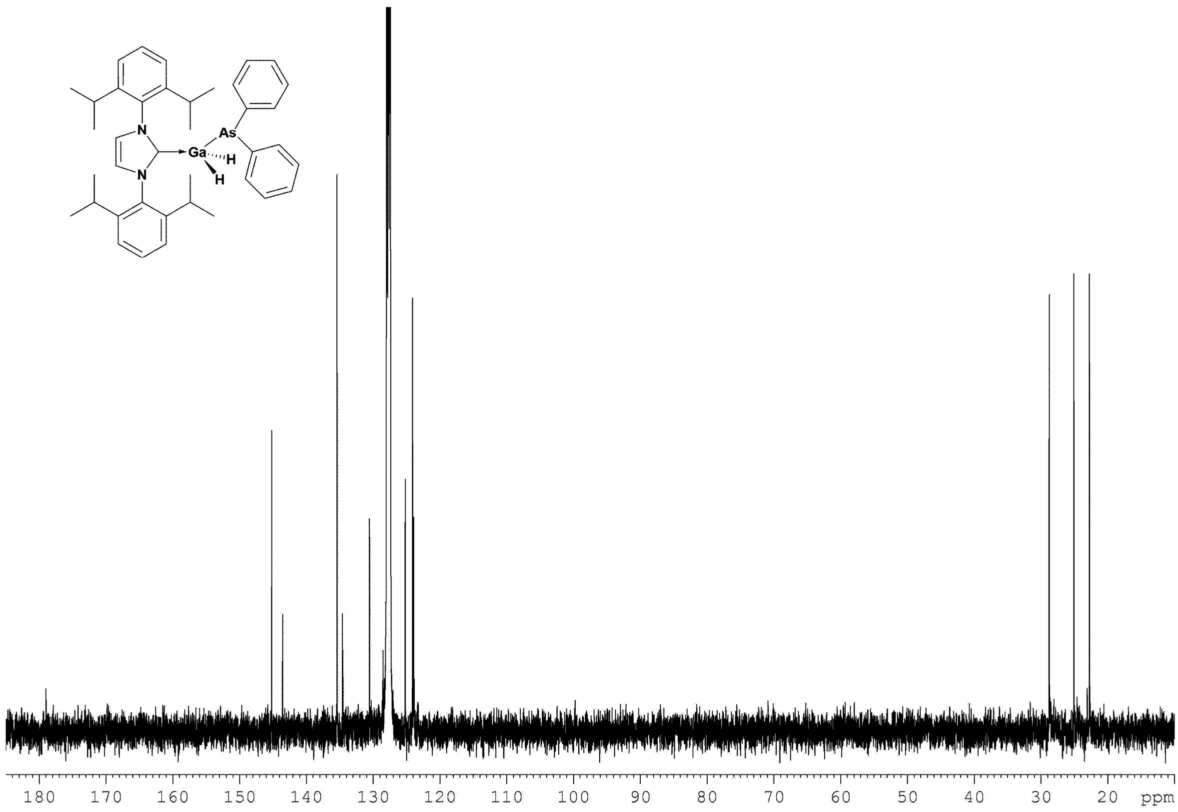


Figure S12: ^{13}C NMR spectrum of **1** in C_6D_6 at 298 K.

IDipp·AlH$_2$AsPh$_2$ (2):

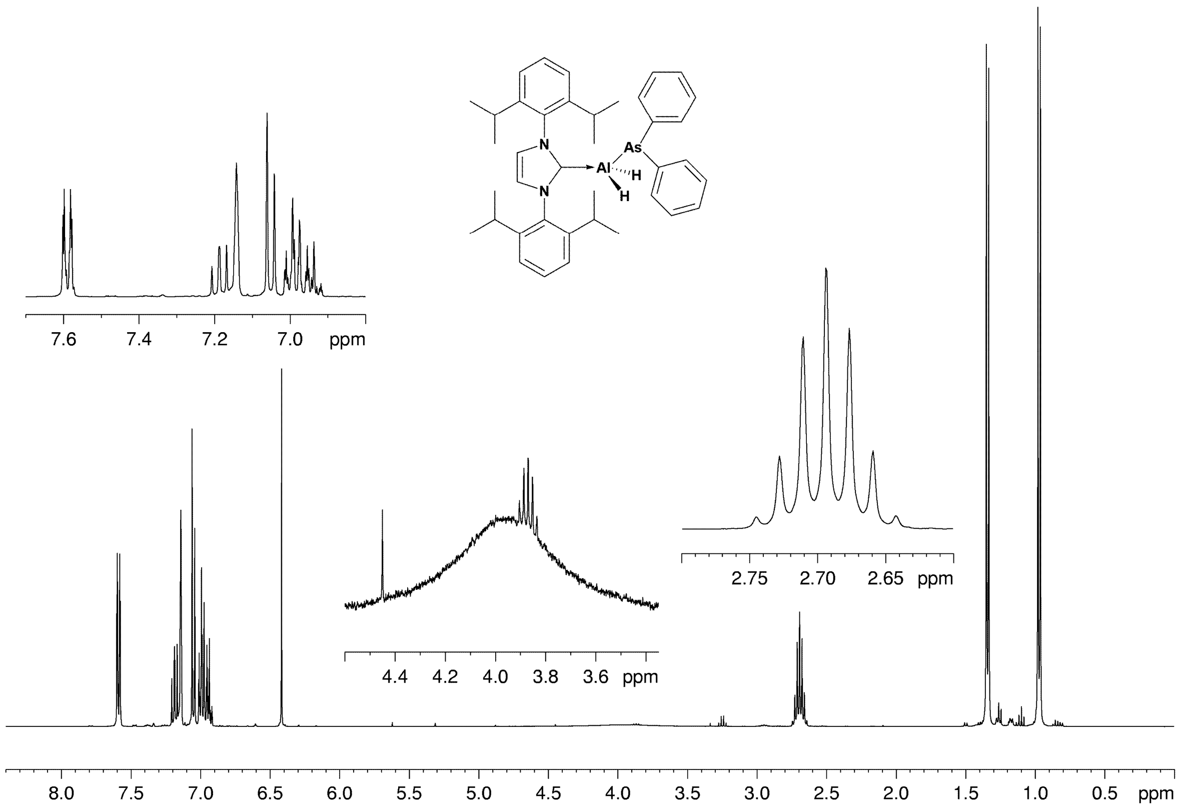


Figure S13: ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K.

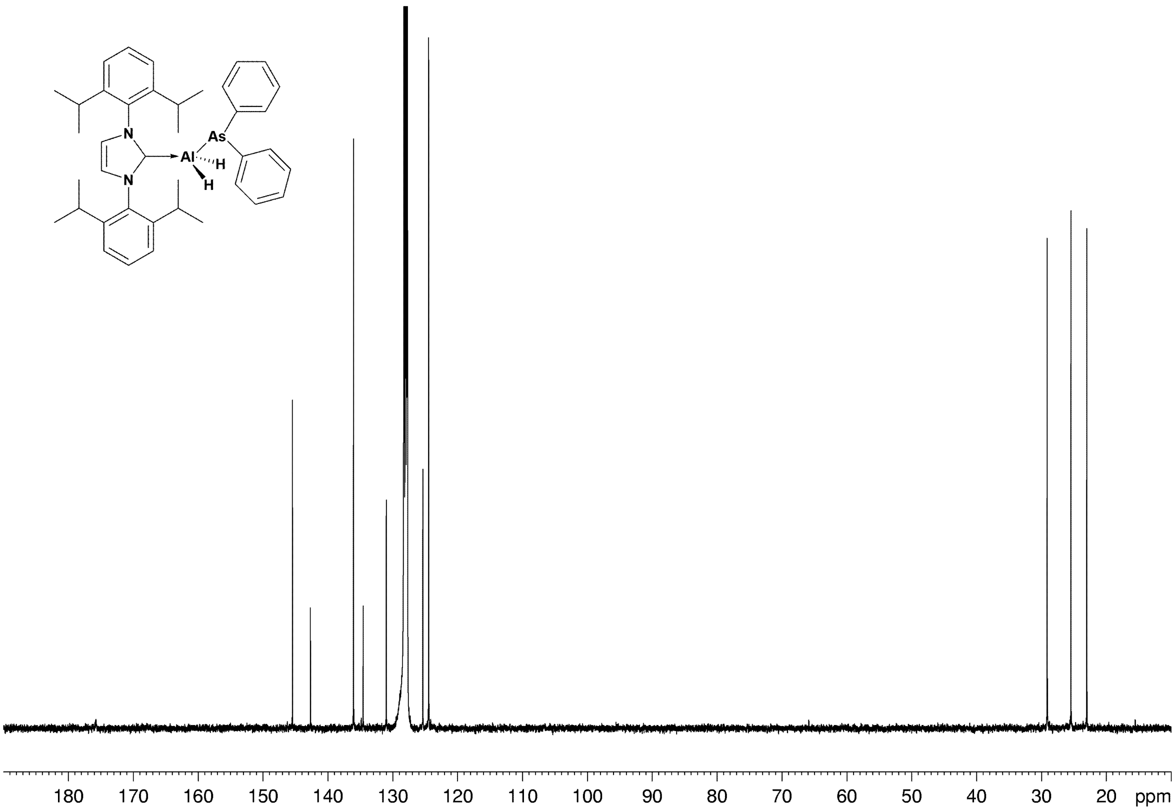


Figure S14: ^{13}C NMR spectrum of **2** in C_6D_6 at 298 K.

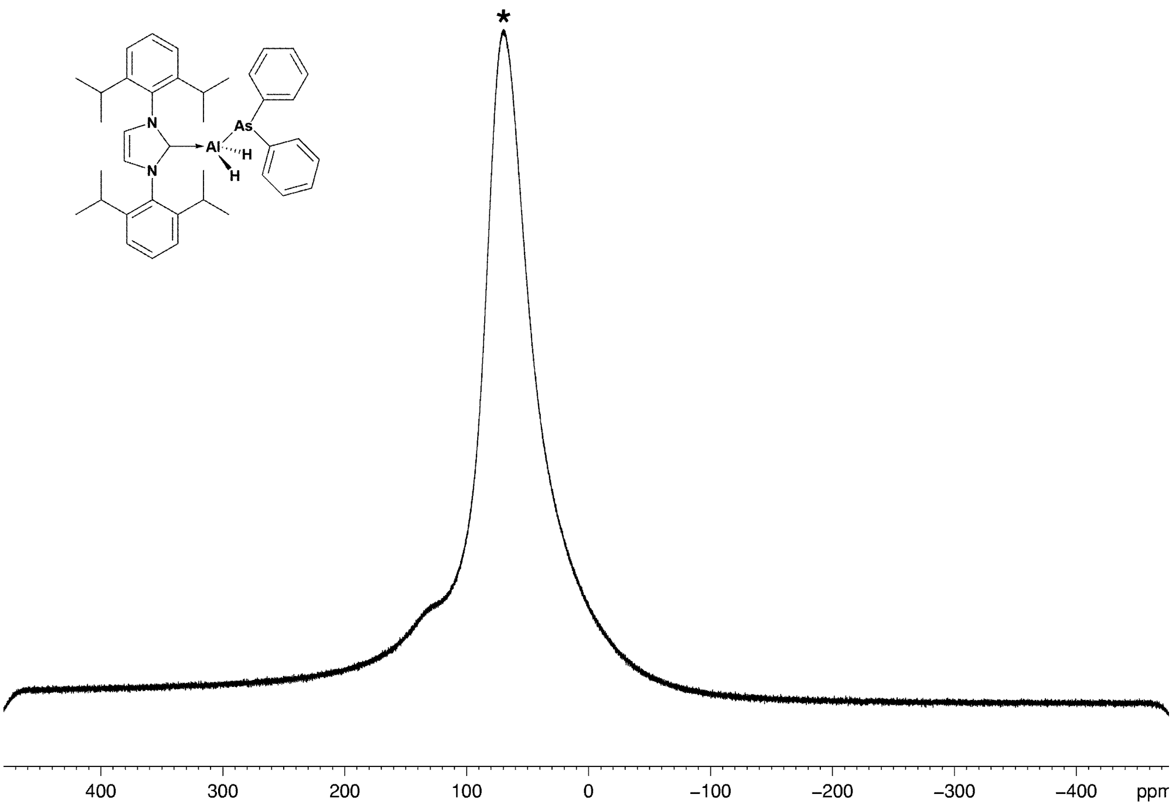


Figure S15: ^{27}Al NMR spectrum of **2** in C_6D_6 at 298 K. * = signal of the NMR tube and the NMR sample head.

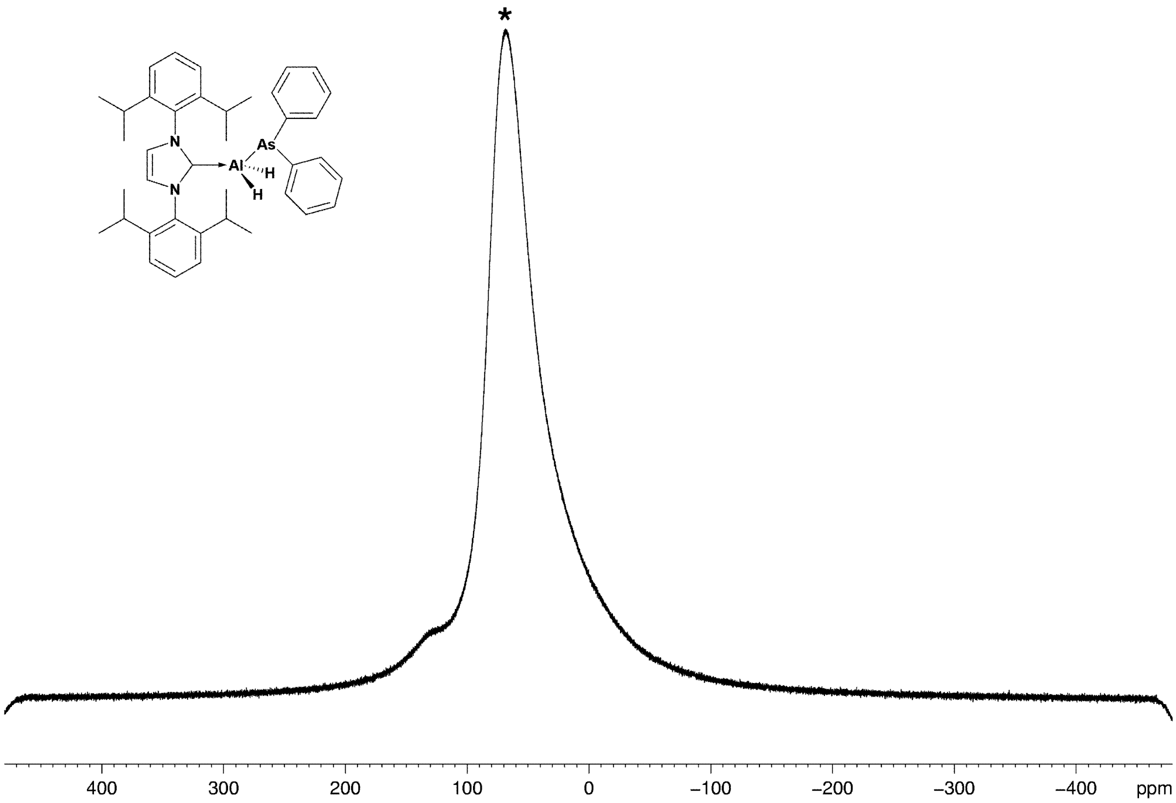


Figure S16: $^{27}Al\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 298 K. * = signal of the NMR tube and the NMR sample head.

IDipp·GaH$_2$AsH$_2$ (3):

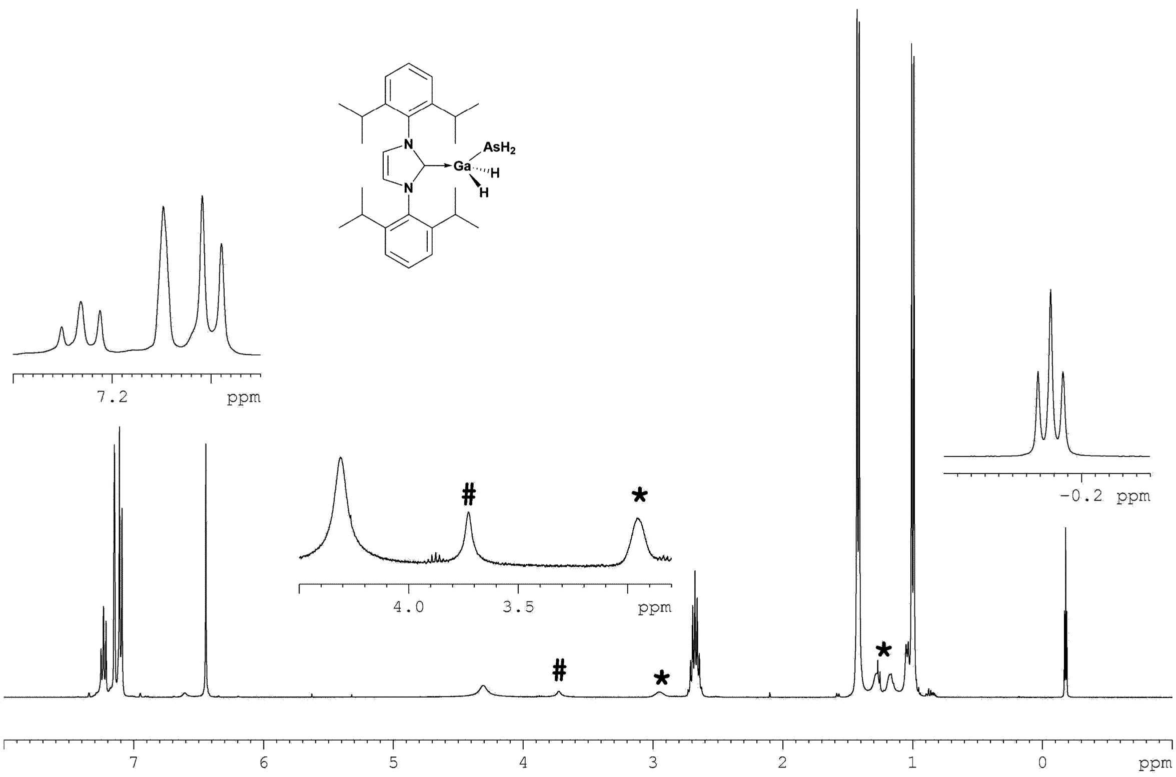


Figure S17: ^{1}H NMR spectrum of **3** in C_6D_6 at 298 K. # = IDippGaH$_3$, formed due to decomposition of **3**. * = unidentified impurity.

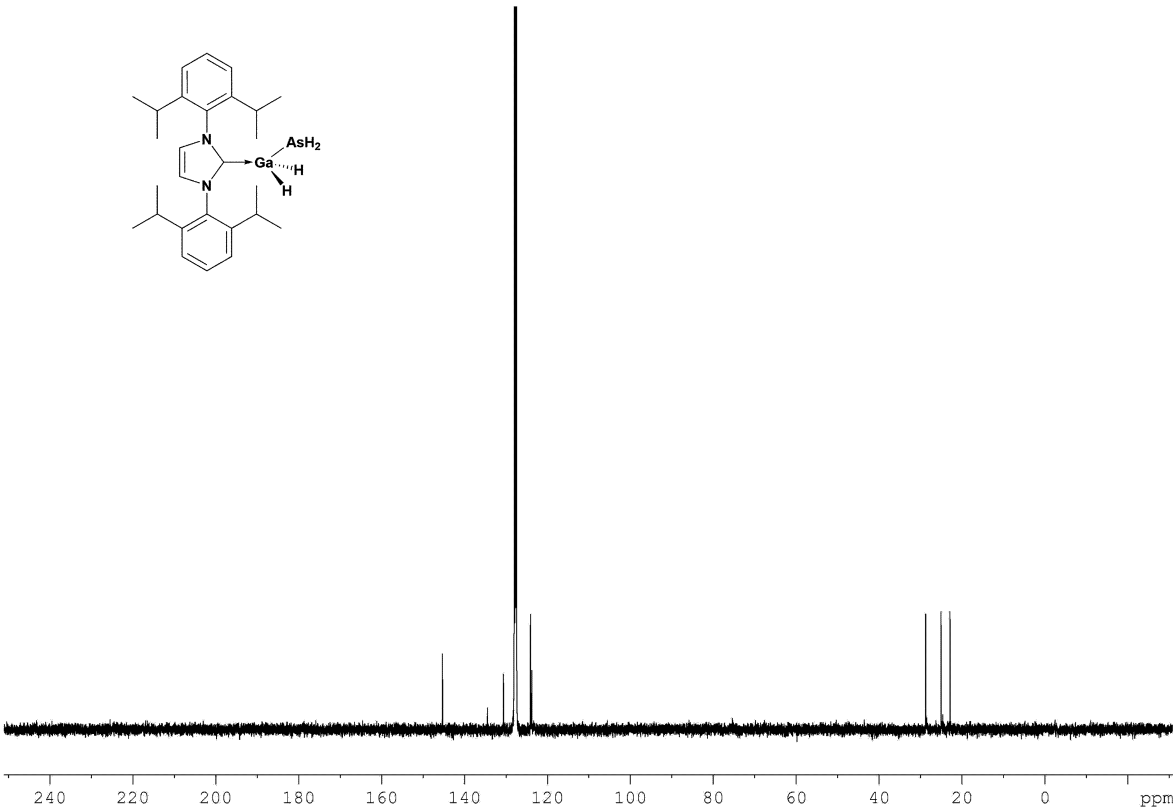


Figure S18: ^{13}C NMR spectrum of **3** in C_6D_6 at 298 K.

IDipp·AlH_2AsH_2 (4):

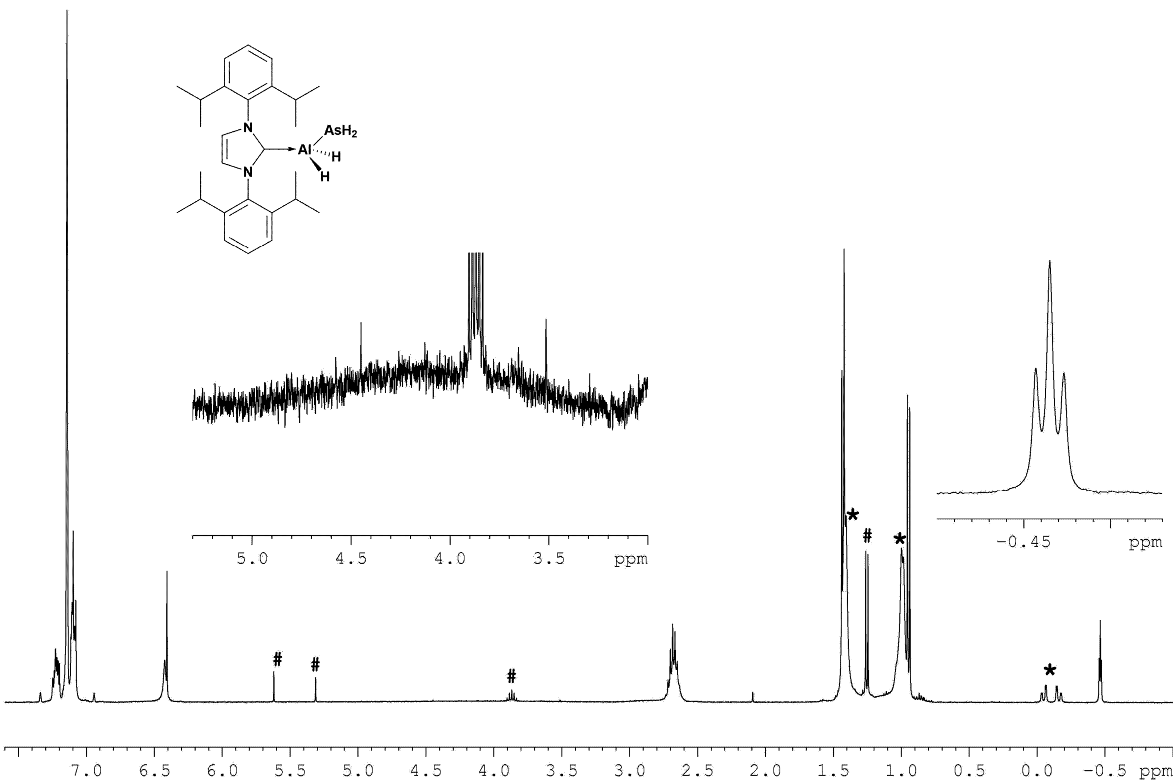


Figure S19: ^{1}H NMR spectrum of **4** in C_6D_6 at 298 K. * = IDipp·$AlH(AsH_2)_2$. # = $IDippH_2$, formed due to hydrolysis of **4**.

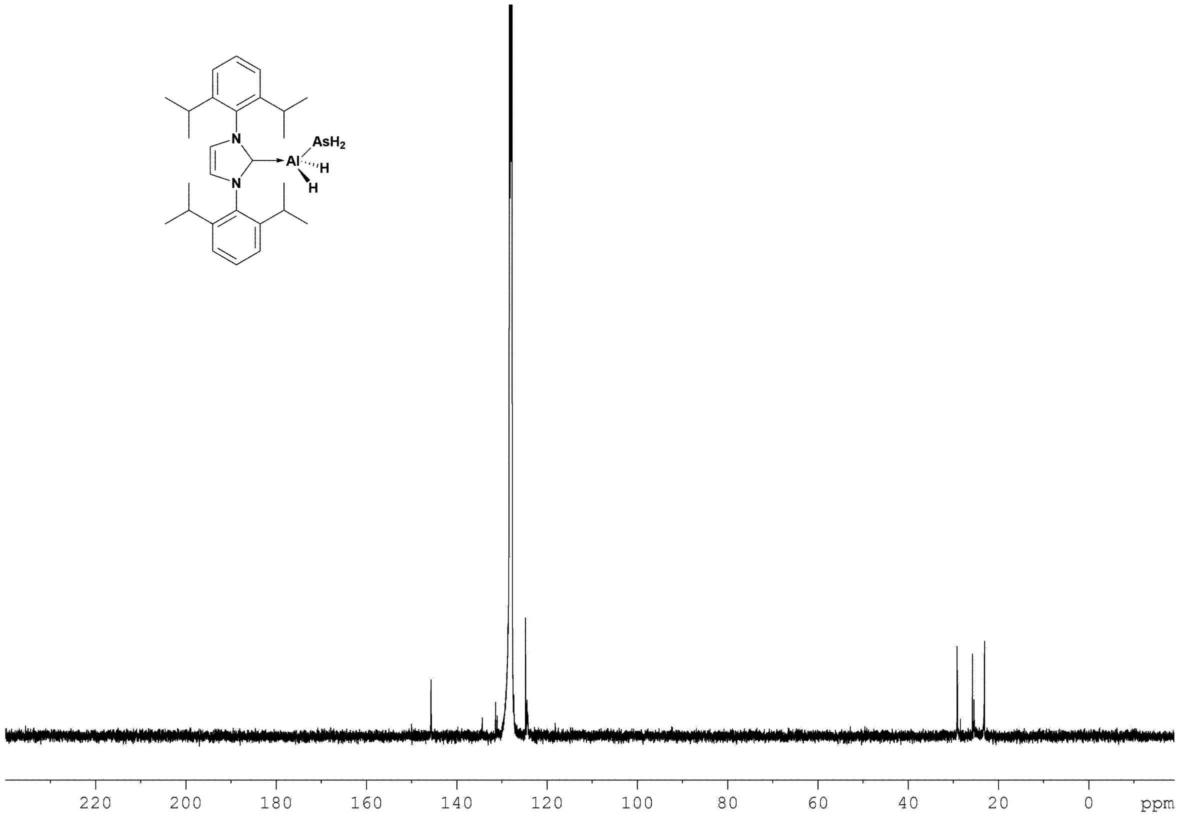


Figure S20: ^{13}C NMR spectrum of **4** in C_6D_6 at 298 K.

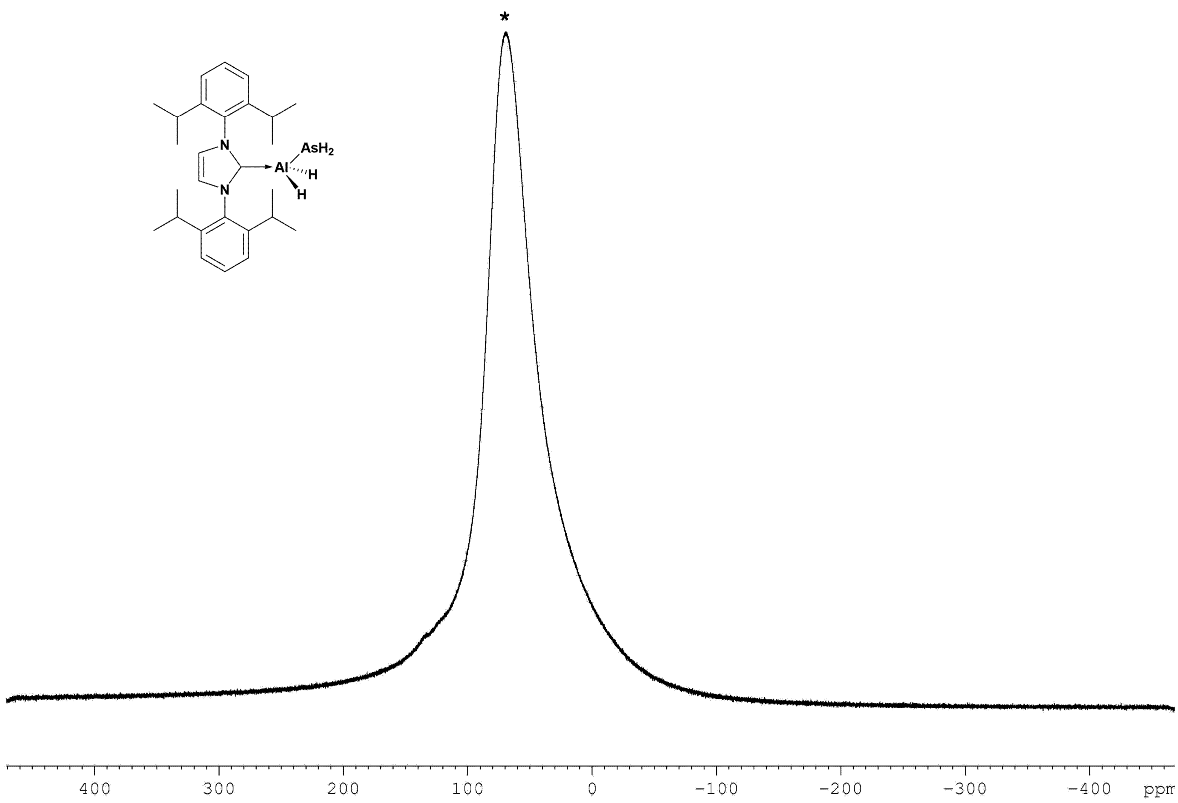


Figure S21: $^{27}Al\{^1H\}$ NMR spectrum of **4** in C_6D_6 at 298 K. * = signale of the NMR tube and the NMR sample head.

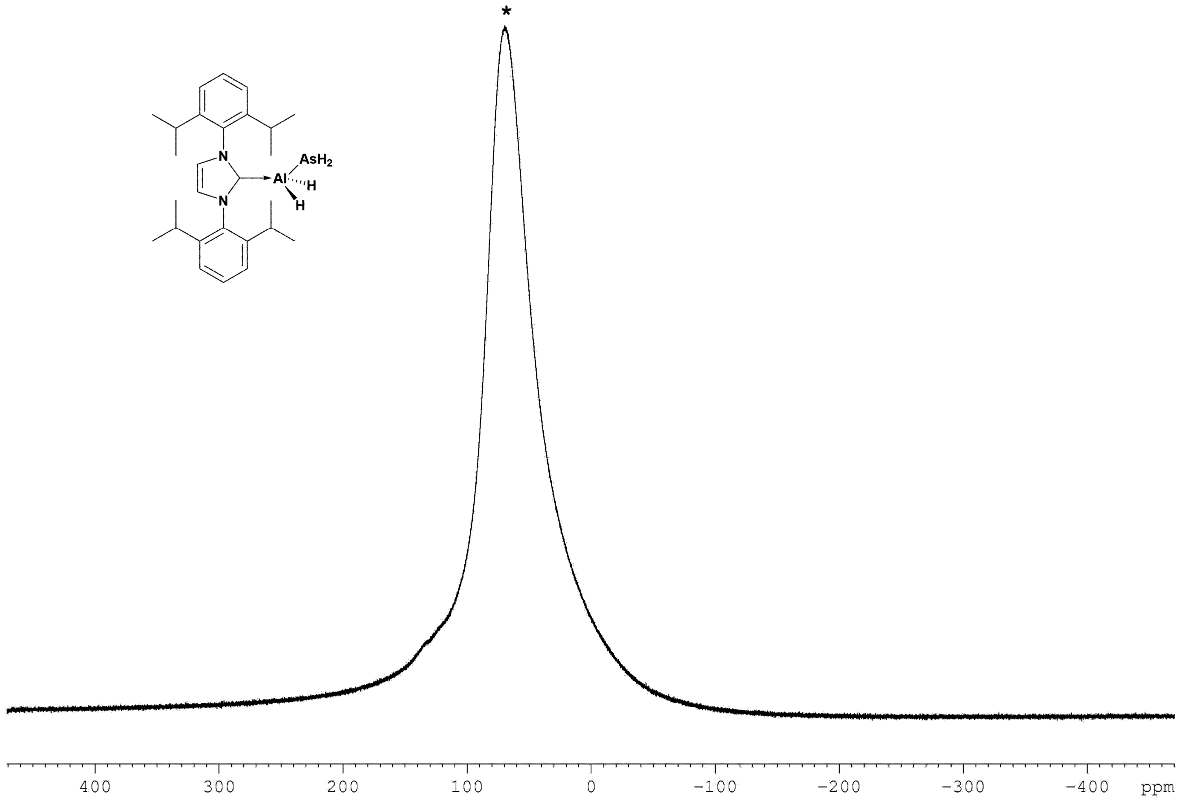


Figure S22: ^{27}Al NMR spectrum of **4** in C_6D_6 at 298 K. * = signal of the NMR tube and the NMR sample head.

IDipp·AlH(AsH$_2$)$_2$ (5):

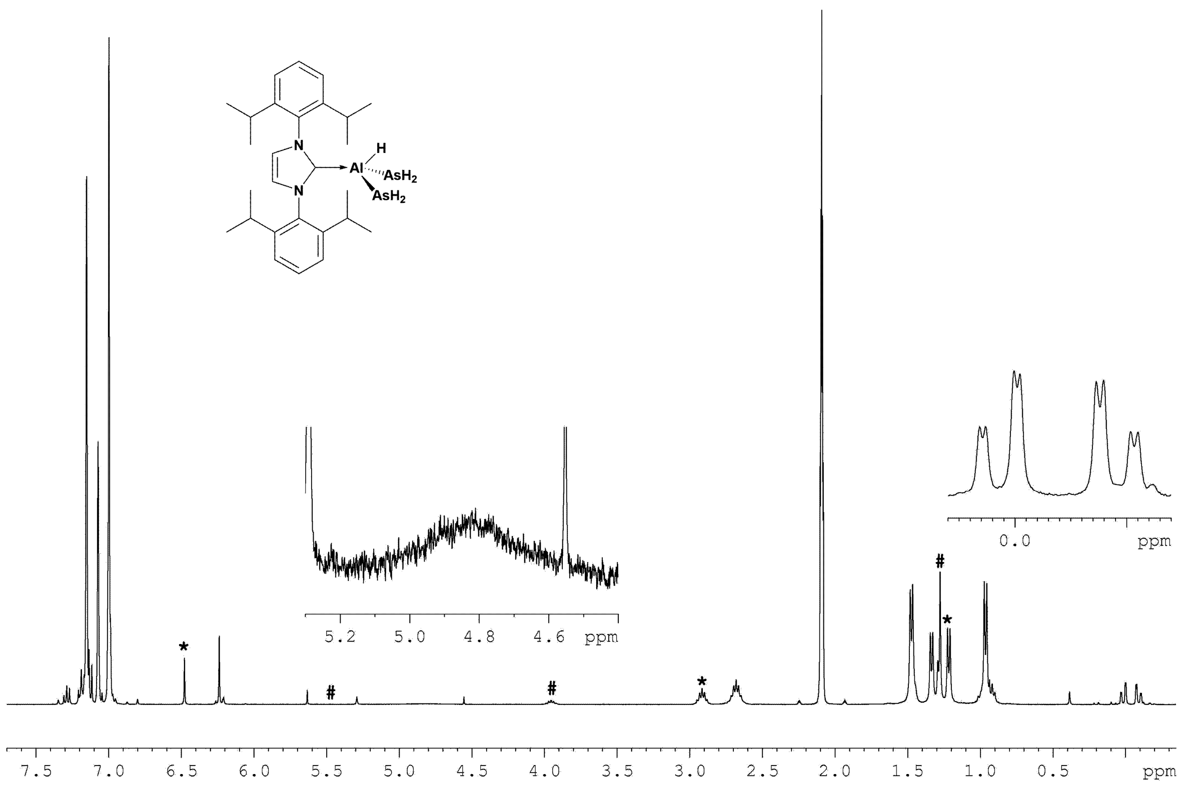


Figure S23: ^{1}H NMR spectrum of **5** in toluene-d$_8$ at 213 K. * = IDipp, # = IDippH$_2$, formed due to decomposition of **5**.

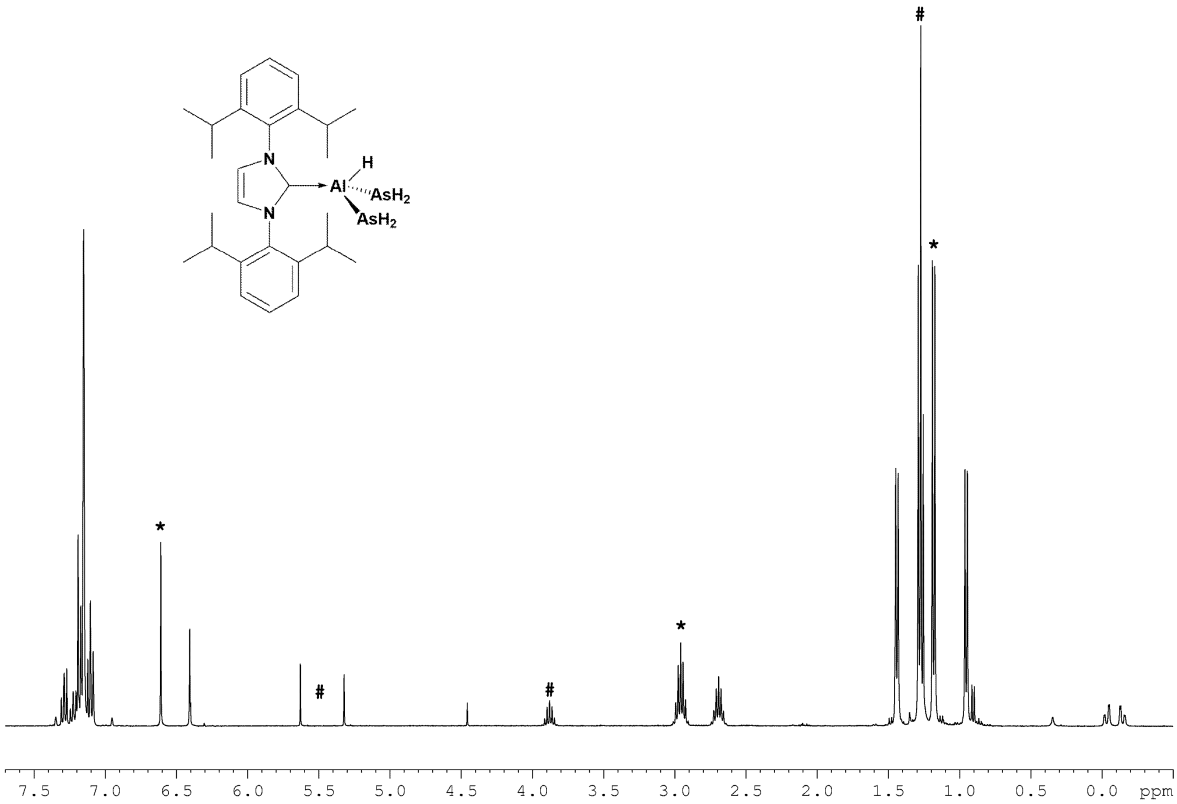


Figure S24: ^{1}H NMR spectrum of **5** in C_6D_6 at 298 K. * = IDipp, # = IDippH$_2$. Here you can see the strong tendency towards decomposition of solutions of **5** at RT compared to Figure S23.

IDipp·GaH(AsH$_2$)$_2$ (6):

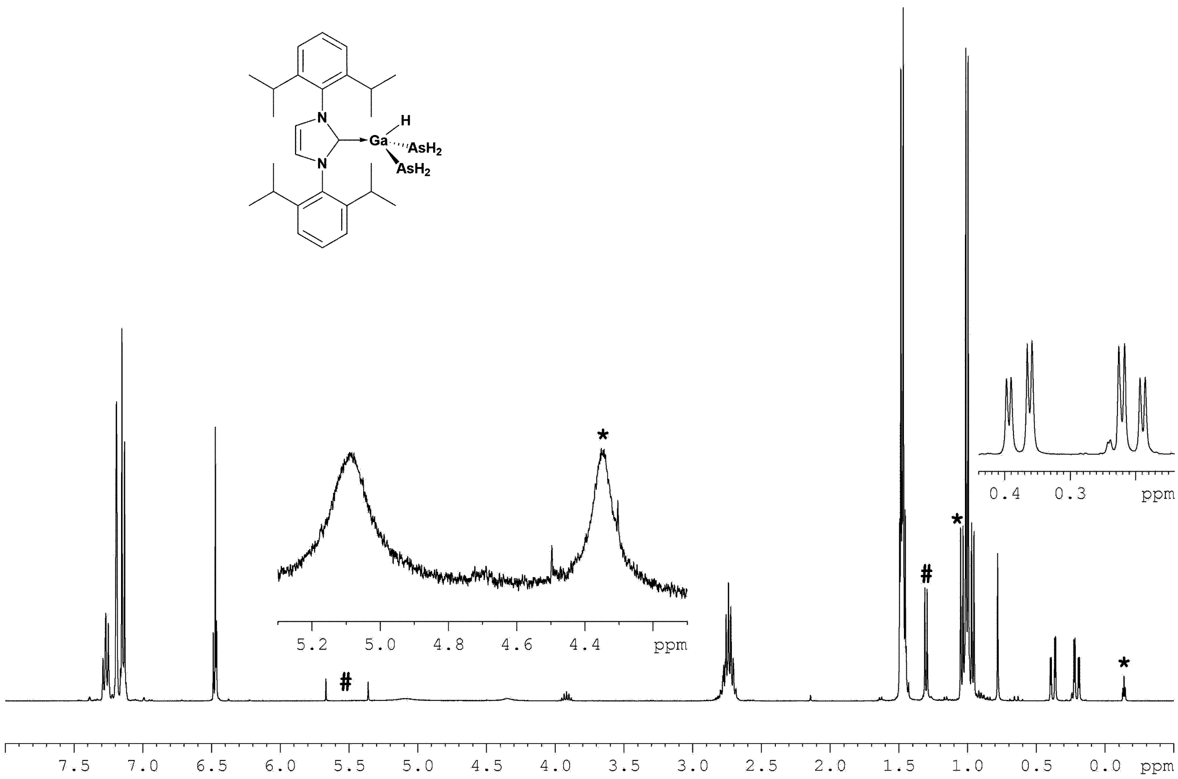


Figure S25: ^{1}H NMR spectrum of **6** in C_6D_6 at 298 K. # = IDippH$_2$, * = IDipp·GaH$_2$AsH$_2$.

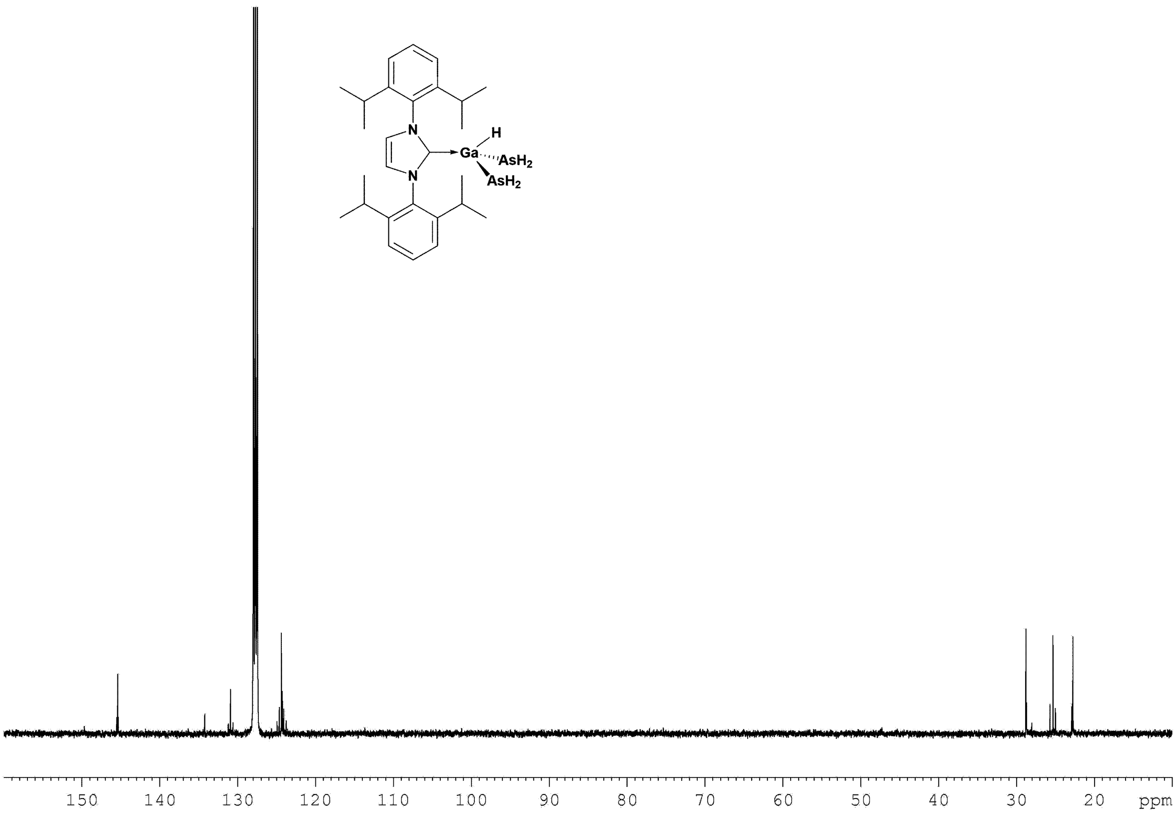


Figure S26: ^{13}C NMR spectrum of **6** in C_6D_6 at 298 K.

IDipp·GaH(PH_2)$_2$ (7):

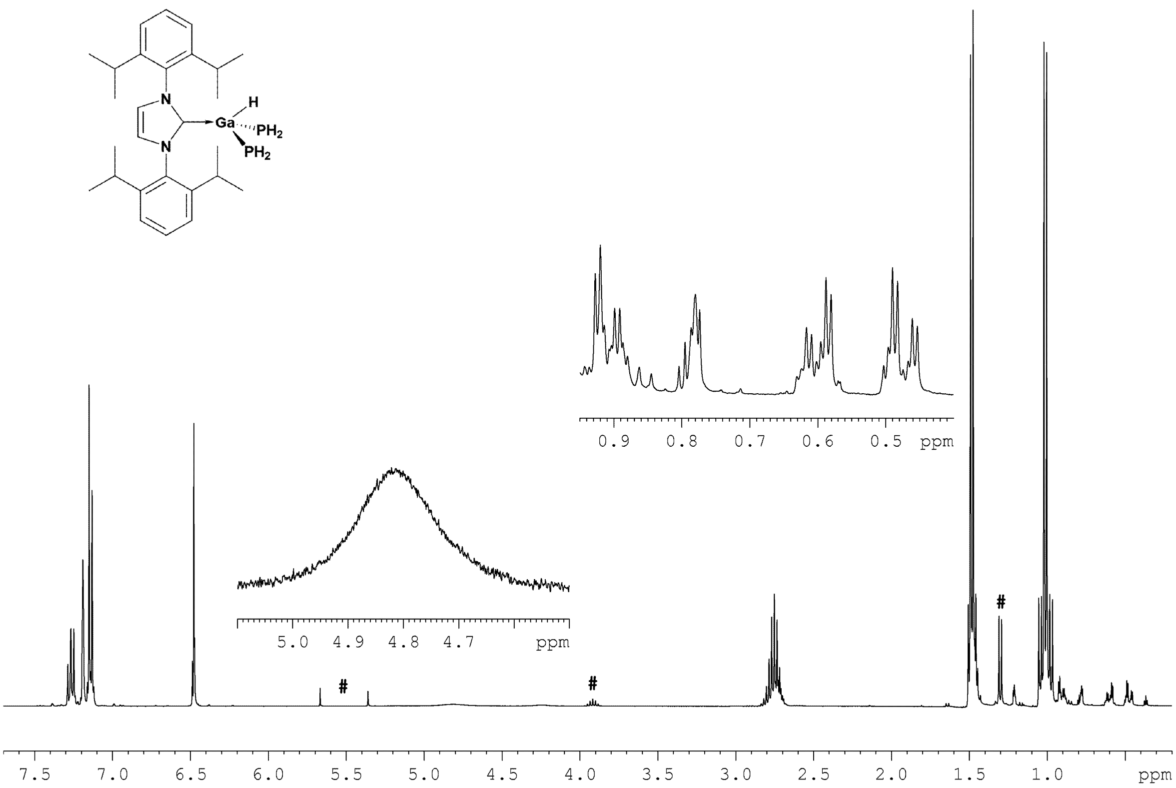


Figure S27: ^{1}H NMR spectrum of **7** in C_6D_6 at 298 K. # = IDippH$_2$.

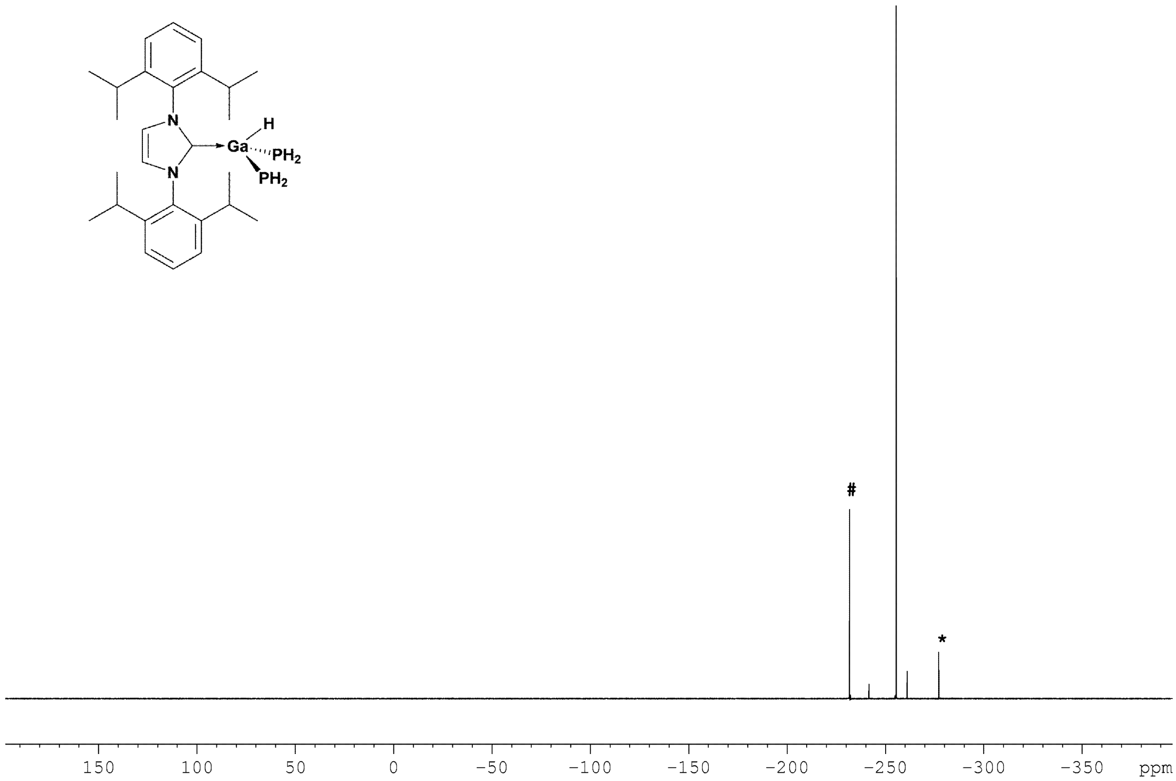


Figure S28: $^{31}P\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at 298 K. # = unidentified impurity, * = IDipp·GaH_2PH_2.

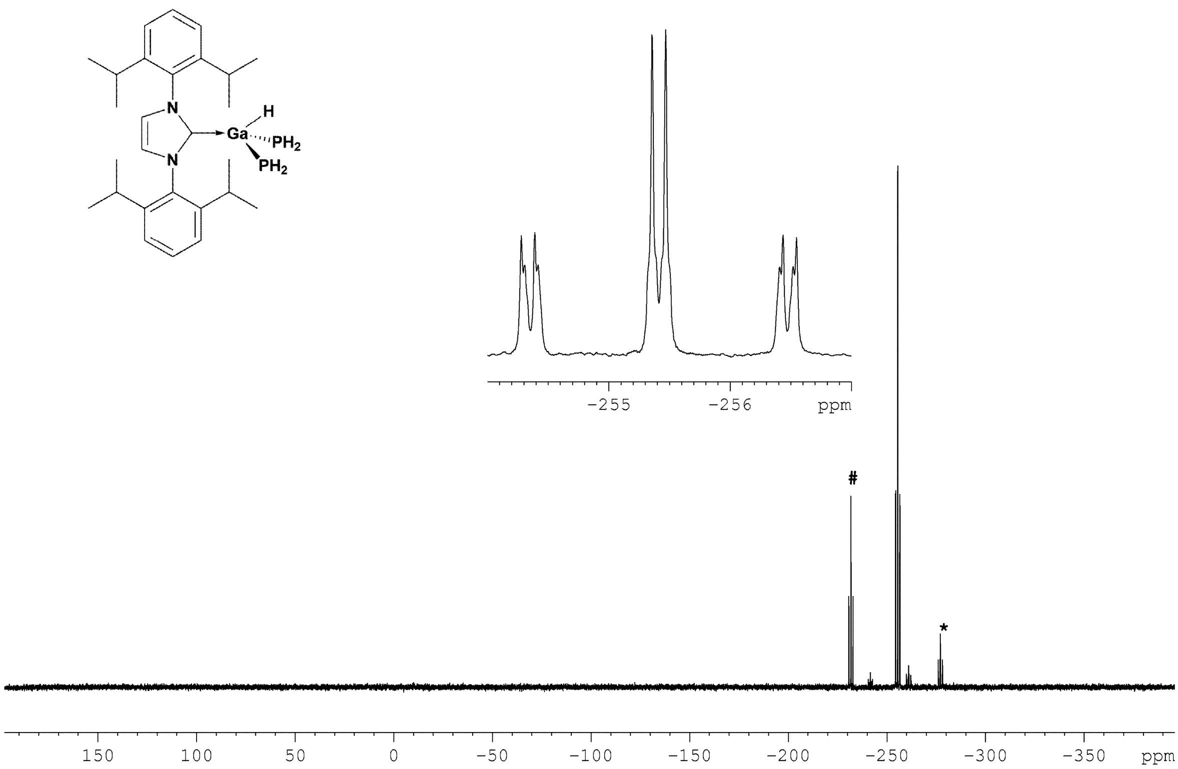


Figure S29: ^{31}P NMR spectrum of **7** in C_6D_6 at 298 K. # = unidentified impurity, * = IDipp·GaH_2PH_2.

IDipp·AlH(PH$_2$)$_2$ (8):

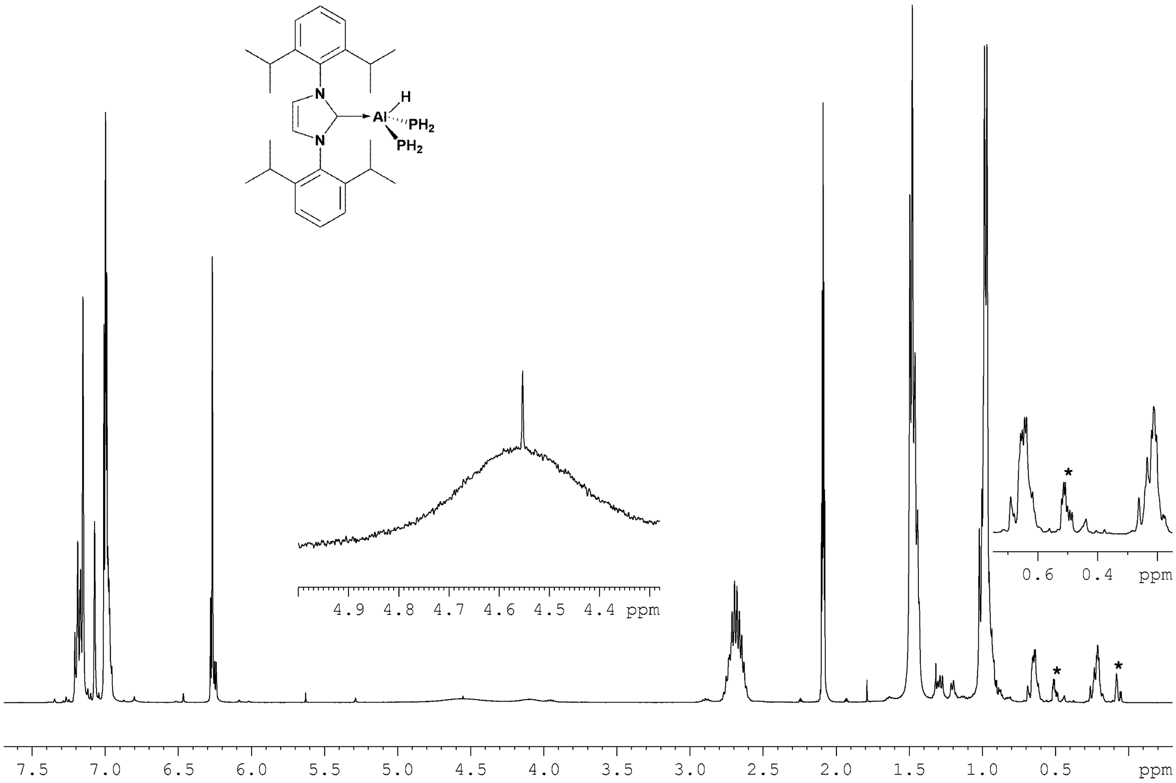


Figure S30: ^{1}H NMR spectrum of **8** in toluene-d$_8$ at 213 K. * = IDipp·AlH$_2$PH$_2$.

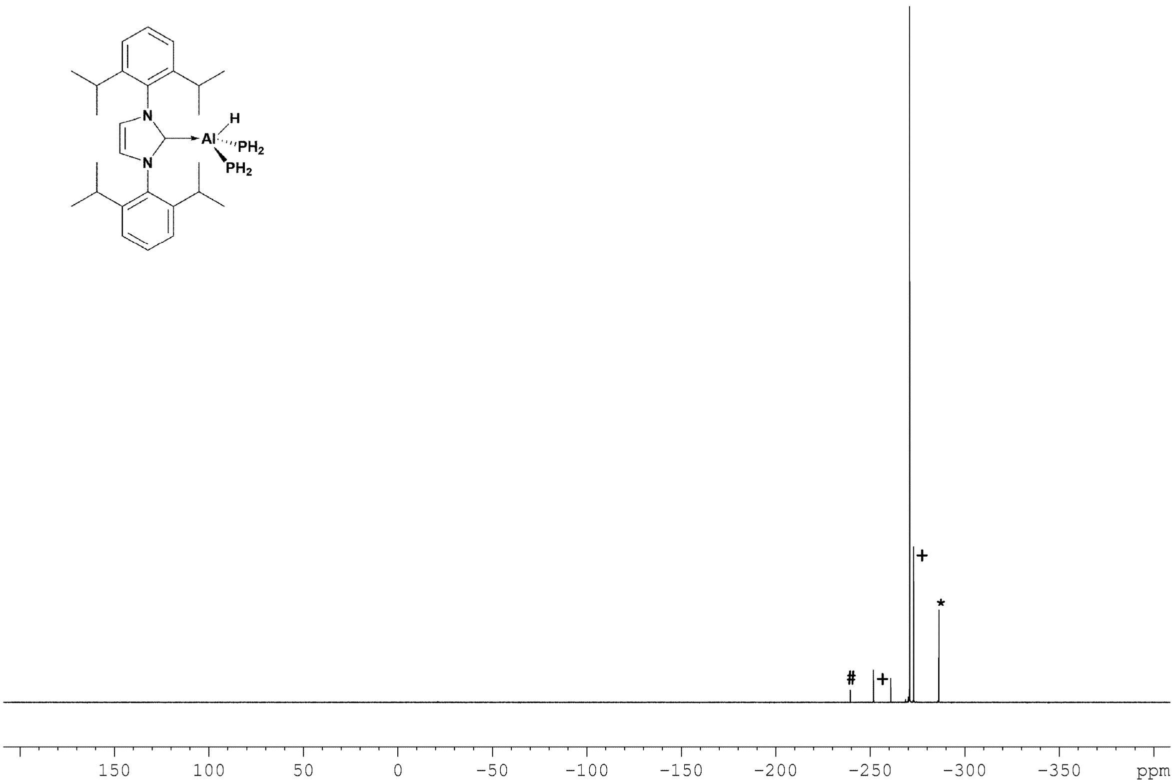


Figure S31: ^{31}P{^{1}H} NMR spectrum of **8** in toluene-d$_8$ at 213 K. # = PH$_3$, * = IDippAlH$_2$PH$_2$, + = unidentified impurity.

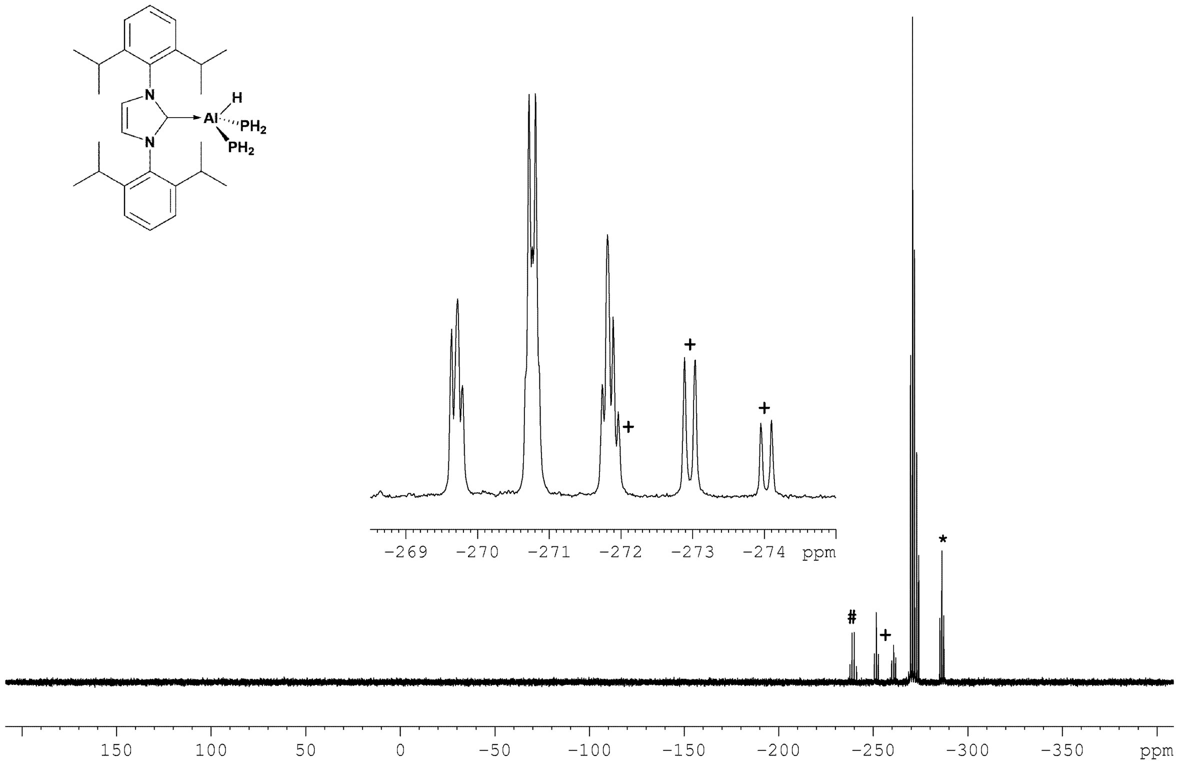


Figure S32: ^{31}P NMR spectrum of **8** in toluene-d$_8$ at 213 K. # = PH_3, * = IDipp·AlH_2PH_2, + = unidentified impurity.

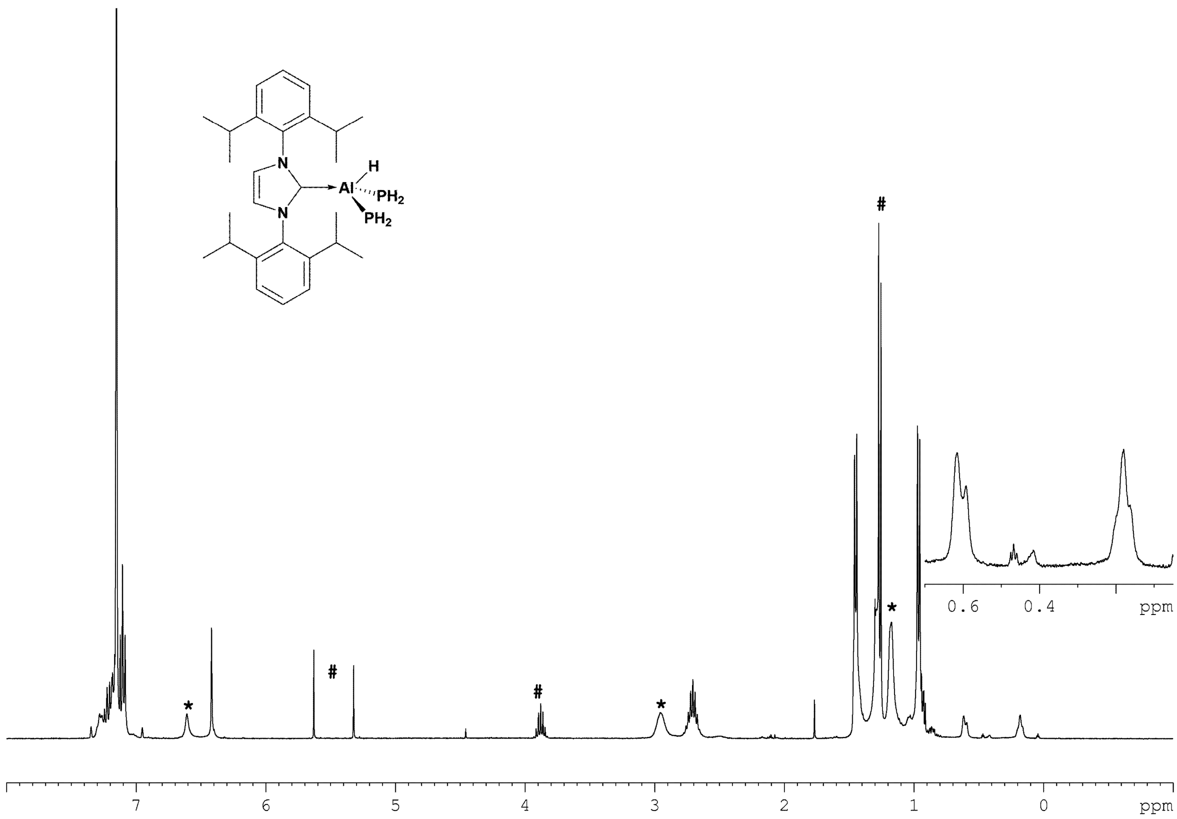


Figure S33: ^{1}H NMR spectrum of **8** in C_6D_6 at 298 K. # = IDippH_2, * = IDipp. Here you can see the strong tendency towards decomposition of solutions of **8** at RT compared to Figure S30.

6.5.3. Crystallographic data

Single crystal X-ray structure determination: Single-crystal X-ray diffraction data were collected using an Oxford Diffraction GV50 diffractometer equipped with a 165 mm Titan S2 CCD area detector. Crystals were selected under degassed inert oil and mounted on MiTeGen MicroLoops. During data collection the crystals were kept at 123(1) K (**1**, **2**, **3**, **5**, **7**, **8**) or 90(1) K (**4**, **6**) using a Cryostream 700 from Oxford Cryosystems. Data collection and reduction were performed with **CrysAlisPro** version 1.171.41.76a (**5**, **8**), version 1.171.41.54a (**1**, **2**, **4**, **6**) and version 1.171.41.21a (**3**, **7**), respectively.[8] For the compounds **1**, **2**, **4**, **5**, **6**, **7** a numerical absorption correction based on gaussian integration over a multifaceted crystal model and an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK have been applied. For the compounds **3** and **8** a multi-scan absorption correction based on an empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK has been applied. Using **Olex2**,[9] the structures were solved with **ShelXT**[10] and a least-square refinement on F^2 was carried out with **ShelXL** (**1**, **3**, **5**, **6**, **7**, **8**)[11] or respectively with **Olex2** (**2**, **4**).[9] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at the carbon atoms have been located in idealized positions and refined isotropically according to the riding model. Figures were created with **Olex2**.[9]

CCDC-2035397 (**1**), CCDC-2035398 (**2**), CCDC-2035399 (**3**), CCDC-20353400 (**4**), CCDC-20353401 (**5**), CCDC-203534002 (**6**), CCDC-20353403 (**7**) and CCDC-20353404 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic data for compounds **1**, **2**, **3**, and **4**.

Compound	1	2	3	4
Data set (internal naming)	**MW238**	**MW342**	**MW391**	**MW384**
CCDC	2035397	2035398	2035399	20353400
Formula	$C_{39}H_{48}AsGaN_2$	$C_{39}H_{48}AlAsN_2$	$C_{27}H_{39.6}As_{0.8}Cl_{0.2}GaN_2$	$C_{27}H_{40.55}AlAs_{1.55}N_2$
$D_{calc.}$ / g · cm^{-3}	1.272	1.195	1.264	1.244
m/mm^{-1}	2.263	1.247	2.042	2.713
Formula Weight	689.43	646.732	528.95	536.296
Colour	clear colourless	clear colourless	clear colourless	clear colourless
Shape	block	block	needle	plate
Size/mm^3	0.42×0.17×0.17	0.63×0.45×0.15	0.32×0.28×0.17	0.30×0.20×0.03
T/K	123.01(10)	123.01(10)	123.00(10)	89.9(4)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$I2/a$
a/Å	10.6343(2)	10.6447(1)	12.35260(10)	18.3591(3)
b/Å	25.4875(5)	25.5162(3)	15.3129(2)	9.0485(1)
c/Å	13.8694(3)	13.7884(2)	14.6980(2)	34.4864(5)
α/°	90	90	90	90
β/°	106.767(2)	106.341(1)	90.1560(10)	91.580(1)
γ/°	90	90	90	90
V/Å^3	3599.37(13)	3593.81(8)	2780.18(6)	5726.78(14)
Z	4	4	4	8
Z'	1	1	1	1
Wavelength/Å	1.54184	1.39222	1.39222	1.54184
Radiation type	Cu K_α	Cu K_β	Cu K_β	Cu K_α
Θ_{min}/°	3.753	3.13	3.764	4.82
Θ_{max}/°	73.869	69.62	74.004	73.44
Measured Refl.	20511	25147	25477	17118
Independent Refl.	7008	8835	7471	5597
Reflections with I > 2(I)	6364	8261	6943	5320
R_{int}	0.0249	0.0220	0.0354	0.0280
Parameters	424	424	321	343
Restraints	38	0	3	14
Largest Peak	0.853	0.3802	0.378	0.6387
Deepest Hole	-0.926	-0.3881	-0.478	-0.3731
GooF	1.060	1.0465	1.040	1.0389
wR_2 (all data)	0.1342	0.0738	0.0823	0.1115
wR_2	0.1299	0.0722	0.0803	0.1101
R_1 (all data)	0.0502	0.0301	0.0330	0.0463
R_1	0.0459	0.0279	0.0306	0.0445

Table S2. Crystallographic data for compounds **5**, **6**, **7**, and **8**.

Compound	**5**	**6**	**7**	**8**
Data set (internal naming)	**MW435**	**MW415**	**MW443**	**MW436**
CCDC	20353401	20353402	20353403	20353404
Formula	$C_{27}H_{40.76}AlAs_{1.88}Cl_{0.12}N_2$	$C_{27}H_{37}As_{1.84}GaN_2$	$C_{27}H_{41}GaN_2P_2$	$C_{27}H_{41}AlN_2P_2$
$D_{calc.}$ / g · cm^{-3}	1.284	1.355	1.218	1.125
m/mm^{-1}	3.176	3.701	2.478	1.795
Formula Weight	565.46	597.16	525.28	482.54
Colour	colourless	clear colourless	clear colourless	colourless
Shape	needle	plate	block	block
Size/mm^3	0.30×0.07×0.04	0.24×0.10×0.04	0.20×0.16×0.04	0.35×0.25×0.25
T/K	122.97(10)	89.9(5)	122.96(18)	122.96(18)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	*I*2/*a*	*I*2/*a*	*I*2/*a*	*I*2/*a*
a/Å	18.5847(5)	18.4649(13)	18.4997(5)	18.4950(4)
b/Å	9.1394(2)	9.1493(5)	8.9746(3)	8.9092(2)
c/Å	34.4659(7)	34.661(3)	34.5230(9)	34.5784(7)
α/°	90	90	90	90
β/°	91.724(2)	91.509(7)	91.657(2)	91.407(2)
γ/°	90	90	90	90
V/Å^3	5851.5(2)	5853.7(7)	5729.4(3)	5696.0(2)
Z	8	8	8	8
Z'	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu K_α	Cu K_α	CuK_α	Cu K_α
Θ_{min}/°	4.761	4.792	2.561	2.556
Θ_{max}/°	73.940	47.228	74.800	73.766
Measured Refl.	16595	8047	16540	16336
Independent Refl.	5680	2626	5636	5489
Reflections with I > 2(I)	4789	2203	4924	4952
R_{int}	0.0486	0.0581	0.0328	0.0231
Parameters	381	301	317	337
Restraints	98	1	0	18
Largest Peak	0.476	0.903	0.771	0.968
Deepest Hole	-0.287	-0.845	-0.656	-0.496
GooF	1.031	1.044	1.035	1.045
wR_2 (all data)	0.1108	0.1896	0.1369	0.1622
wR_2	0.1041	0.1802	0.1303	0.1571
R_1 (all data)	0.0525	0.0841	0.0568	0.0606
R_1	0.0427	0.0726	0.0498	0.0560

Compound 1 (IDipp·GaH$_2$AsPh$_2$): The asymmetric unit contains one molecule of IDipp·GaH$_2$AsPh$_2$. One of the *i*Pr groups at a Dipp substituent is disordered over two positions (78:22). To model this disorder the SIMU restraint was applied. Further, the hydrogen atoms at the gallium atom were located from the difference Fourier map and the Ga-H bond distance was restraint with a DFIX restraint to 1.5 Å.

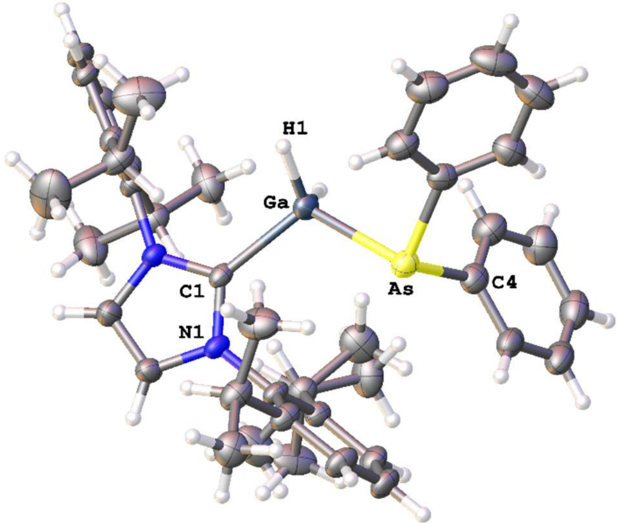


Figure S34: Molecular structure of **1** in solid state. Selected bond lengths [Å] and angles [°]: Ga–As 2.4659(5), Ga–C1 2.068(3), C1–Ga–As 109.33(8), H1–Ga–As–C4 134.4.

Compound 2 (IDipp·AlH$_2$AsPh$_2$): The asymmetric unit contains one molecule of IDipp·AlH$_2$AsPh$_2$. One of the *i*Pr groups at a Dipp substituent is disordered over two positions (64:36). The hydrogen atoms at the aluminum atom were located from the difference Fourier map and refined without restraints.

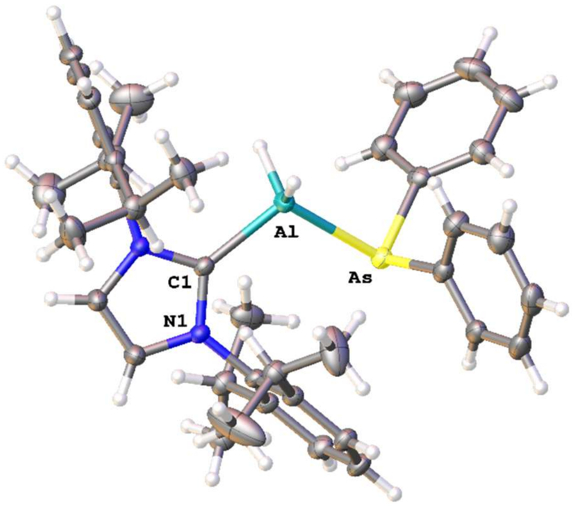


Figure S35: Molecular structure of **2** in solid state. Selected bond lengths [Å] and angles [°]: Al–As 2.4929(4), Al–C1 2.0634(12), C1–Al–As 109.53(3), H1–Al–As–C4 138.1.

Compound 3 (IDipp·GaH_2AsH_2): The asymmetric unit contains 0.8 molecule of IDipp·GaH_2AsH_2 and 0.2 molecules of IDipp·GaH_2Cl, which superpose each other. The hydrogen atoms at the gallium atom and the arsenic atom were located from the difference Fourier map. The As-H distances and the H-As-H angle were restrained by applying the DANG and DFIX restraints.

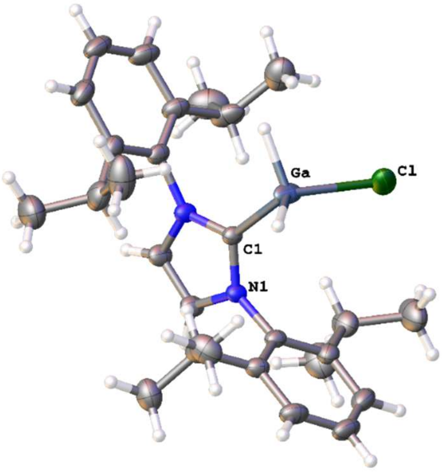


Figure S36: Molecular structure of IDipp·GaH_2Cl in solid state. Chlorine occupation: 20%. Selected bond lengths [Å]: Ga–Cl 2.336(7).

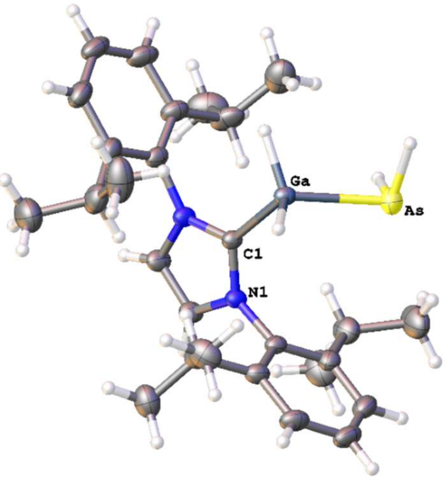


Figure S37: Molecular structure of **3** in solid state. Arsenic occupation: 80%. Selected bond lengths [Å]: Ga–As 2.4503(12).

Compound 4 (IDipp·AlH_2AsH_2): The asymmetric unit contains one molecule with the formula IDipp·AlHXY. The substituents X and Y can be described as a hydrogen atom and two AsH_2 units, which are disordered over three positions. For X an occupancy of 55(AsH_2):32(AsH_2):13(H) and for Y an occupancy of 48(AsH_2):32(H):20(AsH_2) could be identified. This can be interpreted as a co-crystallization of the compounds IDipp·AlH_2AsH_2 (**4**), IDipp·$AlH(AsH_2)_2$ (**5**) and IDipp·AlH_3. However, from a crystallographic point of view it is not possible to unambiguously determine the exact composition of this co-crystallization. Only a theoretical minimum and maximum range of occupancies for the different compounds can be given, which range for the compound IDipp·AlH_2AsH_2 (**4**) from 19 to 45%, for compound IDipp·$AlH(AsH_2)_2$ (**5**) from 55 to 68% and for the compound IDipp·AlH_3 from 0 to 13%. The hydrogen atoms at the aluminum atom and the arsenic atoms were located from the difference Fourier map and the restraints DANG and DFIX were applied. For the arsenic atom As1B it was due to the low occupancy not possible to locate the hydrogen positions.

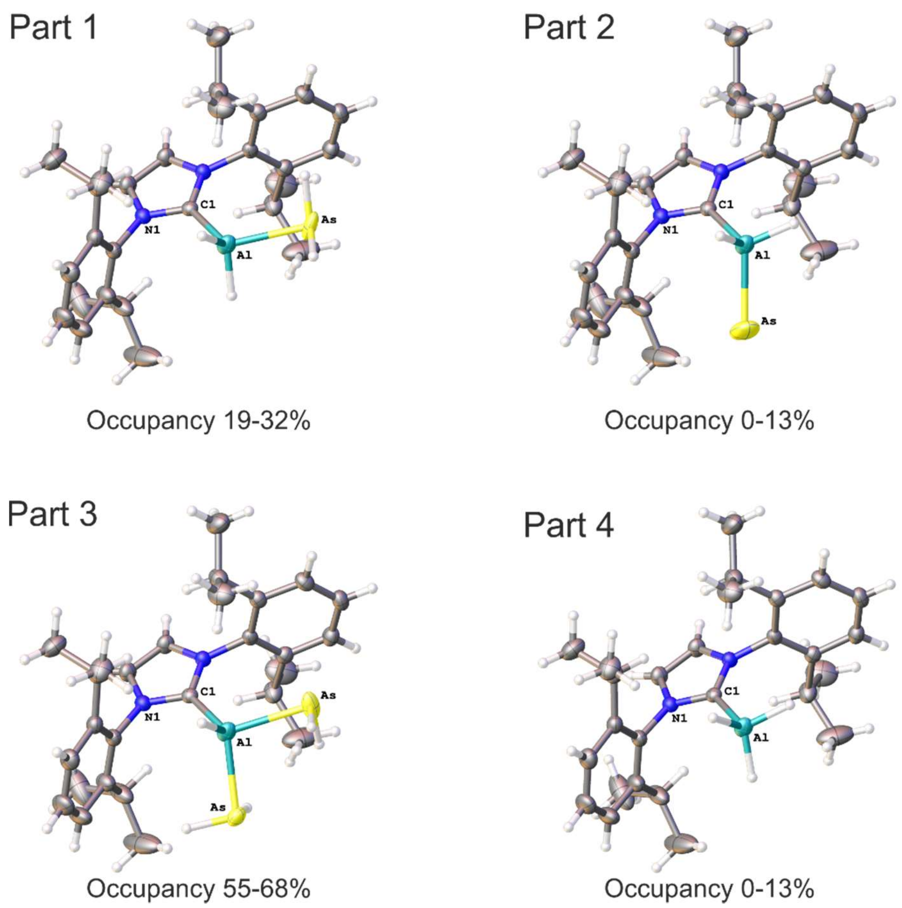


Figure S38: The three co-crystallized compounds IDipp·AlH_2AsH_2 (**4**), IDipp·$AlH(AsH_2)_2$) (**5**) and IDipp·AlH_3 and their possible occupancies.

Compound 5 (IDipp·AlH(AsH_2)$_2$): Compound IDipp·AlH(AsH_2)$_2$ (**5**) co-crystallized with 6% of the starting material IDipp·AlHCl_2. Further, both AsH_2 units are disordered over two positions (57:37). Additionally one *i*Pr group of a Dipp substituent is disordered over two positions (83:17). To model these disorders the restraints SADI and SIMU were applied. The hydrogen atoms at the aluminum atom and the arsenic atoms were located from the difference Fourier map and the restraints DFIX, DANG and SADI were applied.

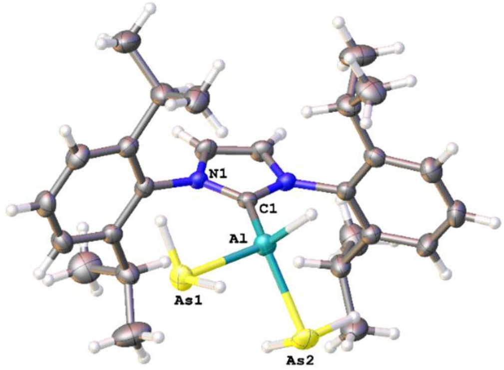


Figure S39: Molecular structure of **5** in solid state (part 1). Arsenic occupation: As1: 57%, As2: 57%. Selected bond lengths [Å]: Al–As1 2.451(4), Al–As2 2.474(3).

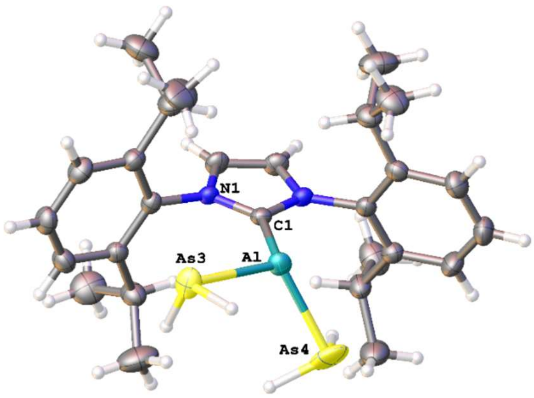


Figure S40: Molecular structure of **5** in solid state (part 2). Arsenic occupation: As3: 37%, As4: 37%. Selected bond lengths [Å]: Al–As3 2.511(6), Al–As4 2.461(4).

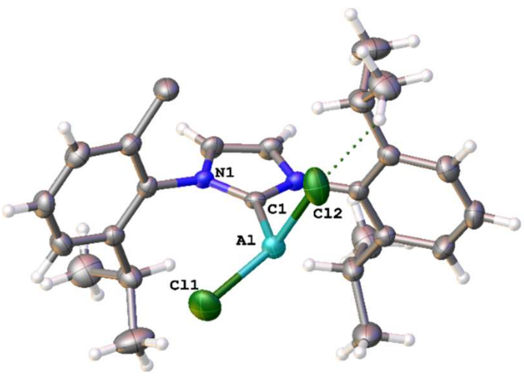


Figure S41: Molecular structure of **5** in solid state (part 3). Chlorine occupation: Cl1: 6%, Cl2: 6%. Selected bond lengths [Å]: Al–Cl1 2.189(14), Al–Cl2 2.102(14).

Compound 6 (IDipp·GaH(AsH_2)$_2$): The overall quality of the crystals of compound **6** was poor, although several attempts to obtain better crystals via recrystallization were undertaken. The measured crystal was a weakly diffracting thin plate (no reflections with an I/σ > 3 above a resolution of 1.05 Å), therefore only reflections up to a resolution of 1.05 Å were taken into account. Compound IDipp·GaH(AsH_2)$_2$ (**6**) co-crystallizes with compound IDipp·GaH_2AsH_2 (**3**) in the ratio 84 to 16.

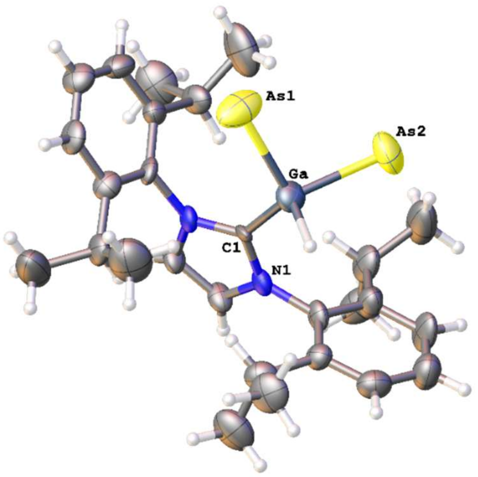


Figure S42: Molecular structure of **6** in solid state. Selected bond lengths [Å]: Ga–As1 2.4412(19), Ga–As2 2.446(2).

Compound 7 (IDipp·GaH(PH_2)$_2$): The asymmetric unit contains one molecule of IDipp·GaH(PH_2)$_2$ (**7**). The hydrogen atoms at the gallium atom and the phosphorus atoms were located from the difference Fourier map and refined without restraints.

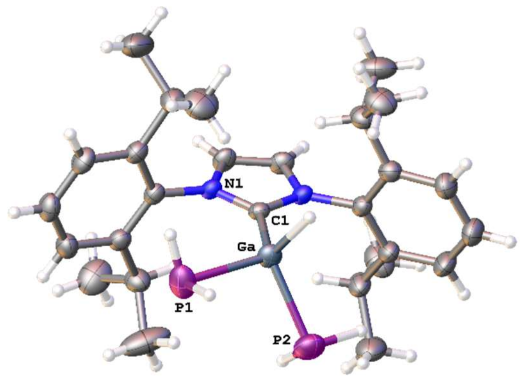


Figure S43: Molecular structure of **7** in solid state. Selected bond lengths [Å] and angles [°]: Ga–P1 2.3574(9), Ga–P2 2.3437(10), Ga–C1 2.075(3), P1–Ga–C1 113.68(7), P2–Ga–C1 112.38(7).

Compound 8 (IDipp·AlH(PH$_2$)$_2$: The asymmetric unit contains one molecule of IDipp·AlH(PH$_2$)$_2$ (**8**). One of the *i*Pr groups at a Dipp substituent is disordered over two positions (76:24). To model this disorder the restraints SADI and SIMU were applied. The hydrogen atoms at the aluminum atom and the phosphorus atoms were located from the difference Fourier map and refined without restraints.

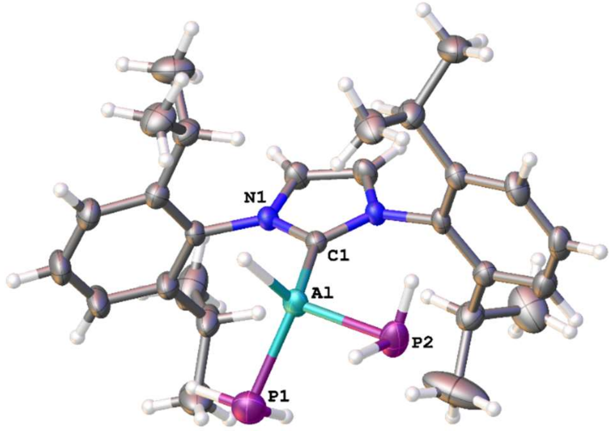


Figure S44: Molecular structure of **8** in solid state. Selected bond lengths [Å] and angles [°]: Al–P1 2.3075(10), Al–P2 2.3418(9), Al–C1 2.066(2), P1–Al–C1 112.04(6), P2–Al–C1 113.91(6).

6.5.4. Computational data

The geometries of the compounds have been fully optimized with gradient-corrected density functional theory (DFT) in form of Becke's three-parameter hybrid method B3LYP[12] with def2-TZVP all electron basis set.[13] Gaussian 09 program package[14] was used throughout. All structures correspond to minima on their respective potential energy surfaces. Basis sets were obtained from the EMSL basis set exchange database.[15] Data for the standard sublimation enthalpies and entropies of NaCl (229.7 kJ mol^{-1}, 157.7 J mol^{-1} K^{-1}) and KCl (222.0 kJ mol^{-1}, 156.5 J mol^{-1} K^{-1}) were taken from the NIST Chemistry Webbook database.[16]

Total energies E°$_0$, enthalpies H°$_{298}$ and entropies S°$_{298}$

Table S3. Total energies E°$_0$, sum of electronic and thermal enthalpies H°$_{298}$ (Hartree) and standard entropies S°$_{298}$ (cal mol^{-1}K^{-1}) for studied compounds. B3LYP/def2-TZVP level of theory.

Compound	E°$_0$	H°$_{298}$	S°$_{298}$
H_2	-1.179649	-1.16627	31.138
NaCl	-622.6050592	-622.60058	54.82
KCl	-1060.244534	-1060.240153	57.115
PH_3	-343.176453	-343.148706	52.381
AsH_3	-2237.710458	-2237.684847	53.259
$AsH(Ph)_2$	-2699.976643	-2699.775462	113.676
$C_4H_8O_2$ (dioxane)	-307.7854057	-307.657205	71.314
$NaPH_2$	-504.8907533	-504.870408	63.818
$KAsH_2$	-2837.067363	-2837.048582	69.780
$KAsPh_2$	-3299.33952	-3299.145215	120.248
$KAsPh_2$·dioxane	-3607.139712	-3606.814955	163.916
IDipp	-1160.453853	-1159.85478	201.948
AlH_3·IDipp	-1404.746619	-1404.121324	210.216
AlH_2Cl·IDipp	-1864.461387	-1863.8398	218.930
$AlHCl_2$·IDipp	-2324.171641	-2323.554103	225.598
GaH_3·IDipp	-3087.182738	-3086.557418	212.980
GaH_2Cl·IDipp	-3546.884942	-3546.263502	222.427
$GaHCl_2$·IDipp	-4006.579704	-4005.963533	225.808
AlH_2AsH_2	-2480.7767615	-2480.7425520	70.435
GaH_2AsH_2	-4163.223595	-4163.189279	72.627
IDipp·AlH_2PH_2	-1746.74819	-1746.109847	222.13
IDipp·GaH_2PH_2	-3429.183794	-3428.545409	225.462
IDipp·AlH_2AsH_2	-3641.2872511	-3640.650401	226.044
IDipp·GaH_2AsH_2	-5323.723883	-5323.08713	228.813
AlH_2AsPh_2	-2943.03969	-2942.829581	121.761
GaH_2AsPh_2	-4625.485371	-4625.275509	127.302
IDipp·AlH_2AsPh_2	-4103.547087	-4102.734791	277.980
IDipp·GaH_2AsPh_2	-5785.984679	-5785.172598	281.037
$(AlH_2AsH_2)_3$	-7442.421483	-7442.312137	127.110
$(GaH_2AsH_2)_3$	-12489.74587	-12489.63658	134.673
$(AlH_2AsPh_2)_3$	-8829.223992	-8828.589139	286.600
$(GaH_2AsPh_2)_3$	-13876.55025	-13875.91482	291.115
IDipp·$AlH(PH_2)_2$	-2088.7487890	-2088.097245	234.179
IDipp·$GaH(PH_2)_2$	-3771.1838562	-3770.532371	237.005
IDipp·$AlH(AsH_2)_2$	-5877.8263943	-5877.177743	237.819
IDipp·$GaH(AsH_2)_2$	-7560.2639038	-7559.615391	241.614

Optimized geometries of the compounds

Table S4. Optimized xyz coordinates (in Angstroms) for studied compounds. B3LYP/def2-TZVP level of theory.

H_2			
1	0.000000000	0.000000000	0.371966000
1	0.000000000	0.000000000	-0.371966000
NaCl			
11	0.000000000	0.000000000	-1.435262000
17	0.000000000	0.000000000	0.928699000
KCl			
19	0.000000000	0.000000000	1.276537000
17	0.000000000	0.000000000	-1.426718000
PH_3			
15	0.000000000	0.128213000	0.000000000
1	0.596216000	-0.641128000	-1.032219000
1	0.596216000	-0.641128000	1.032219000
1	-1.192431000	-0.640945000	0.000000000
AsH_3			
33	0.000000000	0.000000000	0.070769000
1	0.000000000	1.267255000	-0.778460000
1	1.097475000	-0.633627000	-0.778460000
1	-1.097475000	-0.633627000	-0.778460000
$AsH(Ph)_2$			
33	-1.529686000	0.194962000	0.000000000
6	-0.267272000	0.060367000	1.513258000
6	-0.267272000	0.060367000	-1.513258000
1	-1.571989000	1.720465000	0.000000000
6	1.461665000	-0.246846000	3.693412000
6	0.450303000	1.150238000	2.008751000
6	-0.115638000	-1.181735000	2.131250000
6	0.749258000	-1.337664000	3.209393000
6	1.307497000	0.998097000	3.093210000
1	0.343645000	2.125291000	1.549892000
1	-0.678625000	-2.036551000	1.774202000
1	0.859683000	-2.309252000	3.675124000
1	1.856175000	1.853303000	3.468572000
1	2.130062000	-0.364632000	4.537090000
6	1.461665000	-0.246846000	-3.693412000
6	-0.115638000	-1.181735000	-2.131250000
6	0.450303000	1.150238000	-2.008751000
6	1.307497000	0.998097000	-3.093210000
6	0.749258000	-1.337664000	-3.209393000
1	-0.678625000	-2.036551000	-1.774202000
1	0.343645000	2.125291000	-1.549892000
1	1.856175000	1.853303000	-3.468572000
1	0.859683000	-2.309252000	-3.675124000
1	2.130062000	-0.364632000	-4.537090000
$C_4H_8O_2$ (dioxane)			
8	0.225685000	-1.392107000	0.000000000
6	0.225685000	0.725174000	-1.172862000
6	0.225685000	0.725174000	1.172862000
8	-0.225685000	1.392107000	0.000000000
6	-0.225685000	-0.725174000	1.172862000
6	-0.225685000	-0.725174000	-1.172862000
1	1.322238000	0.772670000	-1.230133000
1	1.322238000	0.772670000	1.230133000
1	-1.322238000	-0.772670000	1.230133000
1	-1.322238000	-0.772670000	-1.230133000
1	-0.194548000	1.265255000	-2.022561000

1	-0.194548000	1.265255000	2.022561000
1	0.194548000	-1.265255000	2.022561000
1	0.194548000	-1.265255000	-2.022561000

$NaPH_2$

11	-0.070721000	1.606267000	0.000000000
15	-0.070721000	-1.039811000	0.000000000
1	0.919368000	-1.035885000	1.028264000
1	0.919368000	-1.035885000	-1.028264000

$KAsH_2$

19	-0.039576000	2.026166000	0.000000000
33	-0.039576000	-1.110180000	0.000000000
1	1.028975000	-0.930610000	1.094235000
1	1.028975000	-0.930610000	-1.094235000

$KAsPh_2$

6	1.504996000	0.155291000	-0.445884000
33	0.025706000	1.443446000	-0.610563000
19	0.101121000	0.129453000	2.250754000
6	-1.546507000	0.248730000	-0.429855000
6	-3.931494000	-1.274620000	-0.208050000
6	-1.737343000	-0.934548000	-1.165175000
6	-2.607311000	0.646997000	0.404680000
6	-3.782696000	-0.092789000	0.509182000
6	-2.899851000	-1.687064000	-1.048425000
1	-0.972904000	-1.254863000	-1.862031000
1	-2.517864000	1.576187000	0.961599000
1	-4.583012000	0.257185000	1.151442000
1	-3.010304000	-2.593085000	-1.633366000
1	-4.840152000	-1.857496000	-0.126058000
6	3.844326000	-1.419928000	-0.018886000
6	2.804769000	0.700965000	-0.540265000
6	1.435344000	-1.222741000	-0.152390000
6	2.580910000	-1.990403000	0.060326000
6	3.941296000	-0.061486000	-0.331887000
1	2.915078000	1.753006000	-0.782248000
1	0.473197000	-1.722070000	-0.118109000
1	2.477425000	-3.049174000	0.273018000
1	4.916931000	0.403424000	-0.417999000
1	4.733358000	-2.016874000	0.137785000

$KAsPh_2$·dioxane

6	-0.583674000	-1.952152000	-0.072560000
33	-2.136132000	-1.182687000	-1.018879000
6	-2.633539000	0.328077000	0.137686000
6	-3.463931000	2.709023000	1.470007000
6	-1.897969000	0.881687000	1.206635000
6	-3.817201000	1.012635000	-0.217477000
6	-4.220476000	2.171114000	0.426270000
6	-2.304438000	2.046820000	1.855222000
1	-0.997263000	0.388419000	1.553357000
1	-4.430723000	0.616138000	-1.019998000
1	-5.139181000	2.658250000	0.119303000
1	-1.711278000	2.430019000	2.678771000
1	-3.784319000	3.608472000	1.979662000
6	1.604474000	-3.325339000	1.106969000
6	0.462589000	-2.486077000	-0.847811000
6	-0.497148000	-2.146872000	1.317834000
6	0.580061000	-2.808067000	1.896823000
6	1.529264000	-3.169804000	-0.274645000
1	0.426323000	-2.375727000	-1.927171000
1	-1.302618000	-1.805102000	1.955406000
1	0.607785000	-2.941756000	2.972502000

1	2.306041000	-3.581171000	-0.909637000
1	2.433929000	-3.855301000	1.558348000
19	-0.173558000	1.337844000	-1.322606000
8	2.326548000	1.494903000	-0.269174000
6	4.682699000	1.969318000	-0.599373000
6	4.065489000	-0.076977000	0.362159000
8	5.033047000	0.967980000	0.340804000
6	2.687830000	0.469427000	0.678527000
6	3.308233000	2.537137000	-0.291691000
1	4.693232000	1.553060000	-1.616822000
1	4.049632000	-0.593316000	-0.606499000
1	2.672449000	0.899189000	1.686477000
1	3.320367000	3.044575000	0.680463000
1	5.442045000	2.749847000	-0.533572000
1	4.378280000	-0.784948000	1.129057000
1	1.934223000	-0.314517000	0.610856000
1	3.000687000	3.250766000	-1.058485000

IDipp

6	0.674960000	-0.000061000	1.853488000
6	-0.674915000	0.000151000	1.853504000
7	-1.062430000	0.000181000	0.517812000
6	-0.000003000	-0.000008000	-0.342280000
7	1.062444000	-0.000158000	0.517787000
1	1.379343000	-0.000152000	2.666568000
1	-1.379279000	0.000280000	2.666601000
6	2.435809000	-0.000373000	0.090009000
6	3.085267000	1.227701000	-0.111259000
6	3.084594000	-1.228644000	-0.112192000
6	4.416080000	1.199376000	-0.527433000
6	4.415415000	-1.200728000	-0.528378000
6	5.077373000	-0.000779000	-0.734658000
1	4.940696000	2.131057000	-0.697180000
1	4.939506000	-2.132569000	-0.698867000
6	-2.435805000	0.000376000	0.090067000
6	-3.084599000	1.228638000	-0.112164000
6	-4.415430000	1.200704000	-0.528315000
6	-5.077391000	0.000746000	-0.734534000
1	-4.939527000	2.132537000	-0.698825000
6	-4.416091000	-1.199400000	-0.527282000
1	-4.940708000	-2.131088000	-0.696980000
6	-3.085267000	-1.227707000	-0.111139000
6	-2.379919000	2.563741000	0.074073000
1	-1.393576000	2.364550000	0.491176000
6	-3.116585000	3.476910000	1.064890000
6	-2.165994000	3.265466000	-1.276204000
1	-1.598665000	2.631072000	-1.957893000
1	-3.118903000	3.508866000	-1.751899000
1	-1.614358000	4.198245000	-1.137505000
1	-4.107294000	3.755953000	0.700388000
1	-2.551805000	4.398959000	1.219408000
1	-3.243448000	2.991921000	2.034677000
6	-2.381271000	-2.563037000	0.076099000
1	-1.394748000	-2.364031000	0.492864000
6	-3.118247000	-3.474983000	1.067808000
6	-2.167978000	-3.266026000	-1.273622000
1	-3.121111000	-3.509351000	-1.748906000
1	-1.600472000	-2.632523000	-1.955991000
1	-1.616794000	-4.198969000	-1.134232000
1	-3.244707000	-2.989116000	2.037209000
1	-2.553925000	-4.397197000	1.223016000
1	-4.109161000	-3.753816000	0.703698000

6	2.381278000	2.563038000	0.075947000
1	1.394759000	2.364048000	0.492731000
6	3.118270000	3.475011000	1.067620000
6	2.167970000	3.265989000	-1.273791000
1	3.121097000	3.509298000	-1.749094000
1	1.600454000	2.632467000	-1.956135000
1	1.616789000	4.198937000	-1.134421000
1	3.244740000	2.989172000	2.037034000
1	2.553955000	4.397232000	1.222809000
1	4.109181000	3.753828000	0.703489000
6	2.379915000	-2.563739000	0.074108000
1	1.393589000	-2.364532000	0.491243000
6	2.165939000	-3.265500000	-1.276141000
6	3.116612000	-3.476885000	1.064923000
1	4.107306000	-3.755945000	0.700393000
1	3.243515000	-2.991870000	2.034692000
1	2.551832000	-4.398925000	1.219489000
1	1.598586000	-2.631124000	-1.957827000
1	1.614307000	-4.198275000	-1.137397000
1	3.118831000	-3.508913000	-1.751864000
1	-6.110357000	0.000889000	-1.060192000
1	6.110332000	-0.000936000	-1.060341000

AlH_3·IDipp

6	0.675268000	0.032290000	-1.892198000
6	-0.675275000	0.032235000	-1.892194000
7	-1.072351000	0.021606000	-0.566906000
6	0.000006000	0.015139000	0.266599000
7	1.072354000	0.021707000	-0.566920000
1	1.382577000	0.038199000	-2.701403000
1	-1.382586000	0.038109000	-2.701396000
6	2.462893000	0.006893000	-0.168347000
6	3.100877000	-1.231622000	-0.003511000
6	3.127676000	1.231397000	-0.002848000
6	4.452571000	-1.214743000	0.339108000
6	4.478501000	1.186190000	0.336457000
6	5.135837000	-0.021631000	0.506977000
1	4.975801000	-2.151417000	0.479190000
1	5.021392000	2.111465000	0.477749000
6	-2.462895000	0.006876000	-0.168357000
6	-3.100901000	-1.231607000	-0.003291000
6	-4.452598000	-1.214649000	0.339287000
6	-5.135866000	-0.021494000	0.506874000
1	-4.975843000	-2.151290000	0.479546000
6	-4.478523000	1.186281000	0.336103000
1	-5.021407000	2.111595000	0.477174000
6	-3.127674000	1.231411000	-0.003143000
6	-2.392000000	-2.563743000	-0.199905000
1	-1.331939000	-2.364326000	-0.356201000
6	-2.912065000	-3.286912000	-1.453344000
6	-2.495291000	-3.462812000	1.040795000
1	-2.087284000	-2.964871000	1.920214000
1	-3.529238000	-3.744738000	1.249933000
1	-1.929301000	-4.383153000	0.881243000
1	-3.969955000	-3.539468000	-1.354452000
1	-2.360893000	-4.216348000	-1.612087000
1	-2.800547000	-2.670744000	-2.347900000
6	-2.440979000	2.576750000	-0.183990000
1	-1.376797000	2.395624000	-0.336010000
6	-2.964192000	3.305933000	-1.432238000
6	-2.567595000	3.459230000	1.066868000
1	-3.604812000	3.744863000	1.254041000

1	-2.191733000	2.940148000	1.948481000
1	-1.992936000	4.378679000	0.934710000
1	-2.833814000	2.703994000	-2.333889000
1	-2.429981000	4.247928000	-1.574333000
1	-4.027511000	3.536683000	-1.338547000
6	2.391969000	-2.563722000	-0.200356000
1	1.331937000	-2.364256000	-0.356808000
6	2.912191000	-3.286826000	-1.453760000
6	2.495038000	-3.462865000	1.040315000
1	3.528957000	-3.744754000	1.249637000
1	2.086837000	-2.964981000	1.919677000
1	1.929121000	-4.383224000	0.880600000
1	2.800899000	-2.670567000	-2.348282000
1	2.360951000	-4.216189000	-1.612684000
1	3.970033000	-3.539515000	-1.354709000
6	2.440996000	2.576758000	-0.183598000
1	1.376729000	2.395665000	-0.335053000
6	2.568249000	3.459538000	1.066974000
6	2.963698000	3.305598000	-1.432270000
1	4.027116000	3.536134000	-1.339156000
1	2.832741000	2.703510000	-2.333739000
1	2.429603000	4.247672000	-1.574282000
1	2.192826000	2.940664000	1.948894000
1	1.993482000	4.378927000	0.934877000
1	3.605542000	3.745290000	1.253544000
1	-6.184587000	-0.032569000	0.776587000
1	6.184549000	-0.032762000	0.776725000
13	0.000033000	-0.037597000	2.365479000
1	1.350405000	0.722466000	2.772759000
1	0.000673000	-1.617581000	2.670057000
1	-1.350952000	0.721349000	2.772796000

AlH_2Cl·IDipp

6	0.675410000	0.282765000	-2.020492000
6	-0.675381000	0.282765000	-2.020495000
7	-1.073636000	0.174025000	-0.701455000
6	0.000009000	0.107561000	0.127250000
7	1.073657000	0.174022000	-0.701449000
1	1.382486000	0.350022000	-2.826706000
1	-1.382451000	0.350025000	-2.826713000
6	2.468591000	0.155589000	-0.310045000
6	3.142092000	-1.075488000	-0.279121000
6	3.101029000	1.376651000	-0.030389000
6	4.495981000	-1.052941000	0.054087000
6	4.455504000	1.335883000	0.295467000
6	5.146737000	0.136265000	0.339149000
1	5.047406000	-1.982357000	0.094116000
1	4.974696000	2.257511000	0.523203000
6	-2.468572000	0.155610000	-0.310056000
6	-3.142085000	-1.075461000	-0.279111000
6	-4.495976000	-1.052892000	0.054087000
6	-5.146722000	0.136328000	0.339120000
1	-5.047412000	-1.982299000	0.094133000
6	-4.455476000	1.335937000	0.295420000
1	-4.974659000	2.257576000	0.523136000
6	-3.100998000	1.376684000	-0.030428000
6	-2.471306000	-2.395835000	-0.631844000
1	-1.392060000	-2.244106000	-0.603745000
6	-2.846682000	-2.832293000	-2.058903000
6	-2.785613000	-3.510196000	0.375267000
1	-2.521075000	-3.211605000	1.388631000
1	-3.840657000	-3.790897000	0.355354000

1	-2.206863000	-4.402441000	0.128444000
1	-3.920740000	-3.013108000	-2.141390000
1	-2.329403000	-3.757654000	-2.321215000
1	-2.580287000	-2.076035000	-2.799697000
6	-2.382775000	2.716947000	-0.091244000
1	-1.318382000	2.525433000	-0.228607000
6	-2.857218000	3.544523000	-1.297411000
6	-2.528042000	3.512742000	1.214166000
1	-3.562956000	3.813428000	1.389017000
1	-2.194708000	2.924670000	2.069031000
1	-1.927080000	4.423478000	1.165313000
1	-2.714731000	3.006414000	-2.236592000
1	-2.300878000	4.482456000	-1.357516000
1	-3.917947000	3.790222000	-1.213722000
6	2.471310000	-2.395855000	-0.631873000
1	1.392066000	-2.244077000	-0.603976000
6	2.846907000	-2.832434000	-2.058836000
6	2.785396000	-3.510144000	0.375387000
1	3.840449000	-3.790830000	0.355739000
1	2.520622000	-3.211485000	1.388671000
1	2.206713000	-4.402414000	0.128493000
1	2.580696000	-2.076202000	-2.799724000
1	2.329608000	-3.757776000	-2.321177000
1	3.920966000	-3.013333000	-2.141129000
6	2.382821000	2.716923000	-0.091183000
1	1.318427000	2.525423000	-0.228560000
6	2.528087000	3.512686000	1.214246000
6	2.857283000	3.544520000	-1.297328000
1	3.918015000	3.790201000	-1.213629000
1	2.714792000	3.006433000	-2.236522000
1	2.300956000	4.482461000	-1.357417000
1	2.194749000	2.924596000	2.069097000
1	1.927129000	4.423427000	1.165413000
1	3.563002000	3.813362000	1.389107000
1	-6.197674000	0.127561000	0.600032000
1	6.197688000	0.127483000	0.600067000
13	-0.000001000	-0.018375000	2.214670000
1	-1.358041000	0.668302000	2.675125000
1	1.358139000	0.668095000	2.675137000
17	-0.000154000	-2.174145000	2.602416000

$AlHCl_2$·IDipp

6	-2.212177000	0.045800000	0.674790000
6	-2.212177000	0.045800000	-0.674790000
7	-0.890216000	0.072123000	-1.074466000
6	-0.057298000	0.090765000	0.000000000
7	-0.890216000	0.072123000	1.074466000
1	-3.019789000	0.027565000	1.383217000
1	-3.019789000	0.027565000	-1.383217000
6	-0.526849000	0.049587000	2.478048000
6	-0.338587000	1.267609000	3.147163000
6	-0.447452000	-1.195113000	3.120951000
6	-0.055571000	1.207512000	4.511269000
6	-0.166056000	-1.191210000	4.485344000
6	0.029386000	-0.005352000	5.174394000
1	0.102287000	2.125468000	5.061246000
1	-0.088731000	-2.131885000	5.013962000
6	-0.526849000	0.049587000	-2.478048000
6	-0.338587000	1.267609000	-3.147163000
6	-0.055571000	1.207512000	-4.511269000
6	0.029386000	-0.005352000	-5.174394000
1	0.102287000	2.125468000	-5.061246000

6	-0.166056000	-1.191210000	-4.485344000
1	-0.088731000	-2.131885000	-5.013962000
6	-0.447452000	-1.195113000	-3.120951000
6	-0.465047000	2.620218000	-2.460688000
1	-0.491677000	2.454672000	-1.383508000
6	-1.781376000	3.312631000	-2.853277000
6	0.737418000	3.533627000	-2.737027000
1	1.672525000	3.051238000	-2.454537000
1	0.798769000	3.814598000	-3.790173000
1	0.644491000	4.454132000	-2.157304000
1	-1.808965000	3.523453000	-3.924549000
1	-1.885103000	4.261301000	-2.322227000
1	-2.649380000	2.695006000	-2.614113000
6	-0.664752000	-2.518141000	-2.400458000
1	-0.723800000	-2.315775000	-1.330636000
6	-1.995202000	-3.165481000	-2.820379000
6	0.505313000	-3.492392000	-2.603227000
1	0.590506000	-3.808145000	-3.644918000
1	1.450671000	-3.039295000	-2.306648000
1	0.348579000	-4.390294000	-2.001572000
1	-2.843958000	-2.504128000	-2.635417000
1	-2.160797000	-4.090731000	-2.264210000
1	-1.993336000	-3.411470000	-3.884381000
6	-0.465047000	2.620218000	2.460688000
1	-0.491677000	2.454672000	1.383508000
6	-1.781376000	3.312631000	2.853277000
6	0.737418000	3.533627000	2.737027000
1	0.798769000	3.814598000	3.790173000
1	1.672525000	3.051238000	2.454537000
1	0.644491000	4.454132000	2.157304000
1	-2.649380000	2.695006000	2.614113000
1	-1.885103000	4.261301000	2.322227000
1	-1.808965000	3.523453000	3.924549000
6	-0.664752000	-2.518141000	2.400458000
1	-0.723800000	-2.315775000	1.330636000
6	0.505313000	-3.492392000	2.603227000
6	-1.995202000	-3.165481000	2.820379000
1	-1.993336000	-3.411470000	3.884381000
1	-2.843958000	-2.504128000	2.635417000
1	-2.160797000	-4.090731000	2.264210000
1	1.450671000	-3.039295000	2.306648000
1	0.348579000	-4.390294000	2.001572000
1	0.590506000	-3.808145000	3.644918000
1	0.254519000	-0.026995000	-6.233332000
1	0.254519000	-0.026995000	6.233332000
13	2.006923000	0.431051000	0.000000000
17	2.846719000	-0.475849000	-1.769290000
17	2.846719000	-0.475849000	1.769290000
1	2.106161000	2.011905000	0.000000000

GaH_3·IDipp

6	0.675022000	0.038928000	-2.073300000
6	-0.674998000	0.039008000	-2.073311000
7	-1.072212000	0.021253000	-0.746644000
6	-0.000007000	0.009868000	0.085236000
7	1.072214000	0.021170000	-0.746628000
1	1.382315000	0.049106000	-2.882498000
1	-1.382277000	0.049261000	-2.882520000
6	2.461586000	0.010505000	-0.346579000
6	3.104727000	-1.225509000	-0.183758000
6	3.121327000	1.237022000	-0.176107000
6	4.456173000	-1.204357000	0.159351000

6	4.472173000	1.196584000	0.164342000
6	5.134619000	-0.008946000	0.331121000
1	4.983093000	-2.139322000	0.297180000
1	5.011121000	2.123735000	0.308753000
6	-2.461594000	0.010673000	-0.346626000
6	-3.104888000	-1.225292000	-0.184029000
6	-4.456339000	-1.204033000	0.159053000
6	-5.134640000	-0.008569000	0.331026000
1	-4.983378000	-2.138958000	0.296704000
6	-4.472041000	1.196909000	0.164479000
1	-5.010872000	2.124100000	0.309064000
6	-3.121187000	1.237238000	-0.175950000
6	-2.400052000	-2.559114000	-0.382478000
1	-1.339135000	-2.362126000	-0.535663000
6	-2.919384000	-3.278099000	-1.638533000
6	-2.509155000	-3.460441000	0.856083000
1	-2.107083000	-2.963204000	1.738632000
1	-3.543962000	-3.743464000	1.059482000
1	-1.941745000	-4.380203000	0.698248000
1	-3.978562000	-3.526654000	-1.543040000
1	-2.371411000	-4.209394000	-1.797614000
1	-2.802904000	-2.660653000	-2.531546000
6	-2.428577000	2.580276000	-0.351755000
1	-1.366263000	2.394665000	-0.510591000
6	-2.954666000	3.320906000	-1.591983000
6	-2.544005000	3.455160000	0.905516000
1	-3.579149000	3.741695000	1.102510000
1	-2.162490000	2.930551000	1.781428000
1	-1.968204000	4.374138000	0.775120000
1	-2.832373000	2.724365000	-2.498286000
1	-2.415952000	4.260851000	-1.730612000
1	-4.016157000	3.556983000	-1.491067000
6	2.399721000	-2.559273000	-0.381993000
1	1.338816000	-2.362172000	-0.535122000
6	2.918884000	-3.278463000	-1.638001000
6	2.508792000	-3.460469000	0.856665000
1	3.543569000	-3.743638000	1.060011000
1	2.106876000	-2.963054000	1.739185000
1	1.941220000	-4.380158000	0.698991000
1	2.802412000	-2.661106000	-2.531079000
1	2.370797000	-4.209715000	-1.796940000
1	3.978041000	-3.527121000	-1.542550000
6	2.428915000	2.580116000	-0.352268000
1	1.366544000	2.394628000	-0.510862000
6	2.544693000	3.455454000	0.904652000
6	2.954936000	3.320197000	-1.592855000
1	4.016489000	3.556110000	-1.492193000
1	2.832385000	2.723349000	-2.498921000
1	2.416375000	4.260191000	-1.731739000
1	2.163231000	2.931237000	1.780821000
1	1.969014000	4.374472000	0.774000000
1	3.579912000	3.741910000	1.101369000
1	-6.183322000	-0.016123000	0.601048000
1	6.183296000	-0.016581000	0.601160000
31	-0.000015000	-0.053894000	2.209373000
1	1.342005000	0.694987000	2.605931000
1	0.000374000	-1.620940000	2.501682000
1	-1.342416000	0.694325000	2.605877000

GaH_2Cl·IDipp

6	0.666456000	0.289306000	-2.175401000
6	-0.683960000	0.286763000	-2.173738000

7	-1.080498000	0.178441000	-0.852892000
6	-0.005538000	0.115786000	-0.028813000
7	1.067325000	0.181921000	-0.855792000
1	1.372290000	0.358719000	-2.982411000
1	-1.392364000	0.351791000	-2.978952000
6	2.461643000	0.176112000	-0.462582000
6	3.147420000	-1.048688000	-0.426926000
6	3.080883000	1.403992000	-0.184019000
6	4.500762000	-1.009977000	-0.093489000
6	4.435585000	1.378902000	0.143650000
6	5.139163000	0.186856000	0.189169000
1	5.061817000	-1.933102000	-0.049146000
1	4.944638000	2.306602000	0.370038000
6	-2.473271000	0.159604000	-0.456135000
6	-3.148198000	-1.070720000	-0.428063000
6	-4.500525000	-1.047393000	-0.088624000
6	-5.148048000	0.141184000	0.206838000
1	-5.053109000	-1.976202000	-0.051001000
6	-4.454895000	1.339851000	0.167912000
1	-4.971414000	2.261063000	0.403820000
6	-3.101979000	1.379762000	-0.165102000
6	-2.479826000	-2.390273000	-0.787943000
1	-1.400338000	-2.239991000	-0.762364000
6	-2.861633000	-2.821170000	-2.214998000
6	-2.790782000	-3.507442000	0.216977000
1	-2.515406000	-3.214297000	1.229003000
1	-3.846827000	-3.785198000	0.203476000
1	-2.215630000	-4.399721000	-0.037661000
1	-3.936117000	-3.001503000	-2.293726000
1	-2.345712000	-3.745736000	-2.482509000
1	-2.598141000	-2.062569000	-2.954517000
6	-2.380665000	2.718790000	-0.217280000
1	-1.320371000	2.527086000	-0.382620000
6	-2.878050000	3.571858000	-1.395834000
6	-2.495098000	3.488463000	1.106957000
1	-3.525476000	3.786455000	1.310589000
1	-2.146498000	2.883960000	1.944356000
1	-1.893194000	4.398848000	1.064706000
1	-2.756512000	3.051709000	-2.347931000
1	-2.320253000	4.509349000	-1.449178000
1	-3.935996000	3.818715000	-1.285500000
6	2.486580000	-2.375817000	-0.774215000
1	1.407916000	-2.248845000	-0.678894000
6	2.792620000	-2.771260000	-2.229755000
6	2.879037000	-3.508710000	0.182966000
1	3.933077000	-3.777953000	0.086600000
1	2.675239000	-3.238067000	1.217748000
1	2.293634000	-4.400717000	-0.047580000
1	2.464869000	-2.009284000	-2.939040000
1	2.286419000	-3.705243000	-2.482983000
1	3.865137000	-2.920279000	-2.374309000
6	2.348487000	2.736595000	-0.246120000
1	1.288467000	2.534369000	-0.400244000
6	2.466963000	3.524110000	1.067173000
6	2.829898000	3.578916000	-1.439051000
1	3.886185000	3.837050000	-1.338896000
1	2.707159000	3.045505000	-2.383616000
1	2.262946000	4.510392000	-1.500670000
1	2.127518000	2.928043000	1.914265000
1	1.858602000	4.429834000	1.016964000
1	3.496522000	3.831980000	1.259923000
1	-6.197819000	0.132508000	0.472481000

1	6.190027000	0.189280000	0.450618000
31	-0.003179000	-0.041873000	2.078635000
1	-1.399050000	0.494546000	2.572111000
1	1.340009000	0.614214000	2.574100000
17	0.088256000	-2.289422000	2.345572000

$GaHCl_2$·IDipp

6	0.055111000	-2.348543000	0.674717000
6	0.055111000	-2.348543000	-0.674717000
7	-0.018527000	-1.027619000	-1.075181000
6	-0.066457000	-0.200853000	0.000000000
7	-0.018527000	-1.027619000	1.075181000
1	0.101955000	-3.154600000	1.383535000
1	0.101955000	-3.154600000	-1.383535000
6	-0.010880000	-0.660966000	2.478230000
6	-1.236028000	-0.500605000	3.141048000
6	1.228633000	-0.550735000	3.126512000
6	-1.189617000	-0.213062000	4.504616000
6	1.211096000	-0.267055000	4.490283000
6	0.017716000	-0.098062000	5.173200000
1	-2.113723000	-0.075582000	5.049726000
1	2.147096000	-0.165575000	5.022949000
6	-0.010880000	-0.660966000	-2.478230000
6	-1.236028000	-0.500605000	-3.141048000
6	-1.189617000	-0.213062000	-4.504616000
6	0.017716000	-0.098062000	-5.173200000
1	-2.113723000	-0.075582000	-5.049726000
6	1.211096000	-0.267055000	-4.490283000
1	2.147096000	-0.165575000	-5.022949000
6	1.228633000	-0.550735000	-3.126512000
6	-2.582080000	-0.660583000	-2.449042000
1	-2.410432000	-0.692246000	-1.372790000
6	-3.248712000	-1.988869000	-2.845780000
6	-3.522340000	0.523879000	-2.714218000
1	-3.054757000	1.469553000	-2.441583000
1	-3.816996000	0.578651000	-3.763898000
1	-4.434169000	0.414008000	-2.123809000
1	-3.462346000	-2.015343000	-3.916458000
1	-4.193299000	-2.115373000	-2.312285000
1	-2.612077000	-2.844743000	-2.613080000
6	2.559523000	-0.739127000	-2.412574000
1	2.364617000	-0.794645000	-1.341080000
6	3.228233000	-2.060524000	-2.828213000
6	3.512169000	0.446206000	-2.628727000
1	3.822882000	0.527729000	-3.672271000
1	3.043322000	1.385635000	-2.338048000
1	4.414789000	0.309376000	-2.029297000
1	2.583944000	-2.920460000	-2.634673000
1	4.159445000	-2.205535000	-2.276322000
1	3.468239000	-2.060232000	-3.893602000
6	-2.582080000	-0.660583000	2.449042000
1	-2.410432000	-0.692246000	1.372790000
6	-3.248712000	-1.988869000	2.845780000
6	-3.522340000	0.523879000	2.714218000
1	-3.816996000	0.578651000	3.763898000
1	-3.054757000	1.469553000	2.441583000
1	-4.434169000	0.414008000	2.123809000
1	-2.612077000	-2.844743000	2.613080000
1	-4.193299000	-2.115373000	2.312285000
1	-3.462346000	-2.015343000	3.916458000
6	2.559523000	-0.739127000	2.412574000
1	2.364617000	-0.794645000	1.341080000

6	3.512169000	0.446206000	2.628727000
6	3.228233000	-2.060524000	2.828213000
1	3.468239000	-2.060232000	3.893602000
1	2.583944000	-2.920460000	2.634673000
1	4.159445000	-2.205535000	2.276322000
1	3.043322000	1.385635000	2.338048000
1	4.414789000	0.309376000	2.029297000
1	3.822882000	0.527729000	3.672271000
1	0.028992000	0.130339000	-6.231574000
1	0.028992000	0.130339000	6.231574000
31	-0.468635000	1.872444000	0.000000000
17	0.496145000	2.746941000	-1.798637000
17	0.496145000	2.746941000	1.798637000
1	-2.031982000	2.024670000	0.000000000

AlH_2AsH_2

33	-0.039217000	-0.762177000	0.000000000
13	-0.039217000	1.681659000	0.000000000
1	-0.102134000	2.465623000	1.371999000
1	-0.102134000	2.465623000	-1.371999000
1	1.004130000	-0.820484000	-1.110775000
1	1.004130000	-0.820484000	1.110775000

GaH_2AsH_2

33	-0.028610000	-1.202604000	0.000000000
31	-0.028610000	1.233805000	0.000000000
1	-0.094295000	2.009848000	1.366492000
1	-0.094295000	2.009848000	-1.366492000
1	1.009817000	-1.290856000	-1.112143000
1	1.009817000	-1.290856000	1.112143000

IDipp·AlH_2PH_2

6	-0.155241000	-0.160330000	-0.475656000
7	0.763938000	-1.105469000	-0.175683000
7	0.500693000	1.011665000	-0.322648000
6	1.816675000	0.811121000	0.077109000
6	1.985224000	-0.536260000	0.169360000
6	2.765642000	1.930861000	0.321944000
1	3.724319000	1.545756000	0.664496000
1	2.948478000	2.514130000	-0.584236000
1	2.391805000	2.617851000	1.084996000
6	3.175490000	-1.347189000	0.543376000
1	3.505540000	-1.988135000	-0.278297000
1	4.007360000	-0.697285000	0.808564000
1	2.972268000	-1.992570000	1.401468000
6	-0.109355000	2.321556000	-0.511756000
1	-0.303755000	2.796143000	0.450493000
1	0.551050000	2.955988000	-1.101670000
1	-1.047335000	2.192417000	-1.044713000
6	0.508733000	-2.539738000	-0.190819000
1	-0.491835000	-2.706137000	-0.580647000
1	1.232406000	-3.043440000	-0.831855000
1	0.580064000	-2.949098000	0.817651000
13	-2.168820000	-0.389729000	-0.957564000
1	-2.434997000	0.723545000	-2.081582000
1	-2.314879000	-1.915574000	-1.424431000
15	-3.219325000	0.254475000	1.106832000
1	-3.069334000	-0.999664000	1.760036000
1	-4.542037000	-0.028075000	0.672557000

IDipp·GaH_2PH_2

6	0.678789000	0.339615000	-2.177551000
6	-0.670550000	0.340795000	-2.179188000
7	-1.070782000	0.195366000	-0.861767000

6	0.001618000	0.107268000	-0.032539000
7	1.076000000	0.193193000	-0.859370000
1	1.386461000	0.429607000	-2.980983000
1	-1.376174000	0.431439000	-2.984362000
6	2.470405000	0.169010000	-0.470690000
6	3.150946000	-1.058968000	-0.477884000
6	3.099903000	1.384038000	-0.159305000
6	4.506273000	-1.040209000	-0.150066000
6	4.456107000	1.340283000	0.159651000
6	5.153121000	0.143357000	0.166243000
1	5.062641000	-1.967456000	-0.140298000
1	4.972461000	2.257615000	0.410008000
6	-2.465556000	0.169345000	-0.475493000
6	-3.141675000	-1.061139000	-0.476120000
6	-4.497944000	-1.045631000	-0.152188000
6	-5.149987000	0.137679000	0.154363000
1	-5.050943000	-1.974865000	-0.137841000
6	-4.457374000	1.337147000	0.141845000
1	-4.977938000	2.254095000	0.384598000
6	-3.100432000	1.384078000	-0.173756000
6	-2.467498000	-2.372673000	-0.855258000
1	-1.389011000	-2.229970000	-0.782425000
6	-2.792111000	-2.752251000	-2.310756000
6	-2.827011000	-3.525816000	0.090943000
1	-2.626253000	-3.268250000	1.130190000
1	-3.877261000	-3.811490000	0.003533000
1	-2.228175000	-4.404659000	-0.153988000
1	-3.864406000	-2.915996000	-2.439394000
1	-2.275419000	-3.673751000	-2.587527000
1	-2.488666000	-1.973087000	-3.011863000
6	-2.381709000	2.725067000	-0.209736000
1	-1.313588000	2.532818000	-0.310339000
6	-2.818445000	3.550103000	-1.432126000
6	-2.569537000	3.524401000	1.087428000
1	-3.609461000	3.824837000	1.230218000
1	-2.258428000	2.940339000	1.953244000
1	-1.968667000	4.435842000	1.053593000
1	-2.646705000	3.010551000	-2.365505000
1	-2.260877000	4.488187000	-1.476915000
1	-3.881568000	3.795132000	-1.381535000
6	2.483727000	-2.370743000	-0.868586000
1	1.404412000	-2.232841000	-0.799376000
6	2.817533000	-2.738773000	-2.325086000
6	2.842254000	-3.528712000	0.071747000
1	3.897223000	-3.800886000	-0.000753000
1	2.616217000	-3.284537000	1.108983000
1	2.258151000	-4.411978000	-0.192586000
1	2.517861000	-1.954716000	-3.022452000
1	2.303519000	-3.658693000	-2.611955000
1	3.890721000	-2.900655000	-2.448642000
6	2.376436000	2.722755000	-0.186151000
1	1.309847000	2.528225000	-0.297936000
6	2.550841000	3.507080000	1.122101000
6	2.819915000	3.563624000	-1.395145000
1	3.881758000	3.811555000	-1.333526000
1	2.657199000	3.034394000	-2.336032000
1	2.259613000	4.500398000	-1.433336000
1	2.236465000	2.911078000	1.978519000
1	1.946274000	4.416292000	1.095129000
1	3.588446000	3.809883000	1.276304000
1	-6.203014000	0.124228000	0.406682000
1	6.205471000	0.132048000	0.421512000

31	0.000421000	-0.025184000	2.091896000
1	-1.325776000	0.741659000	2.494669000
1	1.374764000	0.654482000	2.490487000
15	-0.010902000	-2.375731000	2.598643000
1	-1.228874000	-2.369030000	3.327283000
1	0.787425000	-2.239448000	3.763977000

IDipp·AlH_2AsH_2

6	0.706665000	0.846935000	-2.102198000
6	-0.643074000	0.864654000	-2.108424000
7	-1.052135000	0.516298000	-0.834286000
6	0.015021000	0.285402000	-0.023295000
7	1.095084000	0.488339000	-0.824401000
1	1.420193000	1.056214000	-2.877704000
1	-1.343457000	1.091896000	-2.890752000
6	2.489332000	0.382533000	-0.446320000
6	3.151428000	-0.838004000	-0.653068000
6	3.136563000	1.523666000	0.051756000
6	4.507589000	-0.891113000	-0.332165000
6	4.492891000	1.410674000	0.351636000
6	5.172256000	0.218151000	0.164497000
1	5.050771000	-1.815699000	-0.472428000
1	5.023444000	2.268419000	0.743146000
6	-2.450678000	0.435477000	-0.467129000
6	-3.132935000	-0.772657000	-0.684523000
6	-4.491681000	-0.804431000	-0.372313000
6	-5.139947000	0.313830000	0.125962000
1	-5.049802000	-1.718835000	-0.520049000
6	-4.441829000	1.493999000	0.322181000
1	-4.960727000	2.358803000	0.713332000
6	-3.081943000	1.586102000	0.030588000
6	-2.462496000	-2.002260000	-1.282643000
1	-1.383921000	-1.886566000	-1.168759000
6	-2.763532000	-2.110277000	-2.788270000
6	-2.849446000	-3.304401000	-0.568944000
1	-2.682097000	-3.238743000	0.505349000
1	-3.896642000	-3.563404000	-0.736995000
1	-2.245667000	-4.129030000	-0.951794000
1	-3.834598000	-2.237253000	-2.960893000
1	-2.249143000	-2.972507000	-3.218075000
1	-2.442378000	-1.221496000	-3.333569000
6	-2.357340000	2.910615000	0.221533000
1	-1.286390000	2.722578000	0.145987000
6	-2.732328000	3.904001000	-0.891725000
6	-2.602996000	3.522955000	1.607307000
1	-3.644442000	3.822779000	1.739884000
1	-2.342187000	2.816797000	2.395014000
1	-1.989243000	4.417810000	1.730987000
1	-2.510482000	3.503644000	-1.882881000
1	-2.176529000	4.836631000	-0.772606000
1	-3.797700000	4.142660000	-0.861076000
6	2.464642000	-2.060727000	-1.246284000
1	1.386980000	-1.915007000	-1.164390000
6	2.803426000	-2.204627000	-2.740727000
6	2.795698000	-3.356594000	-0.494512000
1	3.846609000	-3.631990000	-0.602396000
1	2.566138000	-3.272223000	0.566986000
1	2.200509000	-4.178647000	-0.896271000
1	2.523520000	-1.316112000	-3.309280000
1	2.275422000	-3.058924000	-3.169880000
1	3.874389000	-2.365837000	-2.882744000
6	2.431607000	2.858132000	0.246516000

1	1.360790000	2.695742000	0.123953000
6	2.635967000	3.425850000	1.658286000
6	2.868178000	3.872569000	-0.823912000
1	3.935706000	4.089934000	-0.746985000
1	2.677015000	3.501952000	-1.832952000
1	2.325722000	4.812558000	-0.701118000
1	2.331211000	2.703751000	2.415320000
1	2.038768000	4.331423000	1.785072000
1	3.678607000	3.695137000	1.838560000
1	-6.195102000	0.264406000	0.364402000
1	6.225080000	0.151890000	0.409108000
13	0.004077000	-0.137286000	2.031514000
1	-1.272392000	0.663891000	2.557860000
1	1.425995000	0.401041000	2.520613000
33	-0.095062000	-2.634606000	2.292045000
1	-1.567231000	-2.669431000	2.694206000
1	0.360421000	-2.526715000	3.744605000

IDipp·GaH_2AsH_2

6	-0.696976000	0.881660000	2.230068000
6	0.652274000	0.894609000	2.234221000
7	1.058449000	0.529964000	0.961983000
6	-0.010523000	0.293899000	0.157079000
7	-1.088623000	0.509379000	0.955482000
1	-1.408565000	1.102763000	3.004083000
1	1.354670000	1.128498000	3.012828000
6	-2.481999000	0.412436000	0.574929000
6	-3.156300000	-0.800398000	0.788309000
6	-3.117427000	1.555148000	0.065385000
6	-4.512081000	-0.843155000	0.464554000
6	-4.474046000	1.452684000	-0.237928000
6	-5.165208000	0.268402000	-0.042643000
1	-5.064338000	-1.761470000	0.610128000
1	-4.995415000	2.312399000	-0.637526000
6	2.454884000	0.450092000	0.589745000
6	3.142205000	-0.754343000	0.810430000
6	4.500231000	-0.782794000	0.494877000
6	5.143271000	0.334985000	-0.011488000
1	5.062060000	-1.694422000	0.645856000
6	4.439846000	1.510947000	-0.213581000
1	4.954097000	2.375457000	-0.611764000
6	3.080391000	1.599212000	0.081772000
6	2.475991000	-1.984365000	1.411825000
1	1.397171000	-1.871819000	1.297767000
6	2.777863000	-2.088978000	2.917404000
6	2.866447000	-3.286052000	0.699273000
1	2.698931000	-3.221324000	-0.375149000
1	3.914339000	-3.542327000	0.867486000
1	2.264311000	-4.111872000	1.082001000
1	3.849449000	-2.211520000	3.090261000
1	2.266793000	-2.952463000	3.348674000
1	2.453079000	-1.200507000	3.461108000
6	2.349389000	2.918593000	-0.120331000
1	1.280572000	2.730515000	-0.019822000
6	2.743362000	3.935235000	0.964728000
6	2.567043000	3.502267000	-1.523275000
1	3.606292000	3.796037000	-1.683628000
1	2.289728000	2.781360000	-2.291962000
1	1.952583000	4.395769000	-1.653080000
1	2.541673000	3.553882000	1.967605000
1	2.182688000	4.863933000	0.837876000
1	3.807201000	4.176107000	0.908951000

6	-2.480266000	-2.024918000	1.389918000
1	-1.401912000	-1.896973000	1.289398000
6	-2.799653000	-2.142423000	2.890948000
6	-2.842391000	-3.326656000	0.663243000
1	-3.893605000	-3.588978000	0.798027000
1	-2.635871000	-3.259016000	-0.404181000
1	-2.247239000	-4.149802000	1.062525000
1	-2.496326000	-1.251477000	3.443235000
1	-2.280074000	-2.999763000	3.324323000
1	-3.871134000	-2.283251000	3.050107000
6	-2.399627000	2.881536000	-0.137953000
1	-1.331658000	2.711988000	-0.001989000
6	-2.584531000	3.433540000	-1.558644000
6	-2.839218000	3.912660000	0.915065000
1	-3.903840000	4.138572000	0.823799000
1	-2.662403000	3.552329000	1.930387000
1	-2.287088000	4.846332000	0.787219000
1	-2.273522000	2.702228000	-2.304318000
1	-1.982208000	4.335214000	-1.688981000
1	-3.623866000	3.704296000	-1.755046000
1	6.198060000	0.288168000	-0.252108000
1	-6.218046000	0.210068000	-0.289253000
31	-0.002039000	-0.175049000	-1.915215000
1	1.294376000	0.564216000	-2.444252000
1	-1.403374000	0.374617000	-2.410219000
33	0.064708000	-2.676574000	-2.083104000
1	1.488109000	-2.740164000	-2.630283000
1	-0.534362000	-2.652467000	-3.485845000

AlH_2AsPh_2

13	-0.960116000	1.742272000	-1.350360000
33	0.038270000	1.176898000	0.797296000
1	-0.351920000	1.182437000	-2.696684000
1	-2.234562000	2.673638000	-1.321732000
6	-1.420580000	-0.105227000	0.246837000
6	-2.719991000	0.143595000	0.726258000
6	-1.222365000	-1.233580000	-0.566233000
6	-3.769314000	-0.712146000	0.422973000
6	-2.276968000	-2.091635000	-0.861435000
6	-3.550175000	-1.836780000	-0.367316000
1	-2.902613000	1.007549000	1.354403000
1	-0.236105000	-1.449690000	-0.955547000
1	-4.758974000	-0.504112000	0.810149000
1	-2.099054000	-2.960362000	-1.483145000
1	-4.368134000	-2.507333000	-0.597914000
6	1.634537000	0.146179000	0.251253000
6	1.998067000	-0.973651000	1.006017000
6	2.484204000	0.561363000	-0.775425000
6	3.165965000	-1.672611000	0.725466000
6	3.661359000	-0.129528000	-1.048889000
6	4.002717000	-1.250471000	-0.302778000
1	1.364350000	-1.303790000	1.820762000
1	2.230027000	1.426060000	-1.375328000
1	3.427459000	-2.541742000	1.316676000
1	4.307081000	0.207582000	-1.850481000
1	4.916319000	-1.790452000	-0.517636000

GaH_2AsPh_2

31	-0.044757000	-2.414616000	0.603119000
33	-0.023464000	-0.546021000	-0.964825000
1	1.313980000	-3.142105000	0.920544000
1	-1.410710000	-2.975731000	1.154178000
6	-1.538731000	0.529915000	-0.294229000

6	-2.799642000	-0.064323000	-0.199453000
6	-1.422560000	1.898328000	-0.045341000
6	-3.914751000	0.688074000	0.149442000
6	-2.539888000	2.649800000	0.305789000
6	-3.788937000	2.048980000	0.406499000
1	-2.920455000	-1.123568000	-0.394451000
1	-0.460242000	2.387130000	-0.124320000
1	-4.882837000	0.207814000	0.222824000
1	-2.430345000	3.710289000	0.497924000
1	-4.656868000	2.635497000	0.679911000
6	1.551093000	0.414945000	-0.254244000
6	2.624717000	0.609106000	-1.124637000
6	1.662269000	0.878010000	1.060160000
6	3.785805000	1.244162000	-0.692543000
6	2.817830000	1.519329000	1.489902000
6	3.884800000	1.700933000	0.615233000
1	2.554417000	0.265636000	-2.149706000
1	0.840116000	0.749565000	1.753581000
1	4.608904000	1.385552000	-1.382089000
1	2.887813000	1.870928000	2.512036000
1	4.785974000	2.197217000	0.952648000

IDipp·AlH_2AsPh_2

13	0.106620000	0.813729000	-0.763827000
33	-2.066620000	1.087456000	0.481678000
7	1.039320000	-1.844072000	0.708748000
7	2.687850000	-0.604886000	0.113876000
6	1.328010000	-0.651115000	0.125773000
6	-0.274500000	-2.398196000	0.961388000
6	-0.828975000	-2.246981000	2.243164000
6	3.518761000	0.457650000	-0.413353000
6	3.925848000	1.482631000	0.453923000
6	2.194413000	-2.525800000	1.046845000
1	2.168928000	-3.492047000	1.515507000
6	3.230758000	-1.745996000	0.674197000
1	4.292342000	-1.893050000	0.752331000
6	-2.059311000	-2.857382000	2.481650000
1	-2.521657000	-2.757433000	3.454340000
6	4.774542000	2.459323000	-0.062984000
1	5.104228000	3.268545000	0.575158000
6	3.489085000	1.557980000	1.909356000
1	2.728338000	0.794785000	2.074215000
6	-0.125685000	-1.496106000	3.366119000
1	0.674876000	-0.902246000	2.923042000
6	-0.899469000	-3.135216000	-0.057624000
6	5.196436000	2.418393000	-1.382163000
1	5.851884000	3.191133000	-1.764038000
6	3.932299000	0.385679000	-1.752028000
6	2.844731000	2.910353000	2.247305000
1	3.568265000	3.726156000	2.192508000
1	2.447899000	2.892193000	3.264550000
1	2.028201000	3.134481000	1.561207000
6	-2.704663000	-3.581935000	1.493062000
1	-3.663740000	-4.040380000	1.698974000
6	4.778532000	1.393307000	-2.214419000
1	5.114213000	1.373992000	-3.242779000
6	-0.262169000	-3.362946000	-1.421508000
1	0.544161000	-2.640056000	-1.543547000
6	-2.131119000	-3.716868000	0.239575000
1	-2.649345000	-4.282109000	-0.522847000
6	-1.238152000	-3.133752000	-2.582565000
1	-2.035553000	-3.879216000	-2.597564000

1	-0.704404000	-3.208445000	-3.532113000
1	-1.695557000	-2.146808000	-2.528759000
6	3.525629000	-0.743481000	-2.688428000
1	2.754809000	-1.334176000	-2.193506000
6	4.659297000	1.251734000	2.858415000
1	5.091225000	0.268594000	2.661151000
1	4.321702000	1.270160000	3.896936000
1	5.455944000	1.991239000	2.753022000
6	0.519150000	-2.477507000	4.360899000
1	-0.241213000	-3.092959000	4.846567000
1	1.055969000	-1.931466000	5.139677000
1	1.226903000	-3.149706000	3.872811000
6	0.358072000	-4.769077000	-1.500140000
1	1.099434000	-4.929667000	-0.715066000
1	0.851108000	-4.913824000	-2.463920000
1	-0.408664000	-5.539992000	-1.396117000
6	4.713642000	-1.679183000	-2.968854000
1	5.518211000	-1.150403000	-3.484373000
1	4.400659000	-2.511645000	-3.602701000
1	5.126800000	-2.093558000	-2.047106000
6	-1.052370000	-0.518350000	4.102258000
1	-1.541268000	0.162686000	3.405486000
1	-0.473434000	0.071492000	4.816276000
1	-1.825091000	-1.042541000	4.668325000
6	2.914107000	-0.224708000	-3.997595000
1	2.054284000	0.415500000	-3.802182000
1	2.576968000	-1.064838000	-4.608402000
1	3.639391000	0.338990000	-4.587605000
1	0.971123000	2.137394000	-0.564587000
1	-0.027974000	0.248023000	-2.257829000
6	-3.414824000	0.279402000	-0.726634000
6	-3.356066000	0.341346000	-2.122211000
6	-4.495194000	-0.385459000	-0.141654000
6	-4.349220000	-0.237716000	-2.905592000
6	-5.487762000	-0.971961000	-0.922207000
6	-5.417840000	-0.898461000	-2.308030000
1	-2.527529000	0.842856000	-2.605100000
1	-4.563162000	-0.439622000	0.938165000
1	-4.285835000	-0.174286000	-3.985528000
1	-6.318372000	-1.479410000	-0.445861000
1	-6.190846000	-1.348897000	-2.918709000
6	-2.351590000	3.010566000	0.106327000
6	-3.436549000	3.506054000	-0.620381000
6	-1.476995000	3.931902000	0.692951000
6	-3.634824000	4.876654000	-0.761906000
6	-1.673263000	5.299489000	0.550732000
6	-2.755307000	5.781044000	-0.179634000
1	-4.137507000	2.823372000	-1.081965000
1	-0.627579000	3.579430000	1.266121000
1	-4.483855000	5.235817000	-1.331849000
1	-0.977675000	5.991327000	1.011174000
1	-2.910187000	6.846954000	-0.291673000

IDipp·GaH$_2$AsPh$_2$

31	0.067921000	0.758099000	-0.761530000
33	-2.077590000	1.007574000	0.519344000
7	1.050567000	-1.893086000	0.735916000
7	2.687028000	-0.640679000	0.136117000
6	1.329043000	-0.698263000	0.153901000
6	-0.257116000	-2.453802000	1.003150000
6	-0.792342000	-2.313991000	2.294243000
6	3.505241000	0.431469000	-0.388950000

6	3.902414000	1.458435000	0.480410000
6	2.213428000	-2.567388000	1.068390000
1	2.197123000	-3.534436000	1.535899000
6	3.241957000	-1.779511000	0.693030000
1	4.304948000	-1.918579000	0.766765000
6	-2.013524000	-2.935739000	2.550138000
1	-2.459871000	-2.845486000	3.531308000
6	4.740367000	2.445838000	-0.034306000
1	5.062643000	3.256299000	0.606128000
6	3.465518000	1.525094000	1.936244000
1	2.716868000	0.749991000	2.100396000
6	-0.080482000	-1.558471000	3.408564000
1	0.716634000	-0.966714000	2.956822000
6	-0.895940000	-3.185688000	-0.010726000
6	5.161871000	2.412941000	-1.353783000
1	5.809424000	3.193191000	-1.733872000
6	3.917253000	0.369123000	-1.728480000
6	2.800314000	2.866942000	2.275556000
1	3.510434000	3.694351000	2.219585000
1	2.404480000	2.842630000	3.293012000
1	1.979376000	3.079460000	1.590941000
6	-2.669819000	-3.659463000	1.568242000
1	-3.620741000	-4.128524000	1.787970000
6	4.753128000	1.386165000	-2.188721000
1	5.087396000	1.373618000	-3.217701000
6	-0.284533000	-3.392393000	-1.389487000
1	0.510191000	-2.658379000	-1.520081000
6	-2.117555000	-3.779434000	0.303611000
1	-2.644816000	-4.342502000	-0.454229000
6	-1.287844000	-3.161944000	-2.526964000
1	-2.075616000	-3.917720000	-2.534715000
1	-0.773329000	-3.218195000	-3.488351000
1	-1.756376000	-2.181495000	-2.451811000
6	3.515406000	-0.757989000	-2.669082000
1	2.756063000	-1.360809000	-2.171148000
6	4.640494000	1.236716000	2.884851000
1	5.087606000	0.260726000	2.686223000
1	4.302839000	1.248505000	3.923454000
1	5.425413000	1.988792000	2.780281000
6	0.571395000	-2.533778000	4.404418000
1	-0.185012000	-3.147069000	4.898931000
1	1.113382000	-1.983254000	5.176467000
1	1.276064000	-3.208165000	3.914869000
6	0.350019000	-4.790157000	-1.496428000
1	1.110516000	-4.949635000	-0.729617000
1	0.823242000	-4.919371000	-2.472307000
1	-0.405122000	-5.571264000	-1.383520000
6	4.710628000	-1.678381000	-2.968199000
1	5.504602000	-1.137181000	-3.487282000
1	4.400569000	-2.509371000	-3.605415000
1	5.136798000	-2.095246000	-2.053546000
6	-1.003276000	-0.576705000	4.144594000
1	-1.496657000	0.099942000	3.446750000
1	-0.420949000	0.017463000	4.852274000
1	-1.773169000	-1.097933000	4.717199000
6	2.885826000	-0.235232000	-3.968171000
1	2.023611000	0.397605000	-3.759408000
1	2.548809000	-1.073454000	-4.581639000
1	3.600344000	0.338782000	-4.561428000
1	0.929082000	2.079754000	-0.635607000
1	-0.102336000	0.139287000	-2.217148000
6	-3.416580000	0.252587000	-0.732401000

6	-3.377152000	0.420405000	-2.119729000
6	-4.466167000	-0.490326000	-0.187522000
6	-4.359689000	-0.132487000	-2.934048000
6	-5.448260000	-1.051306000	-0.999867000
6	-5.398080000	-0.872511000	-2.376716000
1	-2.572292000	0.984960000	-2.571976000
1	-4.518404000	-0.627999000	0.885839000
1	-4.311876000	0.012685000	-4.006846000
1	-6.254950000	-1.621624000	-0.554593000
1	-6.162616000	-1.303186000	-3.011790000
6	-2.360654000	2.943001000	0.215816000
6	-3.482579000	3.466389000	-0.430986000
6	-1.450600000	3.841143000	0.783659000
6	-3.681548000	4.841515000	-0.515360000
6	-1.648038000	5.213506000	0.699994000
6	-2.766484000	5.722695000	0.047556000
1	-4.211532000	2.801793000	-0.875410000
1	-0.571755000	3.466854000	1.295148000
1	-4.558977000	5.222660000	-1.024744000
1	-0.924600000	5.887285000	1.143984000
1	-2.921932000	6.792278000	-0.019843000

$(AlH_2AsH_2)_3$

13	-2.294542000	1.324754000	0.441495000
33	0.000000000	2.245374000	-0.176875000
13	2.294541000	1.324755000	0.441495000
33	1.944551000	-1.122687000	-0.176875000
13	0.000001000	-2.649509000	0.441495000
33	-1.944551000	-1.122687000	-0.176875000
1	-3.379563000	1.951279000	-0.522476000
1	-2.378585000	1.373126000	2.019252000
1	0.000033000	3.690226000	0.265252000
1	-0.000110000	2.513918000	-1.664588000
1	3.379639000	1.951148000	-0.522476000
1	2.378454000	1.373352000	2.019252000
1	3.195813000	-1.845142000	0.265252000
1	2.177172000	-1.256864000	-1.664588000
1	-0.000076000	-3.902427000	-0.522476000
1	0.000131000	-2.746478000	2.019252000
1	-3.195846000	-1.845085000	0.265252000
1	-2.177062000	-1.257054000	-1.664588000

$(GaH_2AsH_2)_3$

31	-2.292164000	1.323356000	0.324476000
33	-0.000032000	2.243697000	-0.293142000
31	2.292141000	1.323394000	0.324476000
33	1.943115000	-1.121821000	-0.293142000
31	0.000022000	-2.646750000	0.324476000
33	-1.943083000	-1.121876000	-0.293142000
1	-3.353195000	1.935865000	-0.653023000
1	-2.367255000	1.366533000	1.889409000
1	0.000000000	3.686604000	0.157395000
1	-0.000288000	2.525347000	-1.778825000
1	3.353106000	1.936020000	-0.653023000
1	2.367080000	1.366837000	1.889409000
1	3.192693000	-1.843302000	0.157395000
1	2.187159000	-1.262424000	-1.778825000
1	0.000089000	-3.871885000	-0.653023000
1	0.000176000	-2.733369000	1.889409000
1	-3.192693000	-1.843302000	0.157395000
1	-2.186871000	-1.262923000	-1.778825000

$(AlH_2AsPh_2)_3$

1	3.673390000	-1.340813000	-0.257185000
13	2.401550000	-0.888647000	-1.092328000
13	-1.973075000	-1.633657000	-1.096725000
13	-0.430367000	2.528359000	-1.085152000
33	-2.190557000	0.810254000	-0.431786000
33	1.796919000	1.493572000	-0.427938000
33	0.392757000	-2.300361000	-0.435266000
1	-1.983111000	-1.599281000	-2.681291000
1	-0.396446000	2.524817000	-2.669721000
6	-2.659407000	1.032199000	1.459123000
6	2.229617000	1.778871000	1.463255000
6	0.426297000	-2.818513000	1.455675000
1	2.378326000	-0.911432000	-2.676984000
1	-2.999217000	-2.511305000	-0.262271000
1	-0.676826000	3.852957000	-0.246062000
6	-3.827537000	1.377816000	-1.368403000
6	3.104352000	2.631133000	-1.363505000
6	0.726417000	-4.000734000	-1.371419000
6	4.893287000	4.249595000	-2.771936000
6	3.271863000	2.465595000	-2.739703000
6	3.835173000	3.614739000	-0.698960000
6	4.726940000	4.417989000	-1.402532000
6	4.162509000	3.272362000	-3.438282000
1	2.712760000	1.706454000	-3.272104000
1	3.715857000	3.758847000	0.366646000
1	5.290250000	5.178384000	-0.875739000
1	4.285508000	3.133050000	-4.505089000
1	5.587980000	4.876043000	-3.317020000
6	2.856568000	2.157447000	4.160407000
6	3.394817000	1.227801000	2.002553000
6	1.382069000	2.518558000	2.287624000
6	1.693955000	2.703358000	3.631444000
6	3.708019000	1.421423000	3.342641000
1	4.060718000	0.646070000	1.377809000
1	0.480285000	2.962216000	1.886520000
1	1.025652000	3.276803000	4.261398000
1	4.616847000	0.993881000	3.747865000
1	3.099610000	2.304256000	5.205339000
6	0.447099000	-3.551248000	4.152650000
6	-0.631350000	-3.553983000	1.996774000
6	1.491687000	-2.453029000	2.278081000
6	1.499119000	-2.815830000	3.621796000
6	-0.616939000	-3.922308000	3.336811000
1	-1.468823000	-3.841445000	1.373771000
1	2.325265000	-1.892968000	1.875169000
1	2.330635000	-2.522550000	4.250177000
1	-1.439858000	-4.497059000	3.743565000
1	0.455119000	-3.835286000	5.197528000
6	1.239304000	-6.357688000	-2.780255000
6	1.218468000	-5.123433000	-0.707629000
6	0.496476000	-4.064232000	-2.747088000
6	0.752699000	-5.238216000	-3.445853000
6	1.471182000	-6.296607000	-1.411369000
1	1.405216000	-5.090910000	0.357526000
1	0.114406000	-3.201992000	-3.278995000
1	0.568397000	-5.276103000	-4.512242000
1	1.852469000	-7.163056000	-0.885158000
1	1.436721000	-7.271930000	-3.325536000
6	-6.121218000	2.123729000	-2.777574000
6	-5.044469000	1.522672000	-0.704168000
6	-3.766908000	1.605066000	-2.744645000
6	-4.909726000	1.975998000	-3.443561000

6	-6.184866000	1.896105000	-1.408117000
1	-5.110273000	1.347673000	0.361451000
1	-2.830178000	1.497505000	-3.276894000
1	-4.849887000	2.151522000	-4.510439000
1	-7.124864000	2.006513000	-0.881561000
1	-7.010159000	2.414305000	-3.323009000
6	-3.312349000	1.367944000	4.155680000
6	-2.890360000	-0.076758000	2.272613000
6	-2.756295000	2.312960000	2.008937000
6	-3.086122000	2.478483000	3.348876000
6	-3.212357000	0.091848000	3.616112000
1	-2.830013000	-1.076239000	1.862537000
1	-2.574958000	3.184433000	1.392691000
1	-3.163551000	3.476442000	3.762457000
1	-3.386070000	-0.777640000	4.237477000
1	-3.565623000	1.498119000	5.200388000

$(GaH_2AsPh_2)_3$

1	3.872431000	0.218273000	-0.103523000
31	2.563650000	0.127889000	-0.973199000
31	-1.171983000	-2.283617000	-0.969492000
31	-1.392734000	2.157320000	-0.967961000
33	-2.324557000	-0.118005000	-0.323154000
33	1.059412000	2.071260000	-0.324217000
33	1.264658000	-1.952077000	-0.325532000
1	-1.222615000	-2.277718000	-2.541083000
1	-1.363903000	2.198253000	-2.539584000
6	-2.814472000	-0.077722000	1.575028000
6	1.341459000	2.470228000	1.574658000
6	1.475525000	-2.395519000	1.572686000
1	2.581952000	0.081483000	-2.544868000
1	-1.746984000	-3.461363000	-0.097814000
1	-2.123330000	3.244655000	-0.095378000
6	-4.067423000	-0.258675000	-1.222261000
6	1.807783000	3.653510000	-1.219860000
6	2.257766000	-3.391373000	-1.224426000
6	2.783229000	5.892477000	-2.577814000
6	2.193085000	3.555094000	-2.557969000
6	1.909072000	4.883015000	-0.569129000
6	2.397914000	5.995198000	-1.246160000
6	2.677698000	4.670363000	-3.231850000
1	2.121345000	2.608970000	-3.079568000
1	1.610844000	4.979106000	0.466586000
1	2.473782000	6.944253000	-0.729845000
1	2.976191000	4.580377000	-4.268907000
1	3.163288000	6.759721000	-3.102831000
6	1.770781000	2.977587000	4.289613000
6	2.640296000	2.606297000	2.072229000
6	0.262624000	2.586774000	2.449883000
6	0.477889000	2.835996000	3.802565000
6	2.852204000	2.864459000	3.420886000
1	3.490189000	2.511704000	1.408236000
1	-0.751250000	2.490590000	2.084895000
1	-0.369472000	2.920516000	4.471163000
1	3.863301000	2.973851000	3.793335000
1	1.937327000	3.175833000	5.341062000
6	1.712301000	-3.021354000	4.286508000
6	0.934071000	-3.581984000	2.074924000
6	2.131917000	-1.526126000	2.442627000
6	2.245942000	-1.837194000	3.794799000
6	1.057797000	-3.894850000	3.423022000
1	0.414413000	-4.265329000	1.415169000

1	2.563948000	-0.605387000	2.073765000
1	2.755406000	-1.150845000	4.459292000
1	0.639109000	-4.820159000	3.799195000
1	1.805318000	-3.264812000	5.337532000
6	3.704550000	-5.355423000	-2.587381000
6	3.265715000	-4.102465000	-0.573541000
6	1.983451000	-3.667419000	-2.565045000
6	2.704622000	-4.644789000	-3.241360000
6	3.982449000	-5.081592000	-1.253195000
1	3.495195000	-3.898887000	0.464119000
1	1.204554000	-3.125536000	-3.086655000
1	2.480330000	-4.851645000	-4.280393000
1	4.761840000	-5.628362000	-0.736830000
1	4.263910000	-6.118034000	-3.114389000
6	-6.491863000	-0.528932000	-2.585187000
6	-5.187176000	-0.776376000	-0.571575000
6	-4.169403000	0.117436000	-2.562736000
6	-5.376466000	-0.018147000	-3.239047000
6	-6.393566000	-0.907139000	-1.251185000
1	-5.125598000	-1.077248000	0.465995000
1	-3.310755000	0.521308000	-3.084231000
1	-5.443528000	0.279993000	-4.277943000
1	-7.256750000	-1.308908000	-0.734916000
1	-7.432037000	-0.631755000	-3.112159000
6	-3.476787000	0.031097000	4.288414000
6	-2.388055000	-1.079133000	2.446134000
6	-3.574081000	0.983055000	2.075891000
6	-3.907558000	1.033016000	3.423815000
6	-2.715717000	-1.022029000	3.797999000
1	-1.804777000	-1.912758000	2.078264000
1	-3.908105000	1.772979000	1.415099000
1	-4.501767000	1.857190000	3.798852000
1	-2.375072000	-1.805246000	4.463370000
1	-3.735028000	0.072525000	5.339216000

IDipp·AlH(PH_2)$_2$

6	-0.091249000	0.028548000	-0.019077000
13	-0.100849000	-0.233022000	2.070632000
15	1.781798000	0.906459000	3.002910000
15	-0.281246000	-2.611019000	2.395426000
1	-1.448821000	0.499116000	2.508108000
1	2.725976000	-0.147814000	2.888929000
1	1.405973000	0.555589000	4.327615000
1	-0.944041000	-2.462468000	3.642460000
1	0.992957000	-2.794220000	2.991624000
7	0.941630000	0.050692000	-0.904735000
6	0.481938000	0.211004000	-2.199222000
6	-0.862372000	0.295275000	-2.128604000
7	-1.200512000	0.179265000	-0.793334000
6	2.357558000	-0.016157000	-0.601038000
1	1.148965000	0.253506000	-3.039900000
1	-1.603581000	0.430834000	-2.894223000
6	-2.577709000	0.271218000	-0.348914000
6	-5.229724000	0.482769000	0.373360000
6	-3.376194000	-0.883256000	-0.380771000
6	-3.075010000	1.529674000	0.024213000
6	-4.418709000	1.605448000	0.385751000
6	-4.712753000	-0.744703000	-0.006890000
6	-2.855631000	-2.238208000	-0.841612000
6	-2.227666000	2.793784000	0.019915000
1	-4.834617000	2.558074000	0.685725000
1	-5.357864000	-1.612513000	-0.012020000

1	-6.270084000	0.564255000	0.662625000
6	5.073030000	-0.126151000	-0.138097000
6	2.970886000	-1.276248000	-0.496211000
6	3.073631000	1.189449000	-0.503656000
6	4.444763000	1.100777000	-0.265820000
6	4.343894000	-1.298678000	-0.255062000
6	2.208785000	-2.579778000	-0.695055000
6	2.430047000	2.556400000	-0.699793000
1	5.026685000	2.007472000	-0.173093000
1	4.850450000	-2.248507000	-0.156788000
1	6.137782000	-0.170137000	0.054043000
6	-3.255185000	-2.509460000	-2.303248000
6	-3.316675000	-3.393649000	0.056389000
1	-1.766365000	-2.215854000	-0.792054000
6	-2.299764000	3.550727000	1.353728000
6	-2.613446000	3.709056000	-1.154457000
1	-1.186626000	2.504213000	-0.121581000
6	2.695642000	-3.713667000	0.215952000
6	2.268758000	-3.024840000	-2.167950000
1	1.162087000	-2.401786000	-0.445379000
6	2.718007000	3.094029000	-2.113417000
6	2.860243000	3.584304000	0.356020000
1	1.350171000	2.436686000	-0.604584000
1	-2.823829000	-4.317603000	-0.250771000
1	-4.393645000	-3.558567000	-0.014291000
1	-3.059091000	-3.215957000	1.099540000
1	-2.890921000	-1.733793000	-2.978671000
1	-4.341696000	-2.555085000	-2.406188000
1	-2.845598000	-3.465037000	-2.637609000
1	-1.603259000	4.391634000	1.342597000
1	-2.037207000	2.898708000	2.186285000
1	-3.297508000	3.955322000	1.535137000
1	-1.971507000	4.592444000	-1.174949000
1	-3.647361000	4.049074000	-1.064238000
1	-2.514905000	3.197411000	-2.113932000
1	2.285491000	4.504021000	0.227136000
1	3.915243000	3.847958000	0.257880000
1	2.690500000	3.210297000	1.365337000
1	2.374762000	2.410606000	-2.891517000
1	3.789562000	3.248580000	-2.257407000
1	2.217771000	4.053119000	-2.263674000
1	3.300250000	-3.220127000	-2.470108000
1	1.860838000	-2.269628000	-2.841048000
1	1.696099000	-3.943910000	-2.309222000
1	2.736903000	-3.402758000	1.259324000
1	3.685174000	-4.072492000	-0.074637000
1	2.009261000	-4.558690000	0.148141000

IDipp·GaH(PH$_2$)$_2$

6	-0.086575000	0.050682000	-0.163322000
31	-0.104688000	-0.292435000	1.944554000
15	1.801706000	0.776403000	2.910778000
15	-0.269150000	-2.685189000	2.160430000
1	-1.443989000	0.428303000	2.393948000
1	2.715434000	-0.301082000	2.773430000
1	1.421260000	0.403704000	4.227370000
1	-1.067341000	-2.615244000	3.332018000
1	0.935825000	-2.860246000	2.887756000
7	0.948735000	0.100004000	-1.043023000
6	0.492152000	0.297681000	-2.335026000
6	-0.852040000	0.377671000	-2.266098000
7	-1.193604000	0.221994000	-0.934188000

6	2.363557000	0.033262000	-0.736848000
1	1.161817000	0.365991000	-3.171983000
1	-1.591238000	0.534501000	-3.029649000
6	-2.569432000	0.303894000	-0.486804000
6	-5.220584000	0.500336000	0.245353000
6	-3.368773000	-0.849122000	-0.542287000
6	-3.065680000	1.553422000	-0.083599000
6	-4.408790000	1.621843000	0.282418000
6	-4.704697000	-0.718519000	-0.163566000
6	-2.847430000	-2.193719000	-1.031161000
6	-2.217413000	2.816784000	-0.059713000
1	-4.823676000	2.567741000	0.604534000
1	-5.350294000	-1.585691000	-0.187070000
1	-6.260515000	0.575740000	0.537816000
6	5.080133000	-0.071024000	-0.276516000
6	2.985764000	-1.224606000	-0.668076000
6	3.070880000	1.240102000	-0.601042000
6	4.442739000	1.154598000	-0.366235000
6	4.359035000	-1.244601000	-0.427930000
6	2.231922000	-2.526910000	-0.901093000
6	2.416796000	2.607786000	-0.750949000
1	5.017965000	2.062423000	-0.245871000
1	4.872176000	-2.193467000	-0.357858000
1	6.145367000	-0.113140000	-0.086540000
6	-3.239467000	-2.432030000	-2.500447000
6	-3.314363000	-3.368435000	-0.161662000
1	-1.758481000	-2.173311000	-0.975383000
6	-2.273778000	3.532638000	1.297399000
6	-2.615917000	3.767716000	-1.200907000
1	-1.178429000	2.531131000	-0.222148000
6	2.714983000	-3.675370000	-0.006531000
6	2.308221000	-2.941969000	-2.381796000
1	1.182321000	-2.358499000	-0.657835000
6	2.715692000	3.204193000	-2.138259000
6	2.824644000	3.594724000	0.351853000
1	1.337132000	2.474801000	-0.674075000
1	-2.814261000	-4.284300000	-0.480711000
1	-4.389868000	-3.535762000	-0.247981000
1	-3.071251000	-3.210301000	0.888184000
1	-2.869062000	-1.642753000	-3.156383000
1	-4.325531000	-2.472477000	-2.610405000
1	-2.830293000	-3.381109000	-2.853326000
1	-1.580803000	4.376523000	1.302593000
1	-1.997281000	2.857594000	2.106913000
1	-3.270606000	3.926715000	1.505056000
1	-1.972571000	4.650313000	-1.202719000
1	-3.647983000	4.106621000	-1.088234000
1	-2.529799000	3.284768000	-2.176276000
1	2.244619000	4.514946000	0.253523000
1	3.878921000	3.869375000	0.279374000
1	2.645355000	3.177527000	1.342438000
1	2.387442000	2.548635000	-2.946344000
1	3.787213000	3.374154000	-2.264029000
1	2.207953000	4.163885000	-2.256346000
1	3.343220000	-3.127180000	-2.678379000
1	1.903660000	-2.174404000	-3.043034000
1	1.740482000	-3.860072000	-2.547338000
1	2.740597000	-3.384208000	1.043152000
1	3.710866000	-4.021665000	-0.290691000
1	2.035231000	-4.523351000	-0.099234000

IDipp·AlH(AsH$_2$)$_2$

6	-0.189917000	0.240681000	-0.307458000
13	-0.090290000	-0.321524000	1.718496000
33	2.160256000	0.222339000	2.659487000
33	-0.616618000	-2.779785000	1.755661000
1	-1.182561000	0.624325000	2.390173000
1	2.835526000	-1.087185000	2.261253000
1	1.729344000	-0.335174000	4.014191000
1	-2.008249000	-2.585543000	2.352712000
1	0.017318000	-2.941461000	3.132065000
7	0.786823000	0.347727000	-1.248964000
6	0.262760000	0.745917000	-2.465287000
6	-1.065463000	0.897284000	-2.287951000
7	-1.331200000	0.581490000	-0.968855000
6	2.212387000	0.150347000	-1.074100000
1	0.880748000	0.886329000	-3.332504000
1	-1.839028000	1.200228000	-2.968667000
6	-2.672503000	0.653359000	-0.423092000
6	-5.258577000	0.838357000	0.513858000
6	-3.540201000	-0.432734000	-0.625643000
6	-3.072380000	1.836744000	0.218891000
6	-4.384345000	1.899292000	0.684352000
6	-4.840650000	-0.310773000	-0.136308000
6	-3.135092000	-1.686082000	-1.391322000
6	-2.158421000	3.044038000	0.372385000
1	-4.725813000	2.791651000	1.191027000
1	-5.535536000	-1.129138000	-0.265212000
1	-6.271967000	0.907913000	0.889126000
6	4.943669000	-0.181946000	-0.901943000
6	2.742127000	-1.142240000	-1.220306000
6	3.016317000	1.282203000	-0.855494000
6	4.393403000	1.081783000	-0.770941000
6	4.126355000	-1.278383000	-1.123793000
6	1.877240000	-2.357545000	-1.524947000
6	2.453653000	2.694130000	-0.752595000
1	5.042840000	1.927993000	-0.592434000
1	4.571154000	-2.258866000	-1.222051000
1	6.015665000	-0.314562000	-0.826544000
6	-3.623472000	-1.617449000	-2.849980000
6	-3.633075000	-2.981612000	-0.736303000
1	-2.045204000	-1.734797000	-1.407278000
6	-2.195889000	3.646440000	1.783035000
6	-2.488689000	4.111308000	-0.686012000
1	-1.133988000	2.715148000	0.199412000
6	2.312800000	-3.612331000	-0.757698000
6	1.846163000	-2.637642000	-3.038196000
1	0.857772000	-2.135724000	-1.208815000
6	2.694822000	3.476097000	-2.056065000
6	3.011399000	3.473551000	0.447130000
1	1.375101000	2.618209000	-0.608964000
1	-3.201131000	-3.842813000	-1.249006000
1	-4.718763000	-3.076306000	-0.801355000
1	-3.346416000	-3.040531000	0.312384000
1	-3.242146000	-0.738815000	-3.371574000
1	-4.714313000	-1.579094000	-2.889730000
1	-3.297839000	-2.502265000	-3.401069000
1	-1.444907000	4.434564000	1.868002000
1	-1.981546000	2.888127000	2.535333000
1	-3.164558000	4.096939000	2.008288000
1	-1.804188000	4.957969000	-0.599078000
1	-3.505848000	4.487570000	-0.556397000
1	-2.407687000	3.715327000	-1.700099000
1	2.489479000	4.428280000	0.540840000

1	4.073206000	3.696441000	0.325104000
1	2.886188000	2.917842000	1.376084000
1	2.261493000	2.973011000	-2.921929000
1	3.763913000	3.596706000	-2.243704000
1	2.251841000	4.472088000	-1.989058000
1	2.846312000	-2.871439000	-3.410153000
1	1.471931000	-1.782265000	-3.603283000
1	1.199160000	-3.490929000	-3.252545000
1	2.397087000	-3.418204000	0.311353000
1	3.271141000	-3.995584000	-1.114175000
1	1.572323000	-4.401710000	-0.892599000

IDipp·GaH(AsH$_2$)$_2$

6	0.198286000	0.233408000	0.422324000
31	0.105817000	-0.401480000	-1.613672000
33	-1.994633000	0.434539000	-2.665342000
33	0.418775000	-2.894400000	-1.509711000
1	1.368973000	0.323051000	-2.242292000
1	-2.868389000	-0.750200000	-2.264358000
1	-1.614798000	-0.214278000	-3.993528000
1	1.242669000	-2.903714000	-2.793351000
1	-0.867795000	-3.213386000	-2.261583000
7	-0.779036000	0.353652000	1.360495000
6	-0.250773000	0.743966000	2.579221000
6	1.079514000	0.875727000	2.404156000
7	1.342485000	0.558060000	1.083183000
6	-2.206196000	0.192484000	1.167543000
1	-0.867466000	0.894059000	3.445708000
1	1.856561000	1.168910000	3.085487000
6	2.679460000	0.653687000	0.531830000
6	5.263672000	0.899538000	-0.399566000
6	3.552902000	-0.436080000	0.677694000
6	3.069608000	1.864826000	-0.060850000
6	4.380889000	1.959267000	-0.523710000
6	4.852265000	-0.282087000	0.194978000
6	3.148085000	-1.733886000	1.363685000
6	2.142602000	3.064867000	-0.189887000
1	4.713786000	2.876221000	-0.991642000
1	5.551972000	-1.101723000	0.283207000
1	6.276998000	0.993569000	-0.769658000
6	-4.939619000	-0.074542000	0.918754000
6	-2.772905000	-1.084698000	1.312349000
6	-2.976686000	1.342666000	0.923971000
6	-4.355320000	1.174826000	0.798984000
6	-4.156505000	-1.188351000	1.175376000
6	-1.946567000	-2.314332000	1.662682000
6	-2.379620000	2.742423000	0.849339000
1	-4.978908000	2.035765000	0.600163000
1	-4.628440000	-2.156354000	1.269360000
1	-6.011710000	-0.181938000	0.811086000
6	3.614610000	-1.750433000	2.830459000
6	3.662574000	-2.981807000	0.633868000
1	2.058867000	-1.791296000	1.359069000
6	2.067419000	3.591435000	-1.630274000
6	2.550213000	4.182571000	0.784743000
1	1.136311000	2.747317000	0.082029000
6	-2.425818000	-3.587223000	0.953577000
6	-1.917859000	-2.534658000	3.186122000
1	-0.921714000	-2.136787000	1.335209000
6	-2.623098000	3.507183000	2.162985000
6	-2.899364000	3.557643000	-0.343136000
1	-1.301222000	2.642920000	0.720920000

1	3.223887000	-3.876198000	1.078841000
1	4.747655000	-3.077423000	0.708956000
1	3.390672000	-2.971154000	-0.420912000
1	3.212387000	-0.910383000	3.398383000
1	4.704194000	-1.701062000	2.890633000
1	3.292149000	-2.671477000	3.320765000
1	1.322968000	4.387467000	-1.697781000
1	1.784556000	2.798154000	-2.321798000
1	3.021921000	4.007680000	-1.958461000
1	1.853363000	5.020686000	0.715137000
1	3.549512000	4.559153000	0.556133000
1	2.555852000	3.832876000	1.818992000
1	-2.357957000	4.504124000	-0.404937000
1	-3.958849000	3.798939000	-0.236985000
1	-2.764314000	3.021697000	-1.282345000
1	-2.217844000	2.977985000	3.026728000
1	-3.691998000	3.651489000	2.334507000
1	-2.154047000	4.492577000	2.121476000
1	-2.924157000	-2.719093000	3.569224000
1	-1.511719000	-1.671868000	3.716098000
1	-1.299468000	-3.400594000	3.431860000
1	-2.527531000	-3.435201000	-0.120678000
1	-3.385839000	-3.932702000	1.342681000
1	-1.702817000	-4.389017000	1.109197000

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Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dappricht, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. F. Fox, *Gaussian 09, Vol. Revision E.01*, Gaussian Inc., Wallingford CT, **2013**.
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6.6. Author contributions

The syntheses and characterization of compounds **1**, **2**, **3**, **4**, **5**, **6**, **7** and **8** were performed by Michael Weinhart.

X-ray structural analyses of **1**, **2**, **3**, **4**, **5**, **6**, **7** and **8** were performed by Michael Weinhart.

Structure refinements of the X-ray structural analyses of **1**, **2**, **3**, **4**, **5**, **6**, **7** and **8** were performed by Michael Seidl.

Computational analyses were performed by Alexey Y. Timoshkin.

The manuscript was written by Michael Weinhart.

The manuscript is submitted and accepted by “Wiley” to be published in “Angew. Chem. Int. Ed.”.

7. Thesis Treasury

The following chapter includes preliminary results and other by-products. These compounds and the corresponding data will be included in future publications or will be used as a basis for future research projects. Some of the obtained compounds could not be fully characterized so far, but all acquired data and knowledge about the described compounds will be presented.

7.1. Substituted Phosphanyltrielanes stabilized only by a LB

Analog to the salt metathesis reaction described in chapter 5, different substituted phosphanyltrielanes can be achieved *via* this pathway (Scheme 1). It is possible to introduce different substituents on the phosphorus atom and the group 13 element, respectively. By screening different alkali metal phosphanides (NaPH*t*Bu, LiP(*t*Bu)$_2$, LiPPh$_2$), phosphanylgallanes containing one organic substituent, two organic substituents or two aromatic substituents could be synthesized. In matter of the aluminum analogue the salt metathesis of the substituted aluminum compound IDipp·AlEt$_2$Cl and NaPH$_2$ afforded the aluminum substituted compound IDipp·AlEt$_2$PH$_2$.

$$\text{IDipp•E'R}_2\text{Cl} \;+\; 2\ \text{MPR'}_2 \xrightarrow[-80\,°\text{C} \rightarrow \text{RT}]{\text{Et}_2\text{O}} \text{IDipp•E'R}_2\text{PR'}_2$$

E' = Ga, Al
R = H, Et
R' = H, *t*Bu, Ph
M = Na, Li

Scheme 26: Salt metathesis reaction for the synthesis of substituted phosphanyltrielanes.

Synthesis of IDipp·GaH$_2$P(*t*Bu)$_2$:

A solution of IDipp·GaH$_2$Cl (0.05 g, 0.1 mmol, 1 eq) in 10 mL Et$_2$O was slowly added to a solution of LiP(*t*Bu)$_2$ (0.031 g, 0.2 mmol, 2 eq) in 10 mL Et$_2$O at –60 °C. The resulting clear solution was warmed up to room temperature overnight and the solvent removed under reduced pressure. The resulting off-white oil was extracted with *n*-hexane and filtered over a celite pad. The solvent of the clear filtrate was removed *in vacuo* to afford IDipp·GaH$_2$P(tBu)$_2$ as a colorless oil (31 mg, 52%).

^{1}H NMR (400.30 MHz, C$_6$D$_6$, 298 K): δ = 1.00 (d, 12H, $^3J_{H,H}$ = 6.90 Hz, *i*Pr-C*H*$_3$), 1.34 (d, 18H, $^3J_{P,H}$ = 10.98 Hz, *t*Bu-C*H*$_3$), 1.51 (d, 12H, $^3J_{H,H}$ = 6.90 Hz, *i*Pr-C*H*$_3$), 2.80 (sept, 4H, $^3J_{H,H}$ = 6.90 Hz, *i*Pr-C*H*), 4.15 (d br, 2H, Ga*H*$_2$), 6.50 (s, 2H, NC*H*C*H*N), 7.14 (d, 4H, $^3J_{H,H}$ = 7.69 Hz, aryl-C$_{meta}$*H*), 7.25 (t, 2H, $^3J_{H,H}$ = 7.69 Hz, aryl-C$_{para}$*H*).

^{31}P{^{1}H} NMR (162.04 MHz, C$_6$D$_6$, 298 K): δ = -2.07 (s, *P*(*t*Bu)$_2$).

^{31}P NMR (162.04 MHz, C$_6$D$_6$, 298 K): δ = -2.08 (m, $^3J_{P,H}$ = 10.98 Hz, *P*(*t*Bu)$_2$).

Synthesis of IDipp·GaH$_2$PH*t*Bu:

A solution of IDipp·GaH$_2$Cl (0.05 g, 0.1 mmol, 1 eq) in 10 mL Et$_2$O was slowly added to a solution of NaPH*t*Bu (0.023 g, 0.2 mmol, 2 eq) in 10 mL Et$_2$O at –30 °C. The off-white suspension was stirred at –30 °C for 24 hours. After removing the solvent *in vacuo* the yellowish residue was suspended in toluene and filtered over a celite pad. The colorless solution was concentrated and stored at –30 °C to afford IDipp·GaH_2PH*t*Bu as colorless needles (24 mg, 43%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = 1.00 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.02 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.32 (d, 9H, $^3J_{P,H}$ = 10.81 Hz, *t*Bu-C*H*$_3$), 1.47 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.49 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.88 (dt, 1H, $^1J_{P,H}$ = 176.32 Hz, $^3J_{H,H}$ = 4.28 Hz, P*H*), 2.71 (sept, 4H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*), 3.98 (s br, 1H, GaH_a), 4.19 (s br, 1H, GaH_b), 6.46 (s, 2H, NC*H*C*H*N), 7.12 (d, 4H, $^3J_{H,H}$ = 7.80 Hz, aryl-$C_{meta}H$), 7.25 (t, 2H, $^3J_{H,H}$ = 7.80 Hz, aryl-$C_{para}H$).

^{1}H{^{31}P} NMR (400.13 MHz, C_6D_6, 298 K): δ = 1.00 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.02 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.32 (s, 9H, *t*Bu-C*H*$_3$), 1.47 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.49 (d, 6H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*$_3$), 1.88 (t, 1H, $^3J_{H,H}$ = 4.28 Hz, P*H*), 2.71 (sept, 4H, $^3J_{H,H}$ = 6.88 Hz, *i*Pr-C*H*), 3.98 (s br, 1H, GaH_a), 4.19 (s br, 1H, GaH_b), 6.46 (s, 2H, NC*H*C*H*N), 7.12 (d, 4H, $^3J_{H,H}$ = 7.80 Hz, aryl-$C_{meta}H$), 7.25 (t, 2H, $^3J_{H,H}$ = 7.80 Hz, aryl-$C_{para}H$).

^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ = -104.00 (s, *P*H*t*Bu).

^{31}P NMR (162.04 MHz, C_6D_6, 298 K): δ = -104.00 (dm, $^1J_{P,H}$ = 176.32 Hz, $^3J_{P,H}$ = 11.25 Hz, *P*H*t*Bu).

Synthesis of IDipp·GaH_2PPh_2:

IDipp·GaH_2Cl (0.05 g, 0.1 mmol, 1 eq) dissolved in 10 mL Et_2O was added to a suspension of $LiPPh_2$ (0.039, 0.1 mmol, 2 eq) in 10 mL Et_2O at –30 °C. The yellow suspension was stirred at –30 °C for 24 hours. After removing all volatiles under reduced pressure the yellow residue was suspended in *n*-hexane and filtered over a celite pad. The colorless solution was concentrated and stored at 6 °C to afford IDipp·GaH_2PPh_2 as colorless needles (37 mg, 58%).

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): δ = 0.99 (d, 12H, $^3J_{H,H}$ = 6.98 Hz, *i*Pr-C*H*$_3$), 1.36 (d, 12H, $^3J_{H,H}$ = 6.98 Hz, *i*Pr-C*H*$_3$), 2.74 (sept, 4H, $^3J_{H,H}$ = 6.98 Hz, *i*Pr-C*H*), 4.23 (d br, 2H, GaH_2), 6.45 (s, 2H, NC*H*C*H*N), 6.93 (t, 2H, $^3J_{H,H}$ = 7.28 Hz, phenyl-$C_{para}H$), 7.00 (t, 4H, $^3J_{H,H}$ = 7.28 Hz, phenyl-$C_{meta}H$), 7.07 (d, 4H, $^3J_{H,H}$ = 7.81 Hz, aryl-$C_{meta}H$), 7.20 (t, 2H, $^3J_{H,H}$ = 7.81 Hz, aryl-$C_{para}H$), 7.43 (t, 4H, $^3J_{H,H}$ = 7.28 Hz, phenyl-$C_{ortho}H$).

^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ = -58.44 (s, *P*Ph$_2$).

^{31}P NMR (162.04 MHz, C_6D_6, 298 K): δ = -58.44 (m, *P*Ph$_2$).

LIFDI-MS (m/z): 644.2088 $[M-H]^+$.

Synthesis of IDipp·$AlEt_2PH_2$:

A solution of IDipp·$AlEt_2Cl$ (0.05 g, 0.1 mmol, 1 eq) in 10 mL Et_2O was added to a suspension of $LiPH_2$·dme (0.026 g, 0.2 mmol, 2 eq) in 10 mL Et_2O at –30 °C. The off-white suspension was warmed up to room temperature overnight. After removing the solvent *in vacuo* the yellowish residue was suspended in *n*-hexane. After filtration over a celite pad the yellowish solution was concentrated and stored at –30 °C to afford IDipp·$AlEt_2PH_2$ as colorless needles (24 mg, 48%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ = -0.42 – -0.12 (m, 4H, ethyl-C*H*$_2$), 0.31 (d, 2H, $^{1}J_{P,H}$ = 168.53 Hz, P*H*), 0.95 (d, 12H, $^{3}J_{H,H}$ = 7.10 Hz, *i*Pr-C*H*$_3$), 1.25 (t, 6H, $^{3}J_{H,H}$ = 8.25 Hz, ethyl-C*H*$_3$), 1.43 (d, 12H, $^{3}J_{H,H}$ = 7.10 Hz, *i*Pr-C*H*$_3$), 2.76 (sept, 4H, $^{3}J_{H,H}$ = 7.10 Hz, *i*Pr-C*H*), 6.42 (s, 2H, NC*H*C*H*N), 7.10 (d, 4H, $^{3}J_{H,H}$ = 7.74 Hz, aryl-C_{meta}*H*), 7.22 (t, 2H, $^{3}J_{H,H}$ = 7.74 Hz, aryl-C_{para}*H*).

^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, 298 K): δ = -284.46 (s, *P*H$_2$).

^{31}P NMR (161.98 MHz, C_6D_6, 298 K): δ = -284.46 (t, $^{1}J_{P,H}$ = 168.53 Hz, *P*H$_2$).

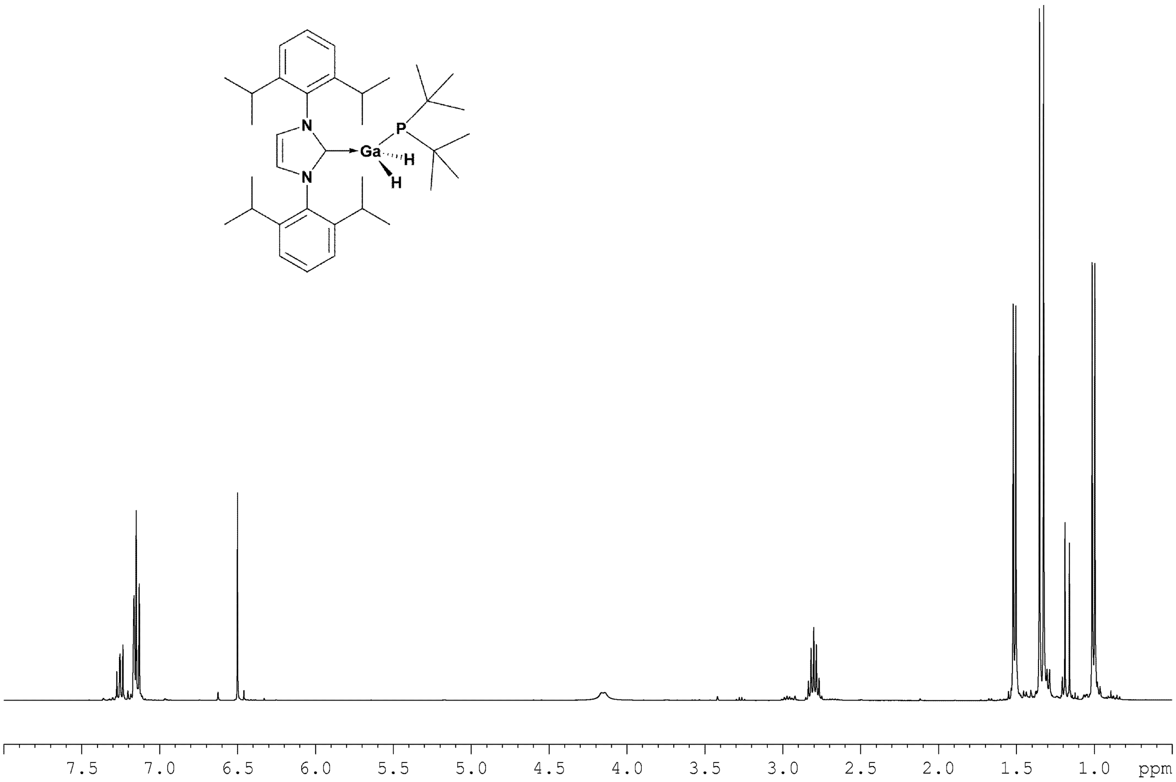


Figure 1: ^{1}H NMR spectrum of IDipp·GaH_2P(*t*Bu)$_2$ in C_6D_6 at 298 K.

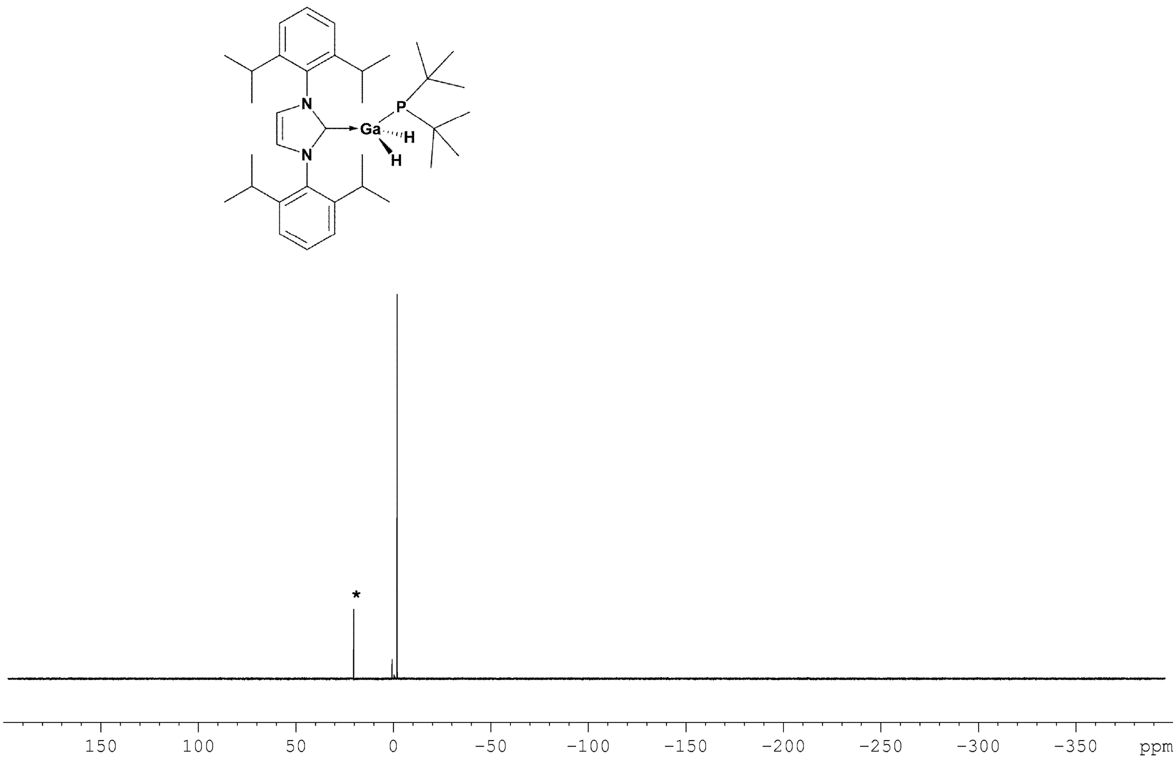


Figure 27: $^{31}P\{^{1}H\}$ NMR spectrum of IDipp·GaH_2P(*t*Bu)$_2$ in C_6D_6 at 298 K. * = HP(*t*Bu)$_2$.

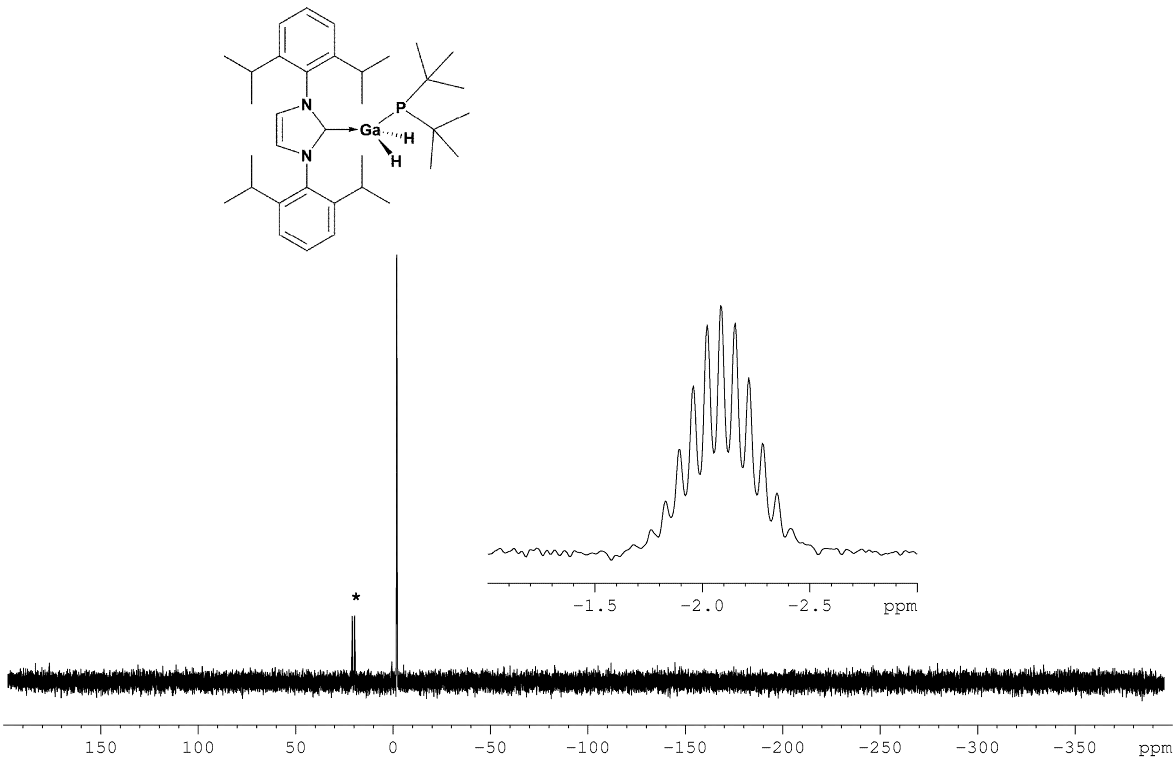


Figure 28: ^{31}P NMR spectrum of IDipp·GaH_2P(*t*Bu)$_2$ in C_6D_6 at 298 K. * = HP(*t*Bu)$_2$.

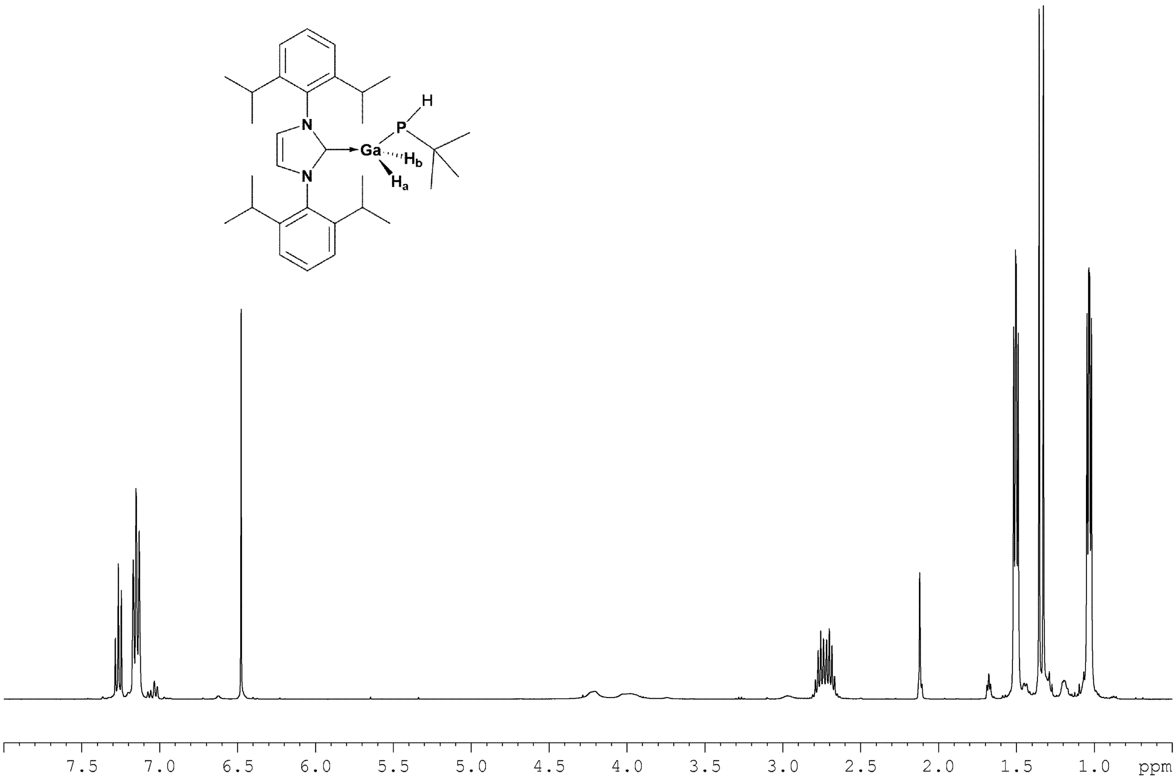


Figure 29: ^{1}H NMR spectrum of IDipp·GaH_2PH*t*Bu in C_6D_6 at 298 K.

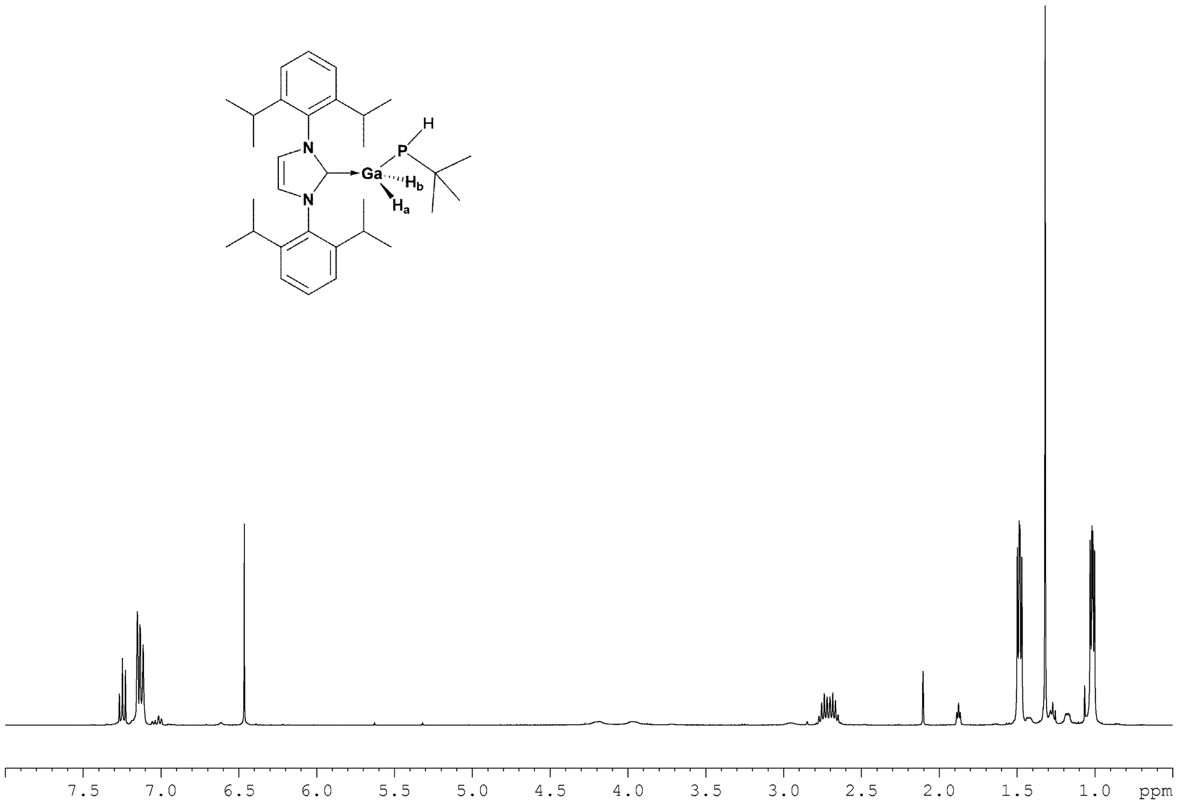


Figure 30: $^1H\{^{31}P\}$ NMR spectrum of IDipp·GaH_2PH*t*Bu in C_6D_6 at 298 K.

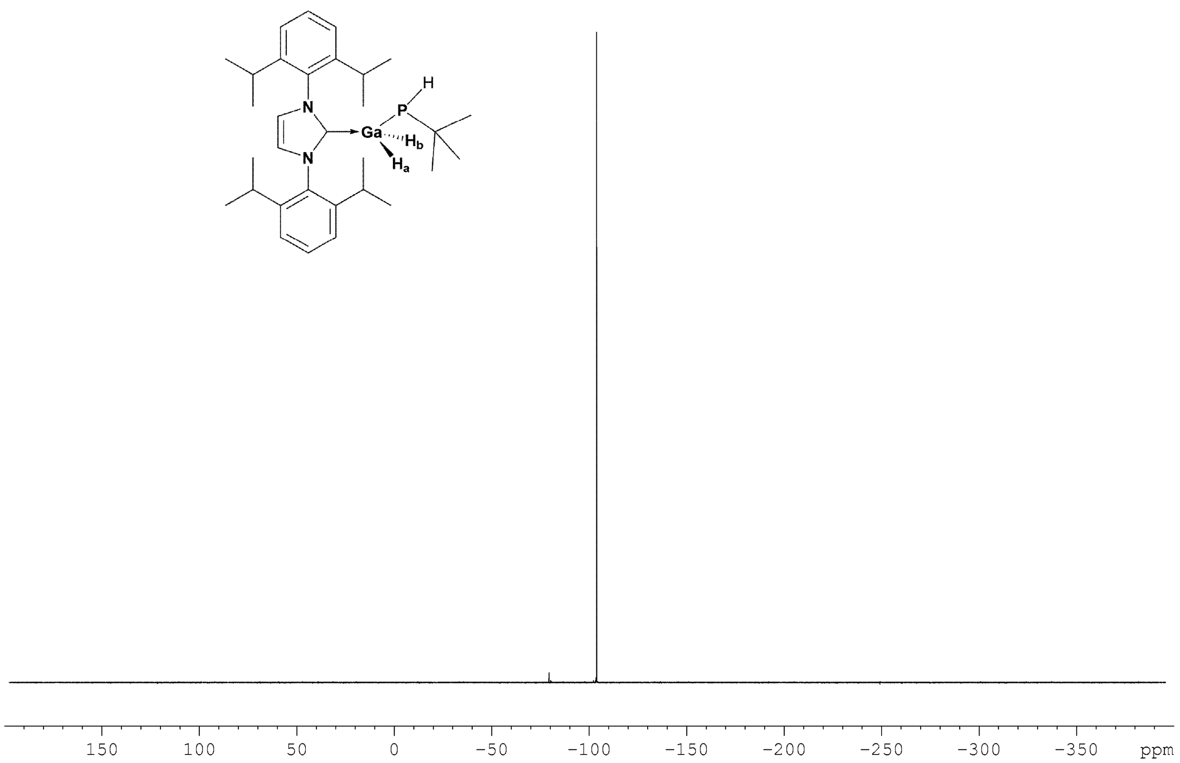


Figure 31: $^{31}P\{^1H\}$ NMR spectrum of IDipp·GaH_2PH*t*Bu in C_6D_6 at 298 K.

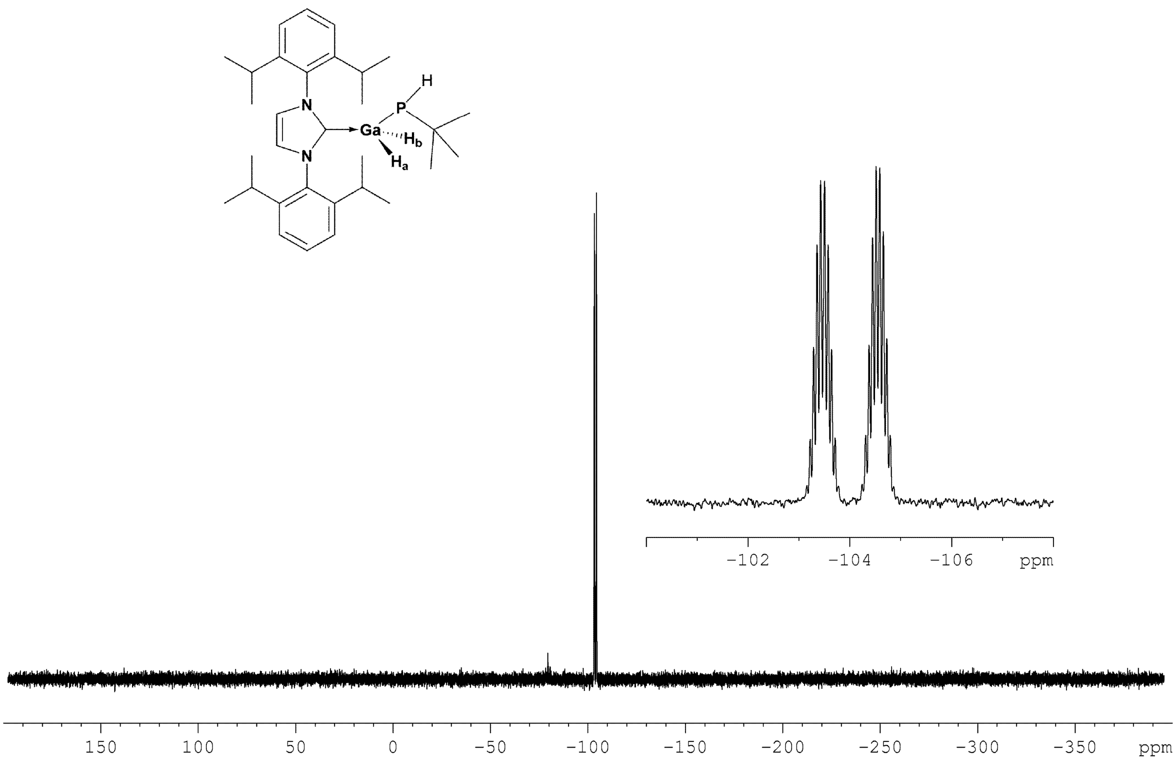


Figure 32: ^{31}P NMR spectrum of IDipp·GaH_2PHtBu in C_6D_6 at 298 K.

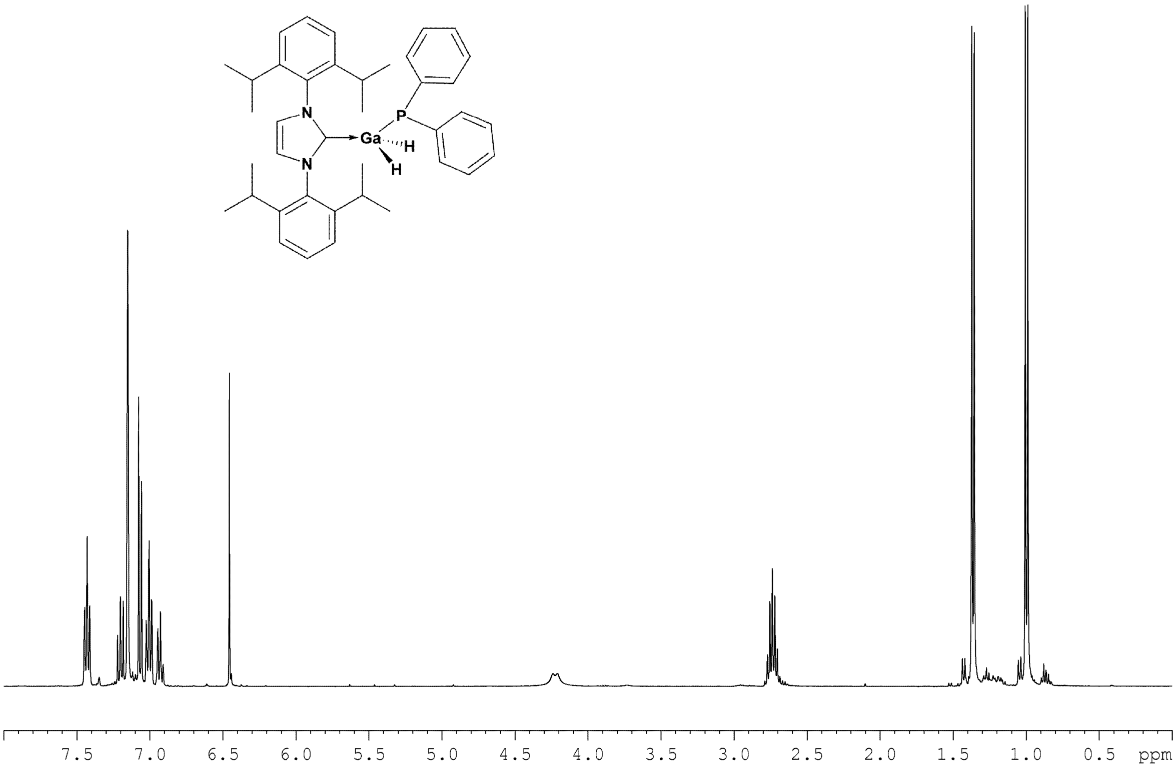


Figure 33: ^{1}H NMR spectrum of IDipp·GaH_2PPh_2 in C_6D_6 at 298 K.

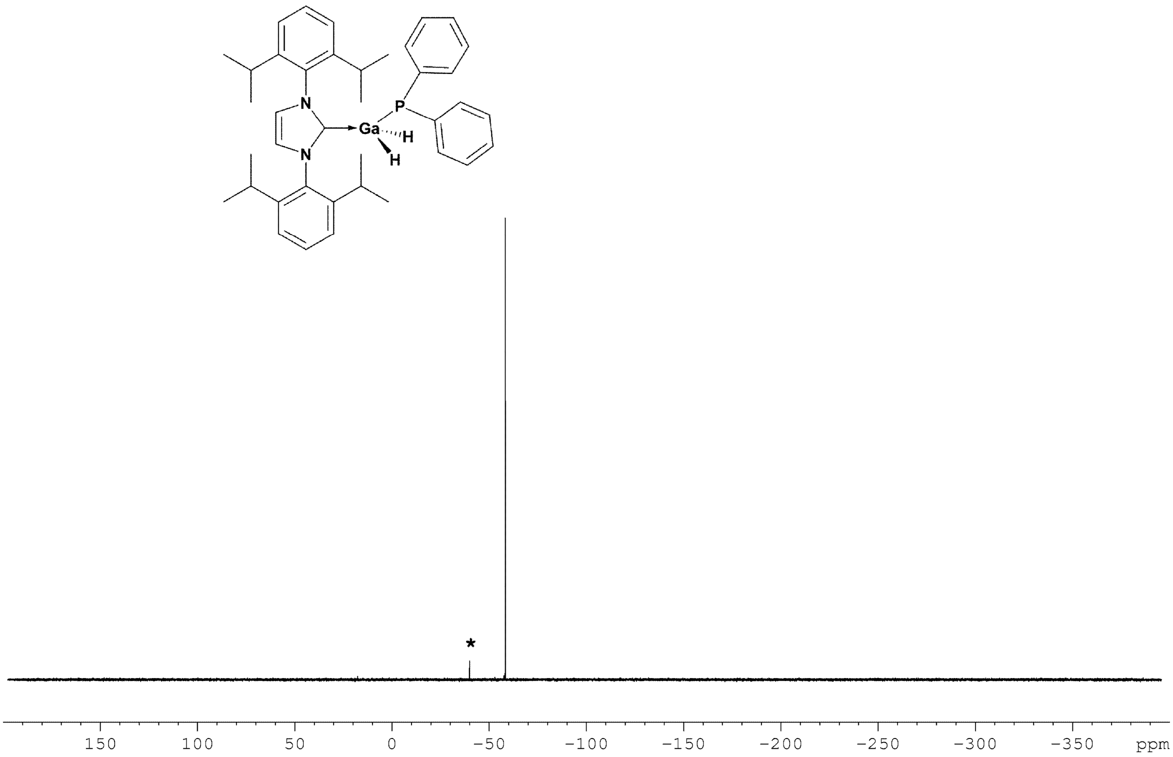


Figure 34: $^{31}P\{^{1}H\}$ NMR spectrum of IDipp·GaH_2PPh_2 in C_6D_6 at 298 K. * = $HPPh_2$.

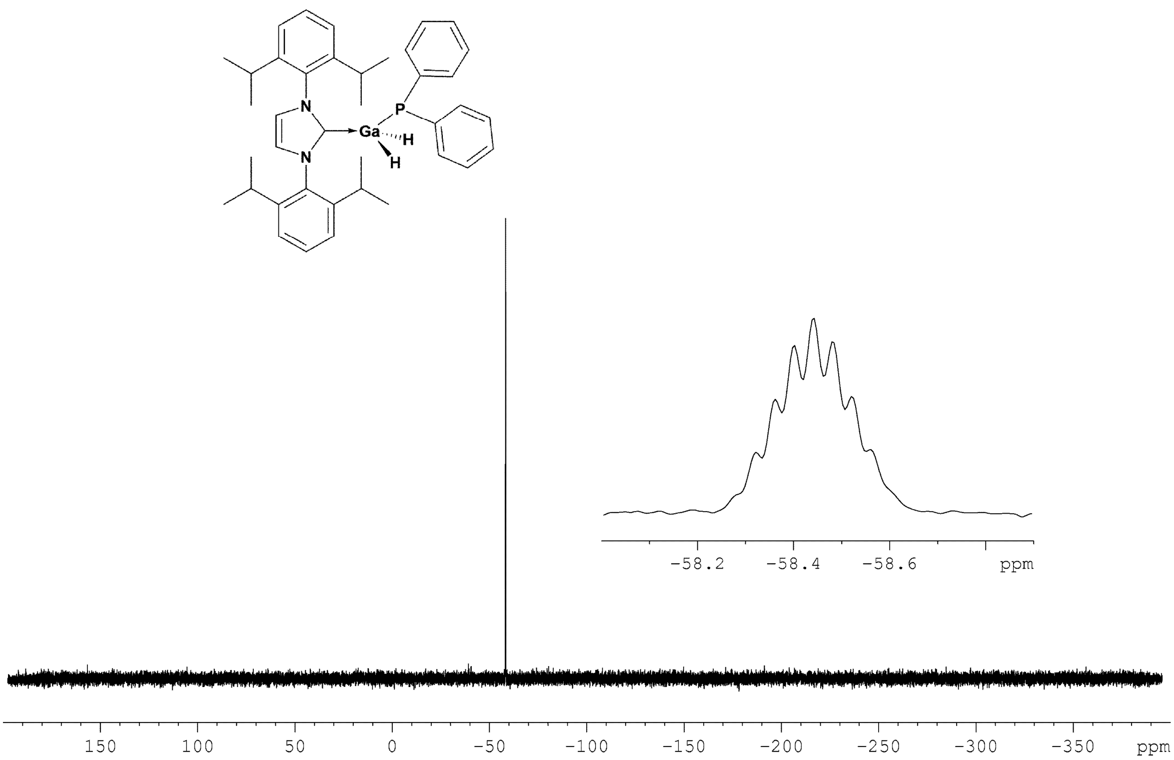


Figure 35: ^{31}P NMR spectrum of IDippGaH_2PPh_2 in C_6D_6 at 298 K.

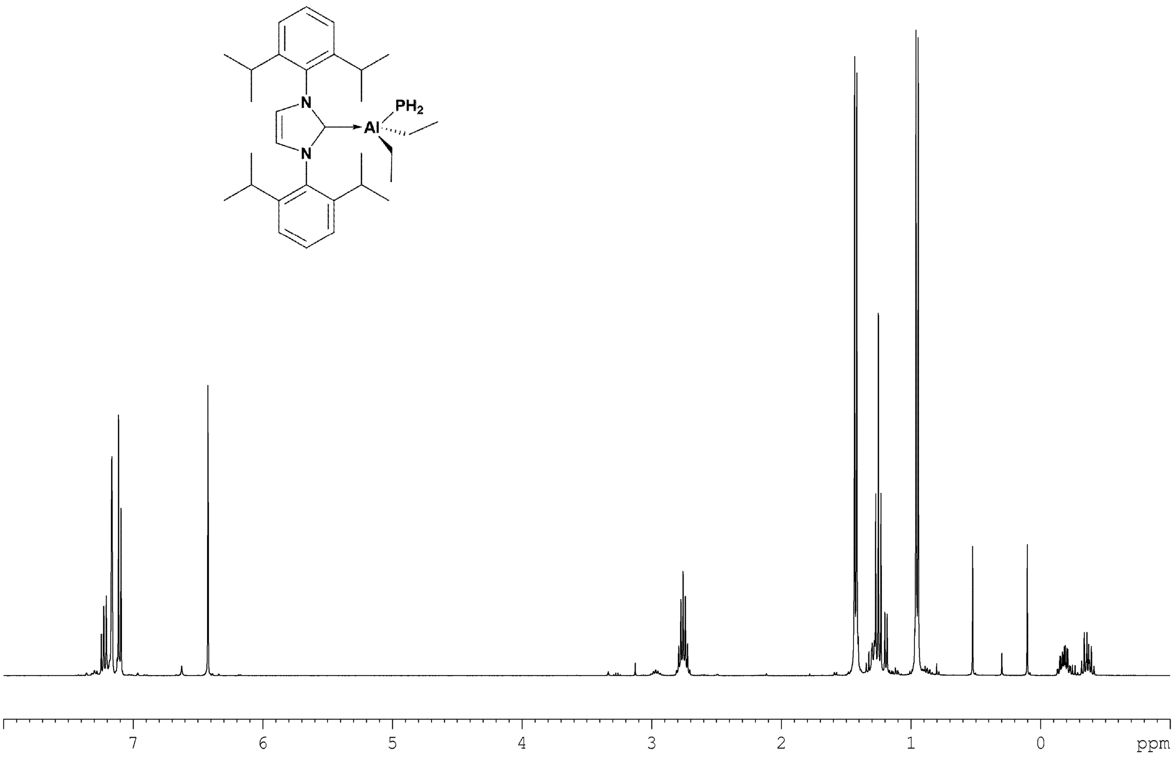


Figure 36: ^{1}H NMR spectrum of IDipp·$AlEt_2PH_2$ in C_6D_6 at 298 K.

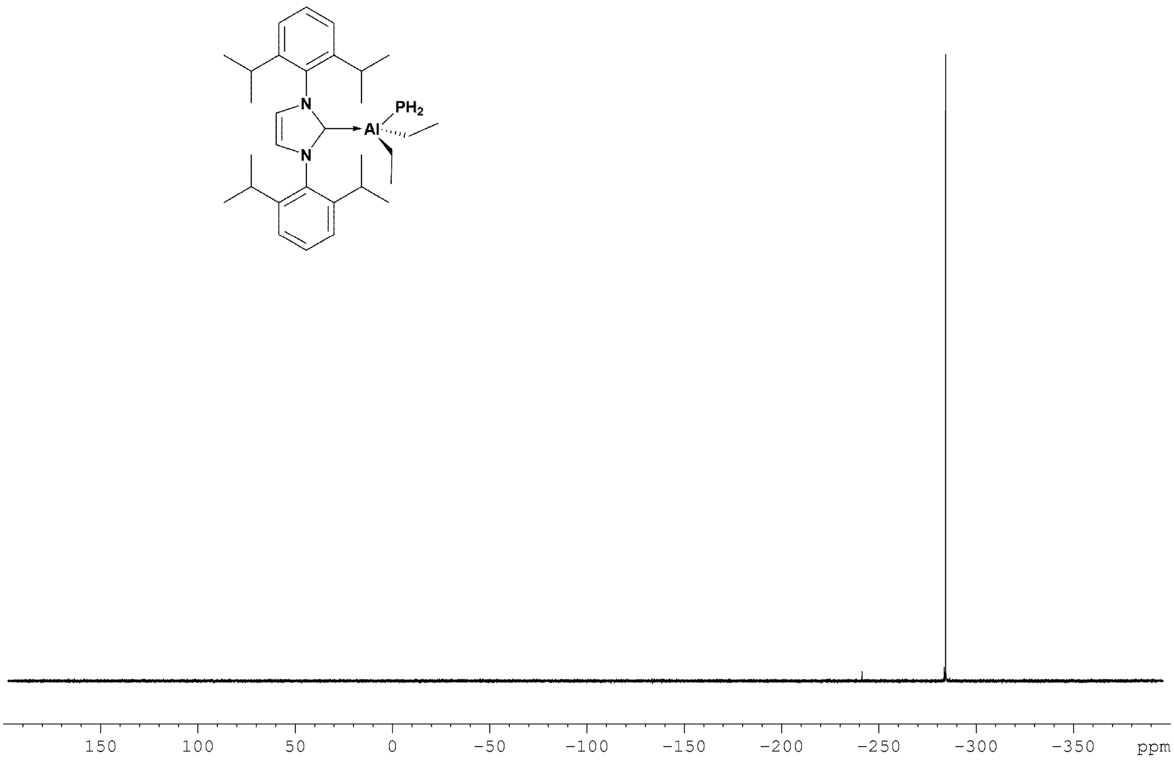


Figure 37: $^{31}P\{^{1}H\}$ NMR spectrum of IDipp·$AlEt_2PH_2$ in C_6D_6 at 298 K.

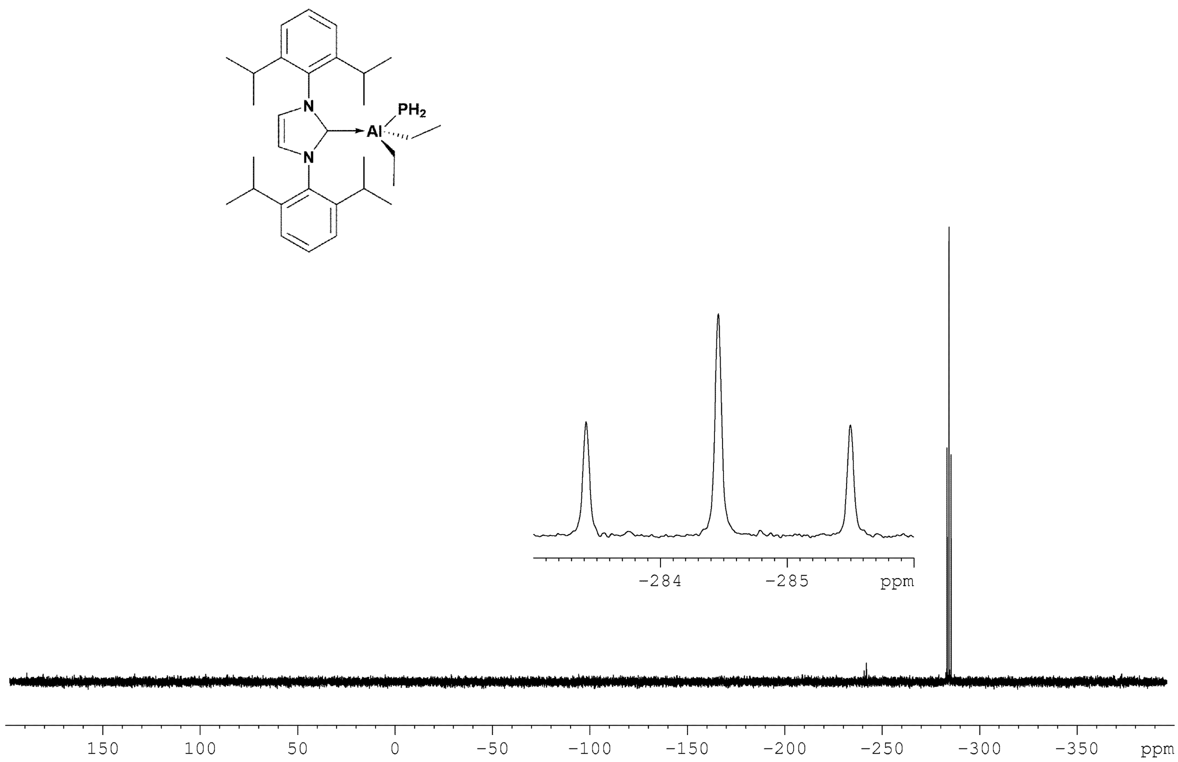


Figure 38: ^{31}P NMR spectrum of IDipp·$AlEt_2PH_2$ in C_6D_6 at 298 K.

Besides IDipp·$GaH_2P(t\text{Bu})_2$, which could only be isolated as an oil, it was possible to achieve suitable crystals for single crystal X-ray diffraction of each compound. The molecular structure of IDipp·$GaH_2PHt\text{Bu}$ (**1**), IDipp·GaH_2PPh_2 (**2**) and IDipp·$AlEt_2PH_2$ (**3**) are depicted in Figure 14 and their crystallographic data summarized in Table 1.

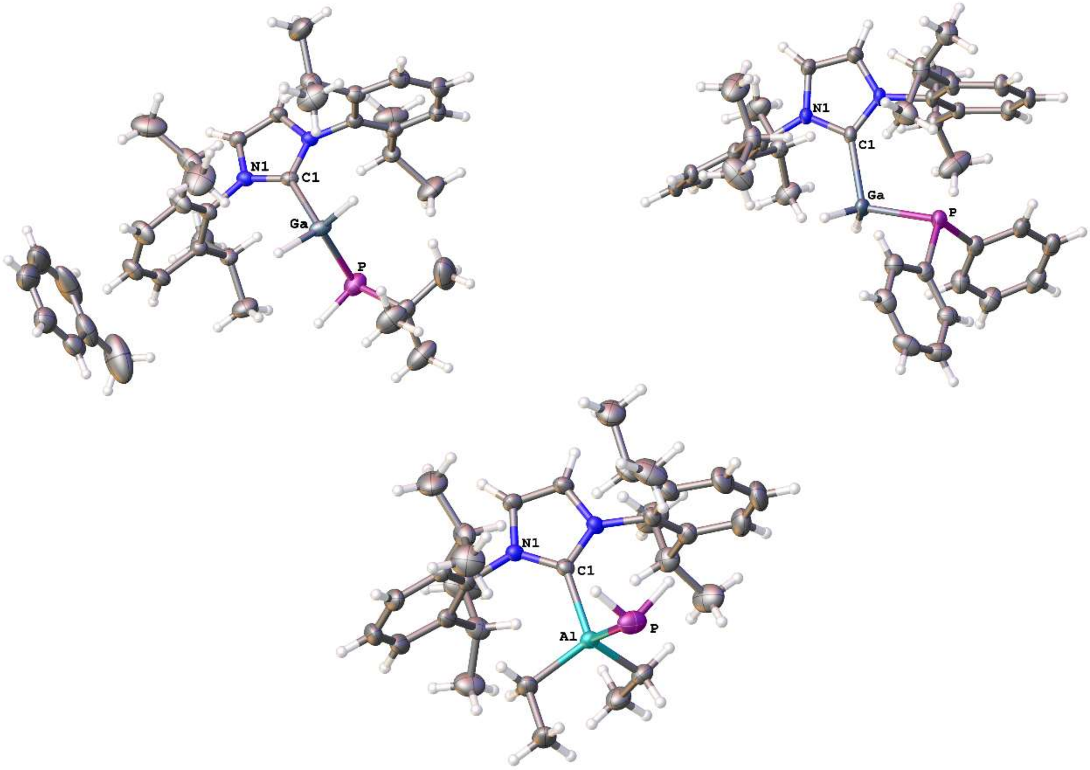


Figure 39: Molecular structure of IDipp·$GaH_2PHt\text{Bu}$ (**1**), IDipp·GaH_2PPh_2 (**2**) and IDipp·$AlEt_2PH$ (**3**) in solid state.

Compound **1** crystallizes in the space group $P2_1/c$ from a concentrated toluene solution at –30 °C with one toluene molecule inside the unit cell. The Ga–P distance in **1** is 2.3538(7) Å and the Ga–C1 bond length is 2.0667(18) Å. The C1–Ga–P angle is 105.94(5)°. Compound **2** crystallizes as colorless needles from a saturated *n*-hexane solution at –30 °C in the space group $P2_1/n$. The Ga–P distance in **2** is very similar to **1** with 2.3754(8) Å and the Ga–C1 bond length (2.073(3) Å) is not affected by the bigger sterical demand of the phenyl substituents on the P atom. However, the sterical demand of two phenyl substituents in **2** compared to one ^{t}Bu substituent in **1** results in a slightly wider C1–Ga–P angle (109.91(7)°). Both, compound **1** and **2**, crystallize in an eclipsed conformation along the Ga–P bond. Compound **3** crystallizes in the space group $P2_1/n$ from a saturated *n*-hexane solution at –30 °C. The Al–P distance is 2.3925(13) Å and the Al–C1 bond length is 2.091(3) Å. The C1–Al–P angle is 108.57(9)° and compared to **1** and **2**, compound **3** crystallizes in a staggered conformation along the Al–P bond (see Figure 14).

Table 1. Crystallographic data for compounds IDipp·GaH_2PH*t*Bu (**1**), IDipp·GaH_2PPh_2 (**2**) and IDipp·$AlEt_2PH_2$ (**3**).

Compound	**1**	**2**	**3**
Data set (internal naming)	**MW305**	**MW313**	**MW233**
Formula	$C_{39}H_{58}GaN_2P_{1.2}$	$C_{39}H_{48}GaN_2P$	$C_{31}H_{50}N_2AlP$
$D_{calc.}$ / g · cm^{-3}	1.047	1.114	1.324
μ/mm^{-1}	1.199	1.675	1.452
Formula Weight	655.60	645.52	508.68
Colour	clear colourless	clear colourless	clear colourless
Shape	block	needle	needle
Size/mm^3	0.56×0.23×0.19	0.48×0.17×0.15	0.61×0.26×0.16
T/K	123.01(10)	122.99(10)	123.00(10)
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	12.2337(2)	10.6427(2)	20.2099(5)
b/Å	13.6490(2)	25.3637(4)	17.4273(3)
c/Å	22.9911(4)	13.7705(2)	20.5912(5)
α/°	90	90	90
β/°	103.955(2)	106.551(2)	118.392(3)
γ/°	90	90	90
V/Å^3	3725.70(11)	3563.17(11)	6380.0(3)
Z	4	4	10
Z'	1	1	2.5
Wavelength/Å	1.39222	1.54184	1.54184
Radiation type	Cu K_β	Cu K_α	Cu K_α
Θ_{min}/°	3.361	3.485	3.519
Θ_{max}/°	72.645	73.837	72.814
Measured Refl.	27388	20389	36814
Independent Refl.	9756	6963	12409
Reflections with I > 2(I)	8953	6111	11113
R_{int}	0.0320	0.0316	0.0195
Parameters	446	404	670
Restraints	0	0	0
Largest Peak	0.754	0.649	3.957
Deepest Hole	-1.616	-0.503	-0.828
GooF	1.052	1.194	1.017
wR_2 (all data)	0.1758	0.1496	0.2802
wR_2	0.1707	0.1444	0.2725
R_1 (all data)	0.0600	0.0523	0.0976
R_1	0.0567	0.0456	0.0915

7.2. Reactivity of Lewis Base stabilized phosphanylgallanes

Pnictogenyltrielanes in general, have a free lone pair at the group 15 element. Small enough group 15 element bonded substituents with low steric demand enable the free lone pair to interact in further reactions e.g. with Lewis acids. To gain more information about this reactivity, especially of phosphanylgallanes, the reaction of IDipp·GaH_2PH_2 and SMe_2·BH_3 (Scheme 2) was investigated. The product IDipp·$GaH_2PH_2BH_3$ proved the accessibility of the lone pair on the phosphorus atom and its donor strength to replace SMe_2 and form the first only LB stabilized parent group 13/15 three membered chain with gallium as group 13 element.

$$\text{IDipp}\bullet\text{GaH}_2\text{PH}_2 \quad + \quad \text{SMe}_2\bullet\text{BH}_3 \xrightarrow[\text{-30°C} \rightarrow \text{RT}]{\textit{n}\text{-hexane}} \text{IDipp}\bullet\text{GaH}_2\text{PH}_2\text{BH}_3$$

Scheme 2: Synthesis reaction of IDipp·$GaH_2PH_2BH_3$.

Synthesis of IDipp·$GaH_2PH_2BH_3$:

With a syringe 0.12 mL of a stock solution of SMe_2·BH_3 (0.06 mmol, 0.5 mmol mL^{-1}) in toluene was added to a solution of IDipp·GaH_2PH_2 (0.03 mg, 0.06 mmol) in 10 mL *n*-hexane at –30 °C. The resulting white suspension was warmed up to room temperature within 1 hour. After removing all volatiles under reduced pressure the white residue was suspended in toluene and filtered over a celite pad. The colorless solution was concentrated and stored at –30 °C to afford IDipp·$GaH_2PH_2BH_3$ as colorless plates (20 mg, 67%).

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): δ = 0.93 (d, 12H, $^3J_{H,H}$ = 6.89 Hz, *i*Pr-C*H*$_3$), 1.32 (d, 12H, $^3J_{H,H}$ = 6.89 Hz, *i*Pr-C*H*$_3$), 1.65 (m br, 3H, B*H*$_3$), 2.25 (dm, 2H, $^1J_{P,H}$ = 302.19 Hz, P*H*$_2$), 2.54 (sept, 4H, $^3J_{H,H}$ = 6.89 Hz, *i*Pr-C*H*), 4.02 (d br, 2H, Ga*H*$_2$), 6.41 (s, 2H, NC*H*C*H*N), 7.02 (d, 4H, $^3J_{H,H}$ = 7.92 Hz, aryl-C_{meta}*H*), 7.17 (t, 2H, $^3J_{H,H}$ = 7.92 Hz, aryl-C_{para}*H*).

^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ = -161.3 (s, *P*H$_2$).

^{31}P NMR (162.04 MHz, C_6D_6, 298 K): δ = -161.3 (tm, $^1J_{P,H}$ = 302.19 Hz, *P*H$_2$).

^{11}B{^{1}H} NMR (128.43 MHz, C_6D_6, 298 K): δ = -38.87 (m, *B*H$_3$).

^{11}B NMR (128.43 MHz, C_6D_6, 298 K): δ = -38.87 (qm, $^1J_{B,H}$ = 99.38 Hz, *B*H$_3$).

CHN: Anal.Calcd. (%) for $C_{27}H_{43}GaN_2P$ + toluene: C 68.14, H 8.58, N 4.67; Found: C 69.19, H 8.73 N 4.75.

LIFDI-MS (m/z): 505.2647 $[M-H]^+$ (3%).

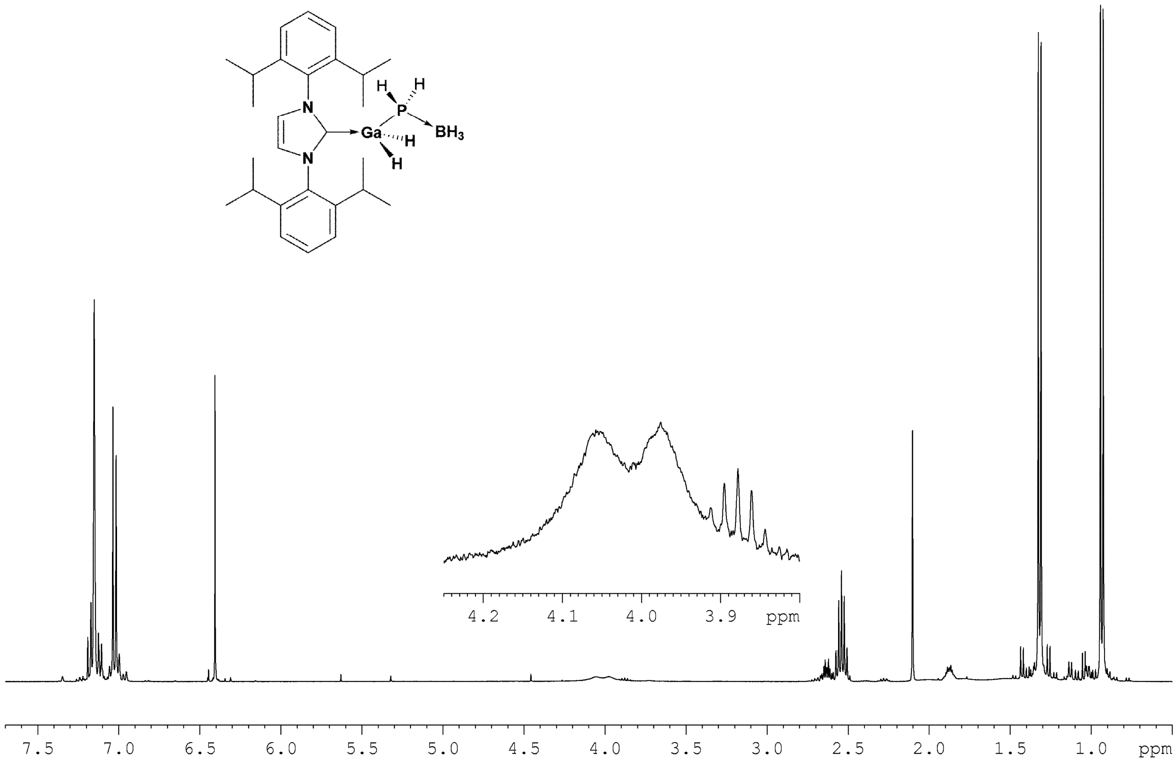


Figure 40: ^{1}H NMR spectrum of IDipp·$GaH_2PH_2BH_3$ in C_6D_6 at 298 K.

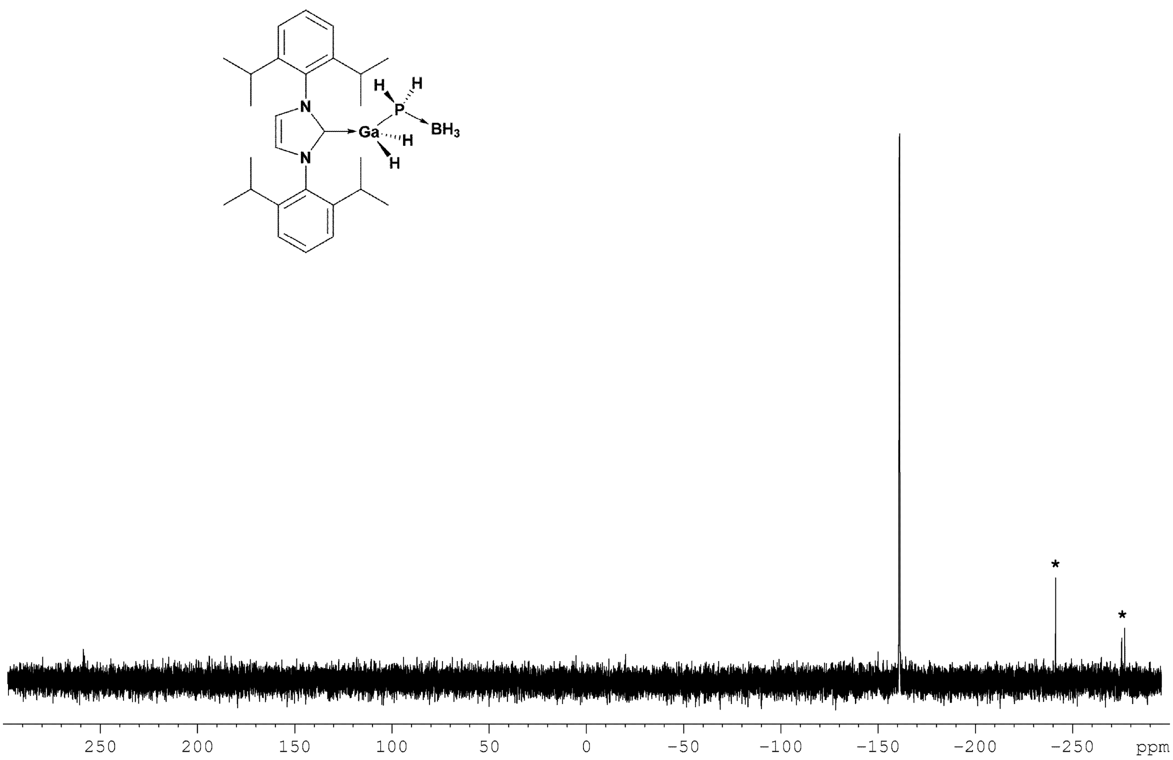


Figure 41: $^{31}P\{^{1}H\}$ NMR spectrum of IDipp·$GaH_2PH_2BH_3$ in C_6D_6 at 298 K. * = unidentified impurities.

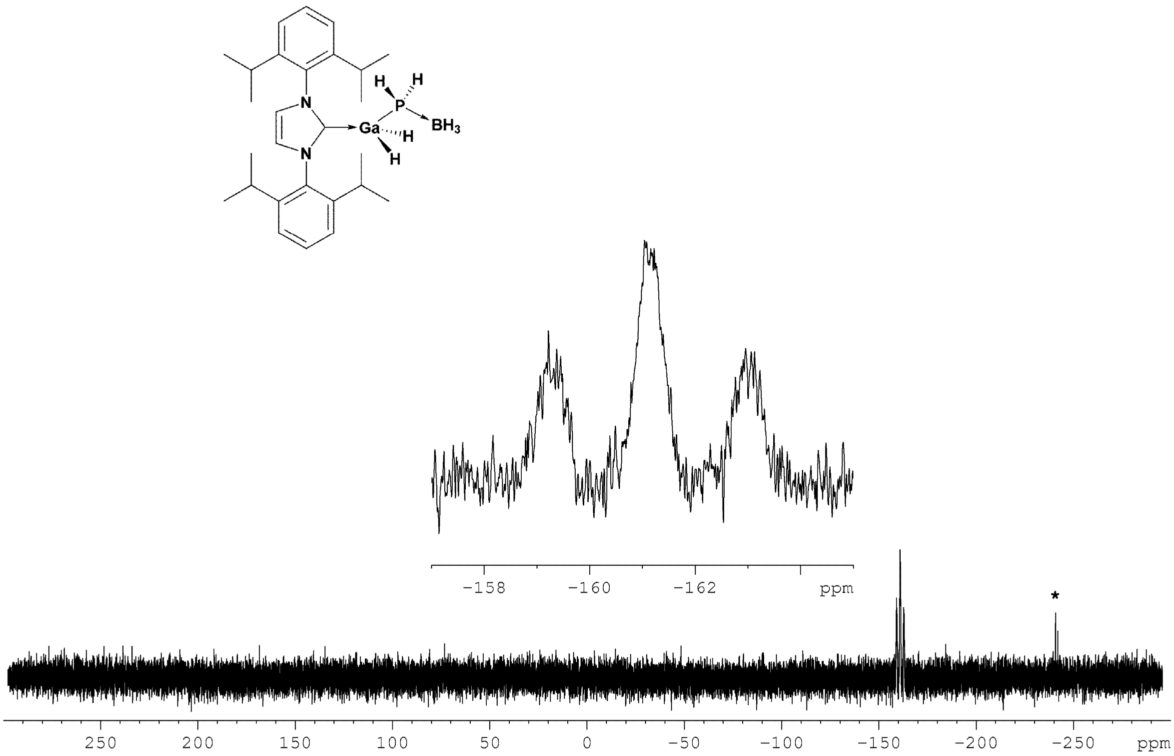


Figure 42: ^{31}P NMR spectrum of IDipp·$GaH_2PH_2BH_3$ in C_6D_6 at 298 K. * = unidentified impurity.

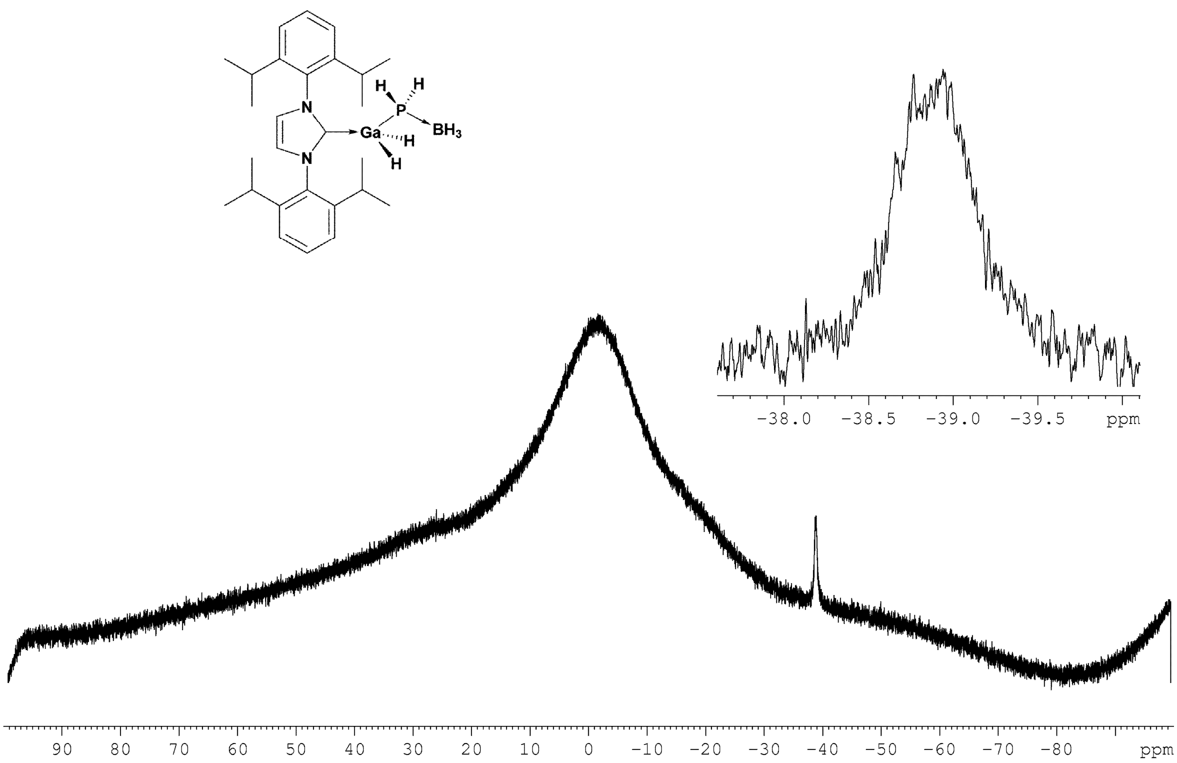


Figure 43: $^{11}B\{^1H\}$ NMR spectrum of IDipp·$GaH_2PH_2BH_3$ in C_6D_6 at 298 K.

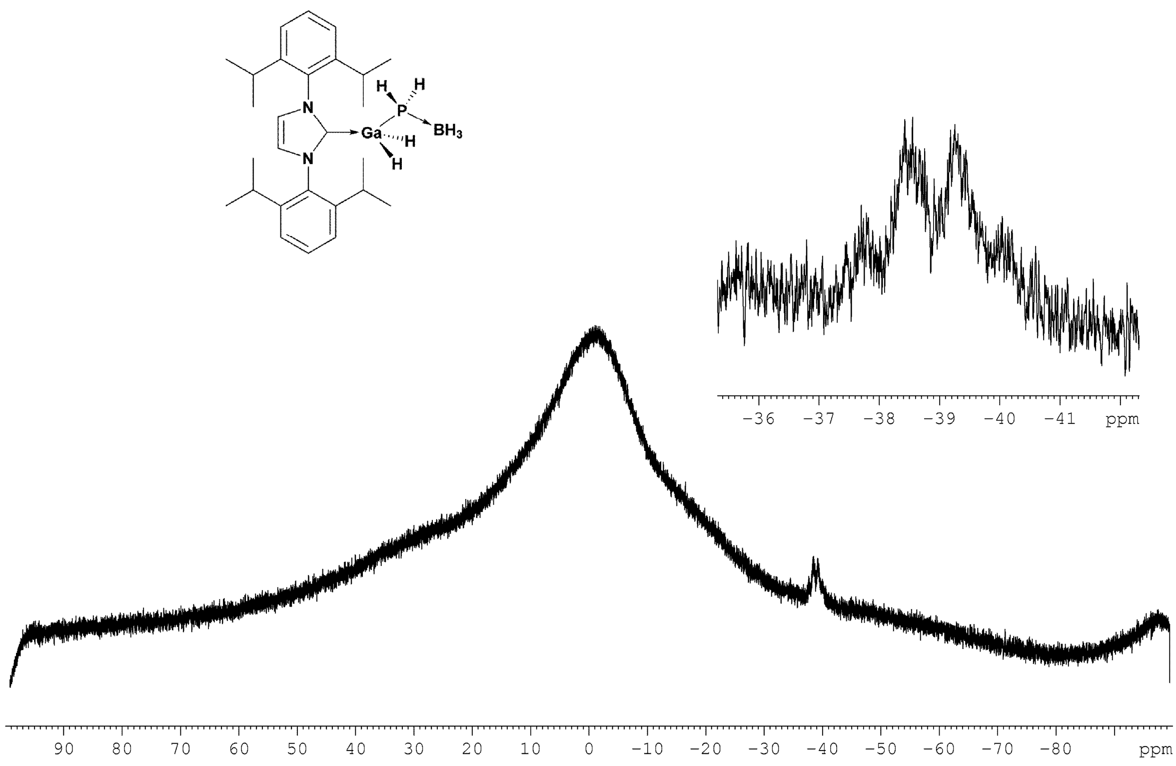


Figure 44: ^{11}B NMR spectrum of IDipp·$GaH_2PH_2BH_3$ in C_6D_6 at 298 K.

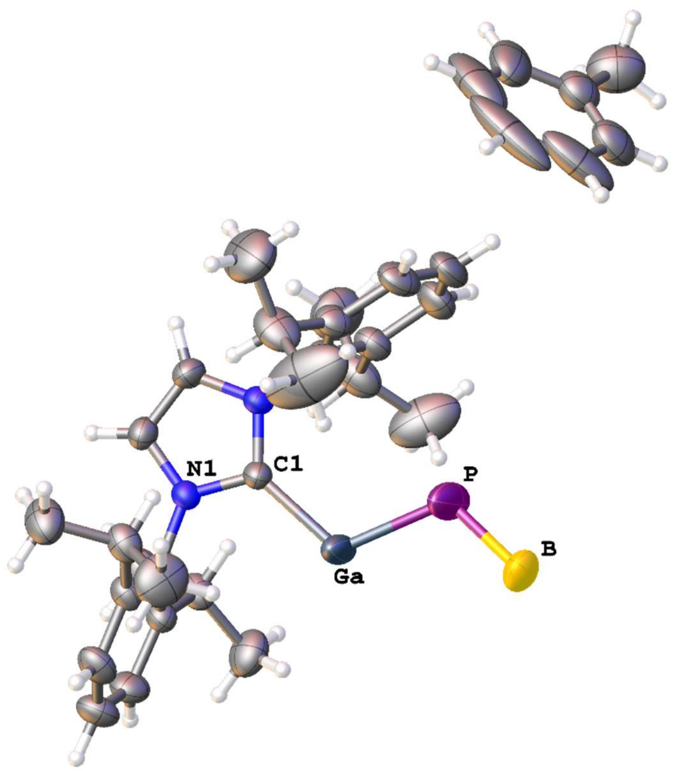


Figure 45: Molecular structure of IDipp·$GaH_2PH_2BH_3$ in solid state. H atoms at the Ga, P and B atom could not be detected.

Table 2. Crystallographic data of IDipp·$GaH_2PH_2BH_3$.

Compound	**IDipp·$GaH_2PH_2BH_3$**
Data set (internal naming)	**MW377**
Formula	$C_{34}H_{44}BGaN_2P$
$D_{calc.}$ / g · cm^{-3}	1.114
μ/mm^{-1}	1.236
Formula Weight	592.21
Colour	clear colourless
Shape	plate
Size/mm^3	0.54×0.48×0.13
T/K	122.97(11)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	17.4915(3)
b/Å	10.3123(2)
c/Å	21.4326(6)
α/°	90
β/°	114.069(3)
γ/°	90
V/Å^3	3529.83(15)
Z	4
Z'	1
Wavelength/Å	1.39222
Radiation type	Cu K_β
Θ_{min}/°	2.498
Θ_{max}/°	74.607
Measured Refl.	19021
Independent Refl.	9353
Reflections with I > 2(I)	7068
R_{int}	0.0285
Parameters	361
Restraints	0
Largest Peak	1.352
Deepest Hole	-1.766
GooF	1.034
wR_2 (all data)	0.2952
wR_2	0.2740
R_1 (all data)	0.1238
R_1	0.1020

7.3. Synthesis and characterization of tris-phosphanidogallanes

After discovering the formation of di-substituted compounds IDipp·E'H(EH_2)$_2$ (E' = Al, Ga; E = P, As) as byproducts and modelling their selective synthesis as discussed in chapter 6, it was obvious to investigate the possibility of the formation of tris-substituted compounds. The first tris-phosphanidogallane IDipp·Ga(PH_2)$_3$ could be obtained by the reaction of IDipp·$GaCl_3$ and $NaPH_2$ (Scheme 3). This reaction shows that tris-pnictogenyltrielanes should be possible and opens a huge field for further studies. IDipp·Ga(PH_2)$_3$ could be characterized *via* NMR and the support of the crystallographic data.

$$\text{IDipp•GaCl}_3 \quad + \quad 4\ \text{NaPH}_2 \xrightarrow[-30°\text{C} \rightarrow \text{RT}]{\text{Et}_2\text{O}} \text{IDipp•Ga(PH}_2)_3$$

Scheme 3: Synthesis reaction of IDipp·Ga(PH_2)$_3$.

IDipp·Ga(PH_2)$_3$ crystallizes in the monoclinic space group *Pc*. The Ga–P distances are in the range of 2.337(3) – 2.358(3) Å. The Ga–C1 bond length is 2.046(8) Å. The Ga atom reveals a tetrahedral geometry and the C1–Ga–P angles are in the range of 106.7(3) – 110.1(3)° (see Figure 24).

Synthesis of IDipp·Ga(PH_2)$_3$:

A solution of IDipp·$GaCl_3$ (0.05 g, 0.09 mmol, 1 eq) in 10 mL Et_2O was added slowly to a suspension of $NaPH_2$ (0.02 g, 0.35 mmol, 4 eq) in 10 mL Et_2O at –30 °C. The white suspension was warmed up to room temperature overnight while the suspension discolored yellowish. After removing the solvent *in vacuo* the yellowish residue was suspended in *n*-hexane and centrifuged for 10 minutes at 2000 rpm. The colorless supernatant was concentrated and stored at –30 °C to afford IDipp·Ga(PH_2)$_2$ as colorless needles (37 mg, 75%).

^{1}H NMR (400.30 MHz, C_6D_6, 298 K): δ = 0.97 (d, 12H, $^{3}J_{H,H}$ = 6.87 Hz, *i*Pr-C*H*$_3$), 0.99 (dt, 6H, $^{1}J_{P,H}$ = 173.87 Hz, $^{4}J_{H,H}$ = 2.55 Hz, (P*H*$_2$)$_3$), 1.50 (d, 12H, $^{3}J_{H,H}$ = 6.87 Hz, *i*Pr-C*H*$_3$), 2.79 (sept, 4H, $^{3}J_{H,H}$ = 6.87 Hz, *i*Pr-C*H*), 6.47 (s, 2H, NC*H*C*H*N), 7.14 (d, 4H, $^{3}J_{H,H}$ = 7.65 Hz, aryl-C_{meta}*H*), 7.26 (t, 2H, $^{3}J_{H,H}$ = 7.65 Hz, aryl-C_{para}*H*).

^{31}P{^{1}H} NMR (162.04 MHz, C_6D_6, 298 K): δ = -231.74 (s, (*P*H$_2$)$_3$).

^{31}P NMR (162.04 MHz, C_6D_6, 298 K): δ = -231.74 (t, (*P*H$_2$)$_3$).

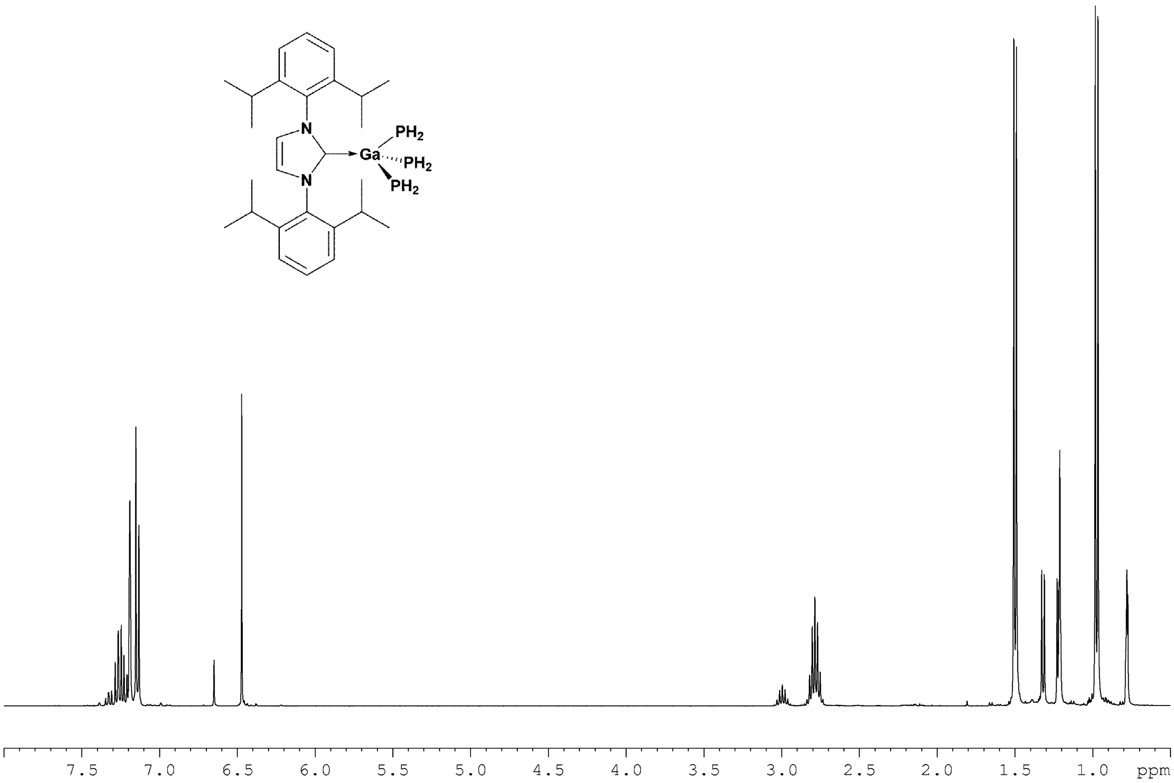


Figure 46: ^{1}H NMR spectrum of IDipp·Ga(PH_2)$_3$ in C_6D_6 at 298 K.

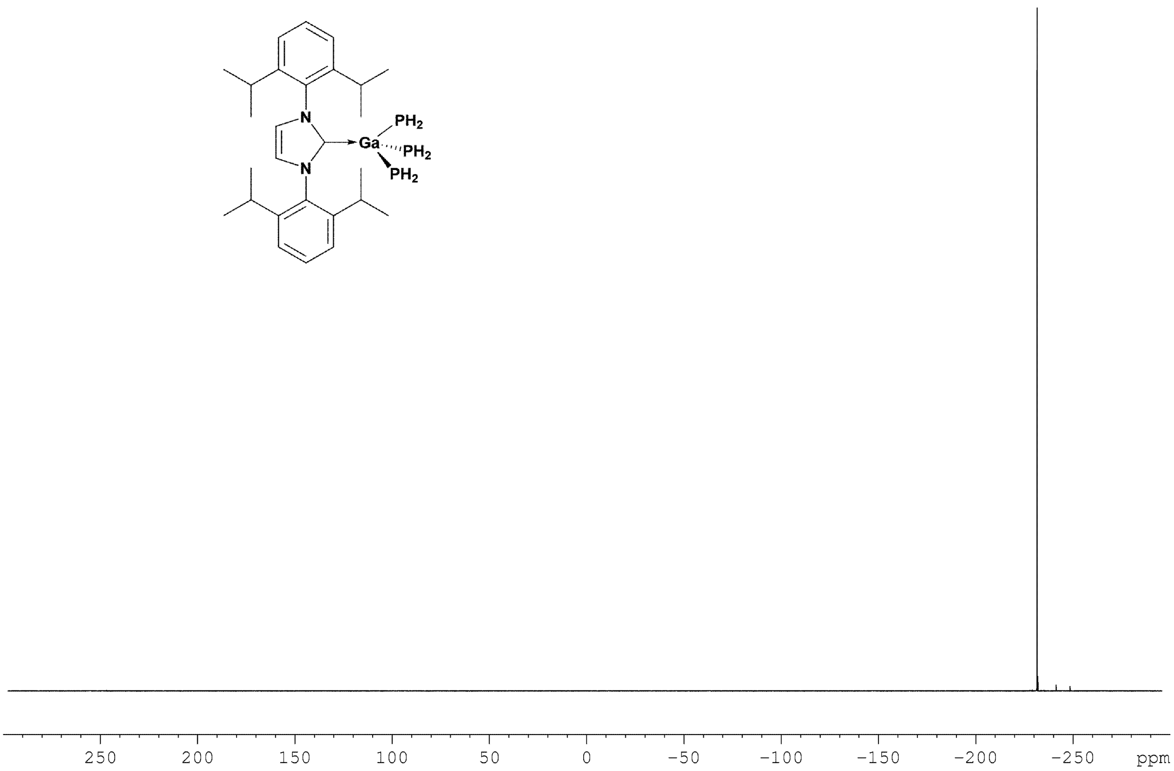


Figure 47: $^{31}P\{^{1}H\}$ NMR spectrum of IDipp·Ga(PH_2)$_3$ in C_6D_6 at 298 K.

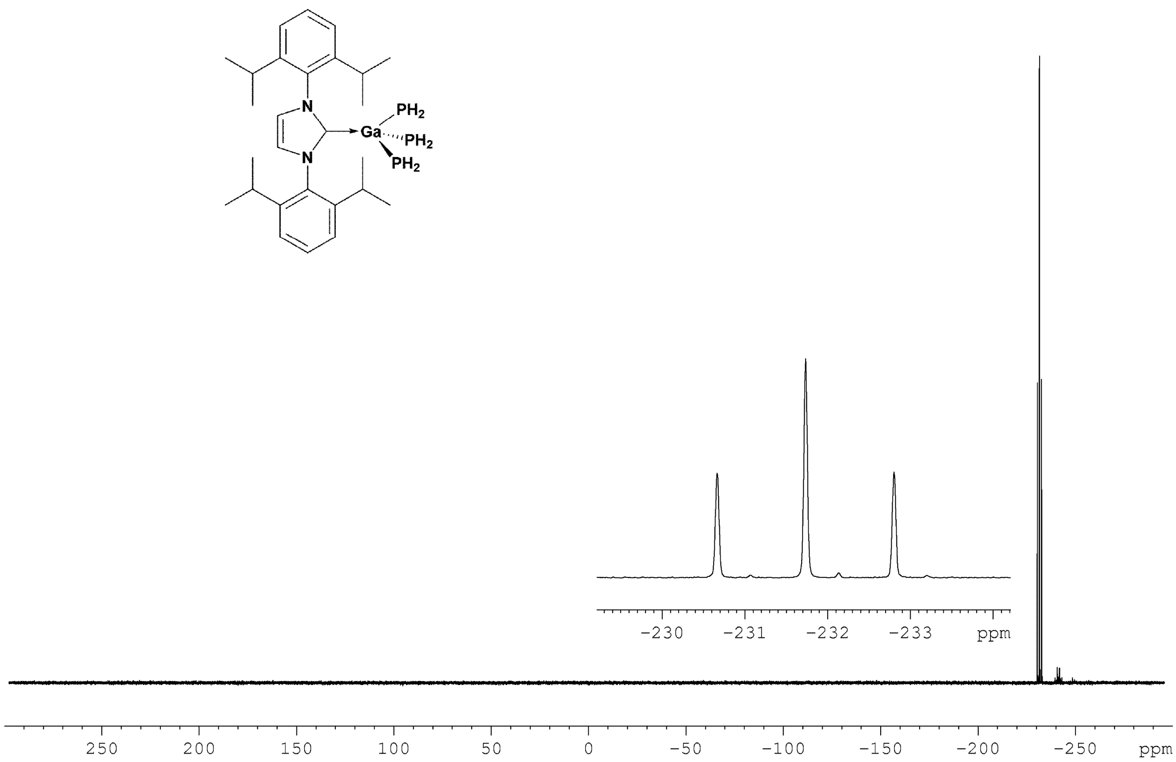


Figure 48: ^{31}P NMR spectrum of IDipp·Ga$(PH_2)_3$ in C_6D_6 at 298 K.

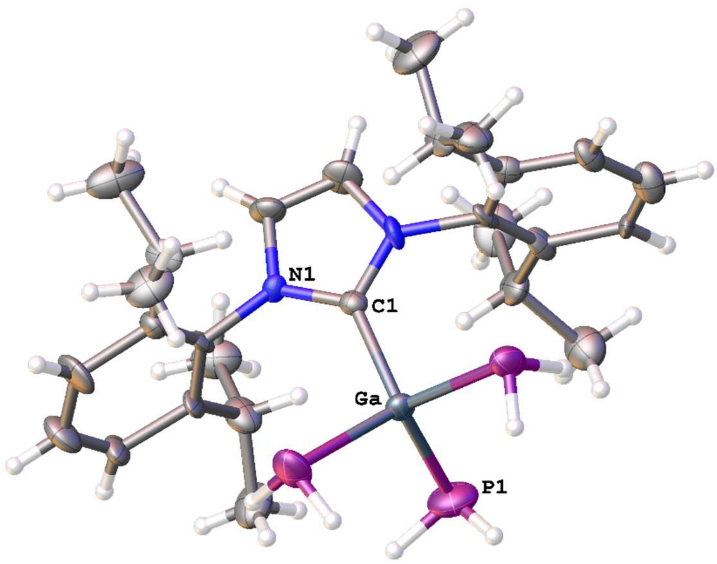


Figure 49: Molecular structure of IDipp·Ga$(PH_2)_3$ in solid state.

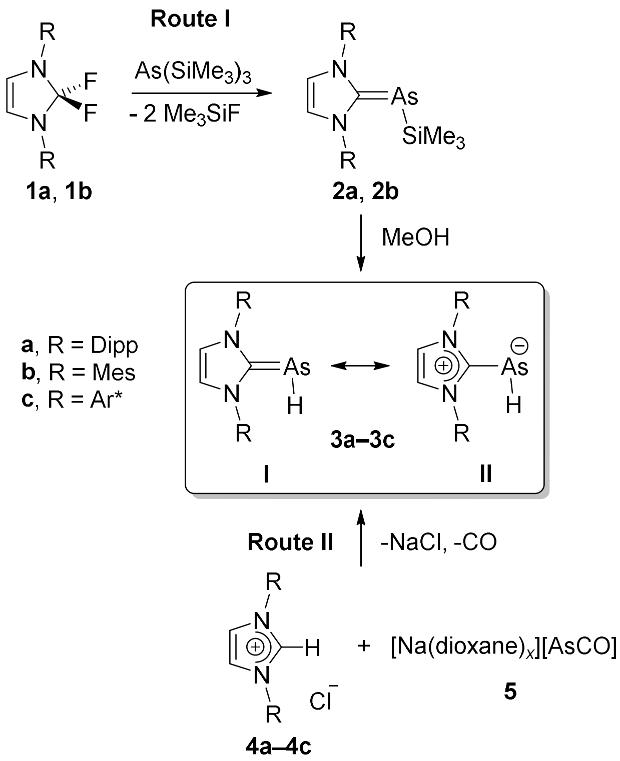
Table 3. Crystallographic data of IDipp·Ga(PH_2)$_3$.

Compound	**IDipp·Ga(PH_2)$_3$**
Data set (internal naming)	**MW446**
Formula	$C_{54}H_{78.5}Ga_2N_4P_6$
$D_{calc.}$ / g · cm^{-3}	1.202
μ/mm^{-1}	2.823
Formula Weight	1108.96
Colour	clear colourless
Shape	needle
Size/mm^3	0.28×0.17×0.15
T/K	122.97(11)
Crystal System	monoclinic
Space Group	*Pc*
a/Å	17.9941(3)
b/Å	17.8831(3)
c/Å	20.8615(4)
α/°	90
β/°	114.084(2)
γ/°	90
V/Å^3	6128.6(2)
Z	4
Z'	2
Wavelength/Å	1.54184
Radiation type	Cu K_α
Θ_{min}/°	2.471
Θ_{max}/°	73.921
Measured Refl.	34801
Independent Refl.	18659
Reflections with I > 2(I)	17049
R_{int}	0.0220
Parameters	1269
Restraints	2
Largest Peak	0.741
Deepest Hole	-0.456
GooF	1.079
wR_2 (all data)	0.1008
wR_2	0.0976
R_1 (all data)	0.0422
R_1	0.0379

8. Conclusion

8.1. N-Heterocyclic Carben-Stabilized Arsinidene

The tremendous interest in the use of carbene-phosphinidene adducts in coordination chemistry led to the question if heavier pnictinidene congeners (NHC)EH (E = As, Sb, Bi) could be suitable ligands in transition metal chemistry as well. To make these compounds available the N-heterocyclic carbene adducts of the parent arsinidene (AsH) were prepared by two different synthetic routes. While route 1 features the reaction of As(SiMe3)3 with 2,2-difluoroimidazolines (1a, 1b) followed by desilylation, route 2 is a salt metathesis reaction of [Na(dioxane)3.31][AsCO] (5) with imidazolium chlorides (4a–4c) (Scheme 1).



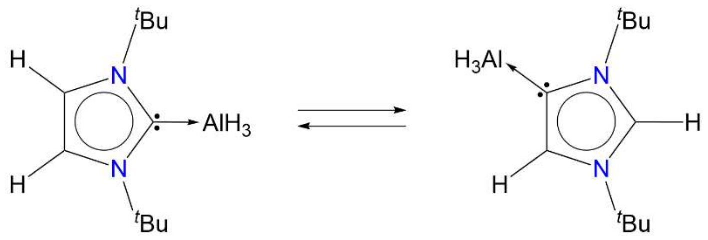
Scheme 1: Preparation of N-heterocyclic carbene-arsinidene adducts; Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl; Ar* = 2,6-bis(diphenylmethyl)-4-methylphenyl.

It was possible to obtain compound **3a** and **3b** *via* both synthetic routes. While the single-reaction route 2 offers a relatively low yield of 13% (**3a**) and 15% (**3b**), respectively, it was possible to increase the yields of these compounds with the use of route 1 to 58% (**3a**) and 64% (**3b**). Compound **3c** was synthesized using route 2 in a yield of 9%. The low yields are the results of the high light sensitivity and instability of the products in solution at ambient temperatures. The corresponding free carbenes could be identified as the decomposition products which reflects the easy removal of the parent arsinidene moiety. It was possible to fully characterize **3a**–**3c** including the molecular structure in the solid state of all three compounds and confirm the dicoordinate nature of the arsenic(I) atoms. To investigate the bonding situation in the N-heterocyclic carbene-arsinidene adducts **3a**–**3c** various computations were carried out, including a comparison with H_3CAsH_2 (featuring a C–As single bond), H_2CAsH and Ph_2CAsH (featuring a C=As double bond).

Route 1 and route 2 exhibit two different synthetic protocols for the preparation of the first NHC adducts of the parent arsinidene. These species now extend the family of N-heterocyclic carbene adducts of parent pnictinidenes, which now comprises EH = NH, PH and AsH. An extension to the heavier antimony (SbH) and bismuth (BiH) analogues might also become possible by application of similar synthetic routes. These new (NHC)AsH species are able to serve as starting material, e.g. for the preparation of unusual arsenic containing main group element compounds and as novel arsenic donor ligands in transition metal chemistry.

8.2. Normal to abnormal I^{t}Bu·AlH_3 isomerization in solution and in the solid state

Compared to normal NHCs, *a*NHCs (abnormal NHCs) could exhibit stronger σ-donating properties which could result in a higher stability of *a*NHC complexes. Due to this energetic stabilization, *a*NHC complexes, like **6a**, may be formed *via* isomerization of the corresponding less stable NHC complexes. It was possible to observe the isomerization of the NHC complex I^{t}Bu·AlH_3 (**6**) into the abnormal carbene complex *a*I^{t}Bu·AlH_3 (**6a**) in a polar solvent and, for the first time, in the solid state (Scheme 2).



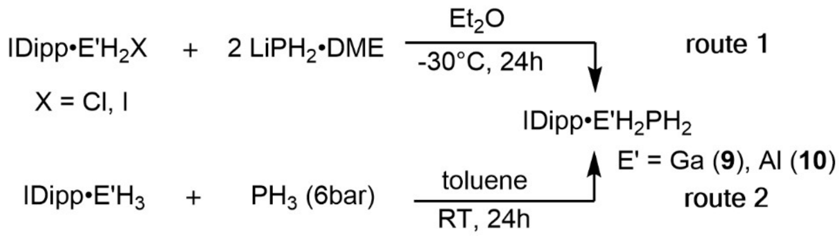
6 **6a**

Scheme 2: Isomerization of **6** into **6a**.

Both **6** and **6a** were structurally characterized by single crystal X-ray diffraction analysis. **6** shows a slow rate of isomerization in non-polar solvents like benzene but the isomerization is promoted by more polar solvents as THF or CD_2Cl_2 which could be shown by NMR studies. Additionally, an isomerization of **6** into **6a** in the solid state within 21 days could be proven by NMR. This is the first example of an isomerization from a normal NHC compound to an abnormal NHC compound in the solid state. In order to shed light on the mechanism involved in the solvent-free isomerization in the solid state, additional computational studies were performed and two different pathways were examined.

8.3. Phosphanylalanes and –gallanes stabilized only by a Lewis Base

It was possible to synthesize and characterize the first parent phosphanylalane and –gallane stabilized only by a Lewis base (LB). The corresponding substituted compounds IDipp·GaH_2PCy_2 (**7**) and IDipp·AlH_2PCy_2 (**8**) could be obtained *via* the salt metathesis reaction of $LiPCy_2$ with IDipp·E'H_2Cl (E' = Al, Ga). However, the LB-stabilized parent compounds IDipp·GaH_2PH_2 (**9**) and IDipp·AlH_2PH_2 (**10**) were prepared *via* two different routes. Route 1 featuring the salt metathesis reaction of $LiPH_2$·DME with IDipp·E'H_2Cl (E' = Al, Ga) and route 2 includes a H_2 elimination reaction between IDipp·E'H_3 (E' = Al, Ga) and PH_3 (Scheme 3). Compound **9** can be isolated in a yield of 67% *via* route 1 and 23% *via* route 2, respectively. Due to higher sensitivity towards decomposition, compound **10** can be isolated in a yield of 55% (route 1) and 20% (route 2), respectively.



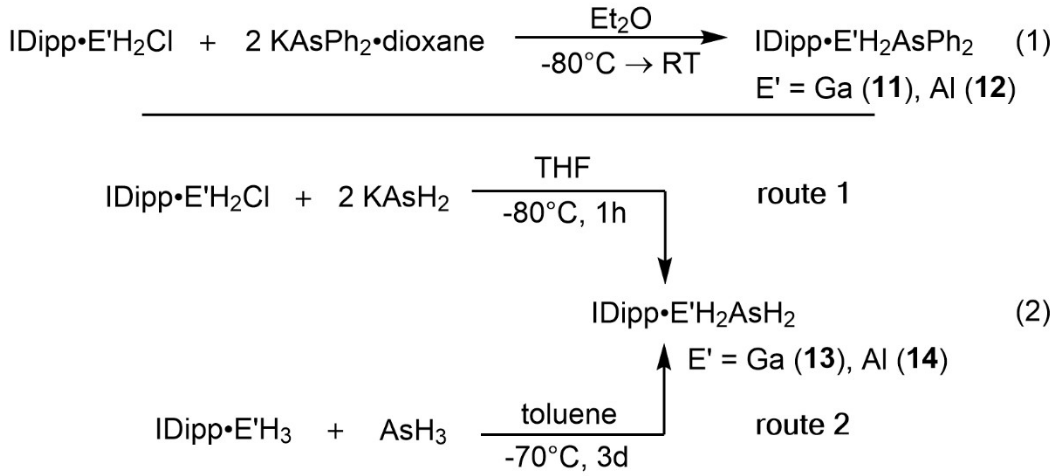
Scheme 3: Different synthetic pathways for the synthesis of LB-stabilized parent phosphanylalanes and –gallanes.

The compounds could be isolated as crystalline solids and their molecular structure in solid state identified by single crystal X-ray analysis. While the parent compounds can be synthesized *via* salt metathesis and H_2 elimination, the organo-substituted compounds **7** and **8** can only be accessed *via* a salt metathesis reaction which was supported by corresponding DFT computations. Moreover, the energetic differences in the reaction pathways and the different stability of all complexes were computed by DFT methods. Route 1 is the first example of an applied salt metathesis reaction to access stabilized phosphanylalanes and –gallanes.

8.4. NHC-stabilized Parent Arsanylalanes and –gallanes

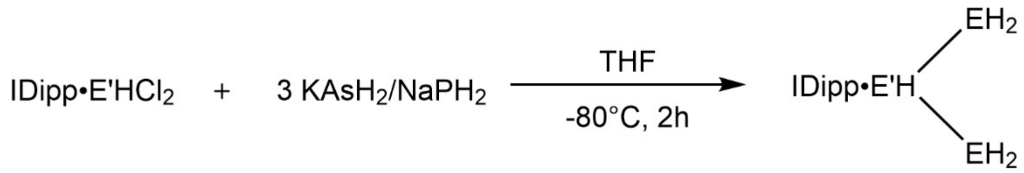
After succeeding in the synthesis and characterization of LB-stabilized parent phosphanylalane and –gallane it was obvious to extend this family of compounds by synthesizing the unprecedented LB-stabilized parent arsanylalanes and –gallanes. While the organo-substituted analogues IDipp·E'H_2AsPh_2 (E' = Ga (**11**), Al (**12**)) were synthesized by a salt metathesis reaction between IDipp·E'H_2Cl (E' = Al, Ga) and $KAsPh_2$·dioxane (**11**: 63%, **12**: 52%; Scheme 4, equation 1), it was possible to obtain the parent compounds by two different synthetic approaches. IDipp·GaH_2AsH_2 (**13**) and IDipp·AlH_2AsH_2 (**14**) could be synthesized *via* a H_2 elimination reaction of IDipp·E'H_3 (E' = Al, Ga) and AsH_3 with a minor yield proven by NMR (Scheme 4, route 2) and *via* a salt metathesis reaction between

IDipp·E'H_2Cl (E' = Al, Ga) and $KAsH_2$ in a yield of 39% for **13** and 40% for **14**, respectively (Scheme 4, route 1).



Scheme 4: Synthesis of organo-substituted LB-stabilized arsanylalanes and –gallanes (1); Different synthetic pathways for the synthesis of LB-stabilized parent arsanylalanes and –gallanes (2).

In contrast to the phosphorus analogues, the arsenic compounds **13** and **14** exhibit a different reactivity forming the branched parent compounds IDipp·E'H(EH_2)$_2$ (E' = Al, Ga; E = P, As) as a side product by AsH_3-caused substitution reactions. It was possible to selectively synthesize IDipp·E'H(AsH_2)$_2$ (E' = Al (**15**), Ga (**16**)) and IDipp·E'H(PH_2)$_2$ (E' = Ga (**17**), Al (**18**)) *via* a salt metathesis reaction of IDipp·E'HCl_2 (E' = Al, Ga) with $KAsH_2$ and $NaPH_2$, respectively (Scheme 5).



15: E' = Al; E = As
16: E' = Ga; E = As
17: E' = Ga; E = P
18: E' = Al; E = P

Scheme 5: Salt metathesis reaction for the synthesis of branched Pnictogenylalanes and –gallanes.

All compounds could be isolated as crystalline solids and their molecular structure in solid state could be identified by single crystal X-ray analysis. The energies of the different reaction pathways, the stability of the corresponding compounds and the differences in the reactivity between the phosphorus compounds and the arsenic analogues were calculated by DFT computations.

These results show that regardless of the rather low E'–As bond stability (E' = Al, Ga) it is possible to synthesize parent arsanylalanes and –gallanes stabilized only by a LB, as well as their branched analogues which may serve as potential chelating ligands in coordination chemistry.

9. Appendices

9.1. Alphabetic List of Abbrevations

Å	Angstroem, 1 Å = $1\cdot10^{-10}$ m
°	degrees (angle)
°C	degree Celsius
Ar*	2,6-bis(diphenylmethyl)-4-methylphenyl
*a*NHC	abnormal NHC
br(NMR)	broad
CAAC	cyclicl(alkyl)(amino)carbene
δ	chemical shift
d(NMR)	doublet
DFT	density functional theory
Dipp	2,6-diisopropylphenyl
dmap	4-dimethylaminopyridine
dme	1,2-dimethoxyethane
ε	dielectric constant
E	element of the 15th group
E’	element of the 13th group
$E°_0$	total energy
EI-MS	electron impact mass spectrometry
ELF	electron localization function
EN	electronegativity
$G°_{298}$	standard Gibbs free energy
$G^{\#}$	barrier of rotation
$H°_{298}$	standard enthalpy
HOMO	highest occupied molecular orbital
HRMS-ESI	high resolution mass spectrometry – electron spray ionization
Hz	Hertz
IDipp	1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
IMe	1,3-di(methyl)imidazole-2-ylidene
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
IR	infrared spectroscopy
J(NMR)	coupling constant
K_{298}	equilibrium constant
K	Kelvin
LA	Lewis acid
LB	Lewis base
LED	light emitting diode

LIFDI-MS	liquid injection field desorption ionization massspectrometry
LUMO	lowest unoccupied molecular orbital
μ	dipole moment
m(NMR)	multiplet
MHz	megahertz
MOCVD	metalorganic chemical vapor deposition
NBO	natural bond orbital
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
NRT	natural resonance theory
ppm	parts per million
rpm	revolutions per minute
s(NMR)	singlet
$S°_{298}$	standard entropy
sept(NMR)	septet
t(NMR)	triplet
T	temperature
T_c	coalescence temperature
THF	tetrahydrofurane
$Tren^{TIPS}$	$N(CH_2CH_2NSi^iPr_3)_3$
VT NMR	variable temperature nuclear magnetic resonance
WBI	Wiberg bond indices

9.2. Acknowledgments

Special thanks go to:

- Prof. Dr. Manfred Scheer for giving me the opportunity to work on this very interesting project, providing excellent working conditions and the freedom to pursue my own ideas in the lab.
- Dr. Gábor Balázs for spending so much time on discussing, giving helpful advice and proof-reading. Without his knowledge, input and help, major parts of this work would not have been possible.
- Prof. Dr. Alexey Timoshkin for all the discussions and putting so much effort into the DFT calculations.
- All staff and co-workers of the Central Analytical Services of the University of Regensburg: X-ray (Dr. Michael Bodensteiner, Sabine Stempfhuber, Birgit Hischa), mass spectrometry department (Wolfgang Söllner, Josef Kiermaier), elemental analysis department (Helmut Schüller, Barbara Baumann) and the NMR department (Anette Schramm, Georgine Stühler, Fritz Kastner) for recording countless spectra and satisfying all special requests.
- The staff of the glass blowing, electronics and mechanics facilities of the University Regensburg.
- My former lab colleagues Felix and Eric for the unforgettable time and all the lifelong memories.
- The gaming group (Boi, Jens, Moritz) for the gaming evenings with so much fun and laughter.
- All present and former members of the Scheer group for a pleasant working atmosphere and an unforgettable time: Maria, Julian, Martin, Claudia, Helena, Anna, Lara, Kevin, Sabrina, Martin, Stephan, Vroni, Lena, Boi, Tobi, Felix, Christoph, Jana and Rebecca (especially for Assi-Mittwoch and Sushi feasts), Robert, Julian, Lukas, Petra, Martina, Schotti.
- My family for the lifelong support.
- And special thanks goes to my wife Corinna for being there for me every minute. No matter if the times are good or bad, you are always supportive and cheerful. You are my safe haven.