Synthesis and Reactivity of Hetero-Pnictogen Diazonium Analogs Stabilized by Transition Metal Units

Lisa Zimmermann,[a] Christoph Riesinger,[a] Gábor Balázs,[a] and Manfred Scheer*[a]

Dedicated to Professor Wolfgang Weigand on the occasion of his 65th birthday.

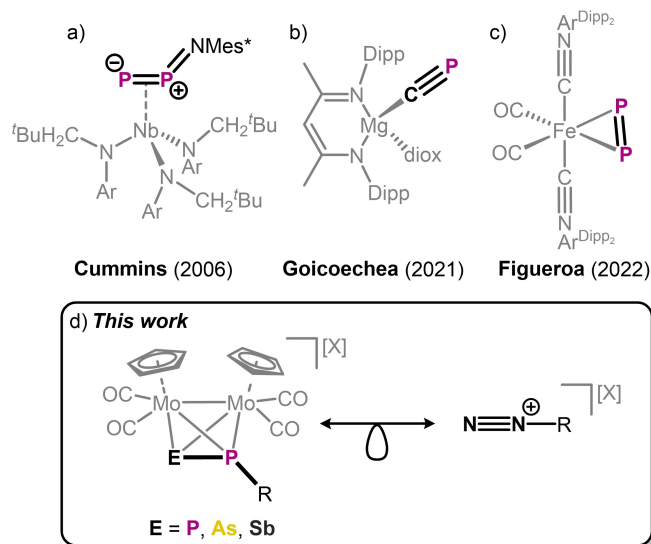The reactivity of the mixed dipnictogen complexes [{CpMo(CO)$_2$}$_2$($\mu,\eta^{2:2}$-PE)] (E=P, As, Sb) towards different group 14 electrophiles is reported. The resulting library of cationic compounds [{CpMo(CO)$_2$}$_2$($\mu,\eta^{2:2}$-EPR)]$^+$ (R=Mes (2,4,6-C$_6$H$_2$Me$_3$), CH$_3$, CPh$_3$, SnMe$_3$) represents formally inorganic diazonium homologs which are stabilized by transition metal units. Modifying the steric and electronic properties of the electrophile drastically impacts the respective P–R bond lengths and is accompanied by increasing (SnMe$_3$ > CPh$_3$ > CH$_3$) dynamic behavior in solution. In contrast to the well-studied organic analogs, the prepared compounds are stable at room temper-

ature. The subsequent reaction of the model substrate [{CpMo(CO)$_2$}$_2$($\mu,\eta^{2:2}$-P$_2$Me)][OTf] ([OTf]$^-$=[CF$_3$SO$_3$]$^-$) with different N-heterocyclic carbenes (NHCs) leads to an addition at the unsubstituted P atom which is also predicted by computational methods. NMR spectroscopy confirms the formation of two isomers *sync/gauche*-[{CpMo(CO)$_2$}($\mu,\eta^{2:1}$-P(NHC)PMe)-{CpMo(CO)$_2$}][OTf]. X-ray crystallographic characterization and additional DFT calculations shed light on the spatial arrangement as well as on the possible formation pathways of the isomers.

Introduction

Numerous organic nitrogen-containing compounds provide molecules with functionality and specific reactivity. Thus, functional nitrogen-containing groups such as amines, imines, enamines, imides, azides or diazonium cations play a key role in designing molecules with targeted properties. In contrast, little is known about compounds containing functional groups of the heavier pnictogens P, As, Sb and Bi, respectively. Such rare homologs already discovered are phosphaalkenes and -alkynes as the respective homologs to imines and nitriles. In fact, since the first discovery of phosphaalkynes by Gier[1] and further investigations by Tyler,[2] their reactivity including their di-[3] and oligomerization[4] tendency has been studied intensely.[5] Particularly phosphaalkynes are often used for the synthesis of valuable ligands via dimerization[6] or cyclocondensation reactions,[7] and their coordination chemistry was studied.[8] The selected example clearly shows that obtaining easy access to a larger variety of such heavier homologs of group 15 functional groups would allow an in-depth study of their interesting

properties and reactivity. Nevertheless, most of them need additional stabilization to allow for their isolation. This stabilization can take place either by sterically demanding organic substituents or by coordination to transition metal units. As regards the latter possibility, Cummins and co-workers reported the synthesis of [(η^2-Mes*NPP)Nb(N{(CH$_2$^{t}Bu)(Mes)}$_3$] (Mes*= 2,4,6-^{t}Bu$_3$C$_6$H$_2$, Mes=3,5-C$_6$H$_3$Me$_2$), a compound featuring a diphosphaazide ligand, which can serve as molecular P$_2$ source (Scheme 1a).[9] Moreover, the same group synthesized another P$_2$ source, the diphosphorus bisanthracene adduct P$_2$(C$_{14}$H$_{10}$)$_2$,

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               anorganische-chemie-scheer/startseite/index.html

Scheme 1. Selected examples of compounds containing phosphorus-based heavier homologs of well-known nitrogen-containing functional groups; Ar=3,5-C$_6$H$_3$Me$_2$, Dipp=2,6-C$_6$H$_3$^{i}Pr$_2$, diox=dioxane, Ar^{Dipp2}=2,6-(2,6-C$_6$H$_3$^{i}Pr$_2$)C$_6$H$_3$, Mes*=2,4,6-^{t}Bu$_3$C$_6$H$_2$.

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which was found to transfer P_2 units efficiently to 1,3-cyclohexadiene.[10] Furthermore, very recently, the Cummins group succeeded in synthesizing the anthracene-based molecular precursor $[(C_{14}H_{10})N_3P]$ as a source for phosphorus mononitride PN, which was successfully transferred to an iron center.[11] In 2021, Goicoechea et al. reported the heavier cyanide analog (Scheme 1b) as a magnesium cyaphido ($C\equiv P^-$) derivative, which was synthesized by the reduction of $^iPr_3SiOCP$ with Mg(I) sources.[12]

In addition, the group of Figueroa succeeded in isolating the mononuclear iron complex $[(CNAr^{Dipp2})_2(CO)_2Fe(\eta^2-P_2)]$ ($Ar^{Dipp2} = 2,6-(2,6-C_6H_3^iPr_2)C_6H_3$) featuring a first side-on coordinated P_2 ligand at one metal, which can be considered as the heavier dinitrogen homolog (Scheme 1c).[13] Earlier on, several complexes bearing P_2 units were synthesized, which, however, require additional stabilization by at least two transition metals.[14]

Diazonium salts $[N\equiv N-R][X]$ (R = aryl, alkyl) were first reported as early as 1858[15] and have been important starting materials in organic syntheses ever since. Nevertheless, they have serious drawbacks as they are known to be temperature-sensitive and explosive depending on their substituent R and the introduced counterion $[X]^-$.[16] Notably, aliphatic diazonium salts spontaneously explode due to dinitrogen release and thus their relevance in organic synthesis is limited.[17] Hence, the generation and stabilization of such species with aromatic as well as aliphatic substituents and the introduction of heavier pnictogen atoms to obtain heteroatomic species are valuable targets. To date, according to our knowledge, only two reports of Niecke and Burford, respectively, on the synthesis of $[P\equiv NC_6H_2^tBu_3][X]$ ($[X]^- = [AlCl_4]^-$, $[GaCl_4]^-$) as well as one report from Schulz and coworker on the synthesis of $[As\equiv NC_6H_2tBu_3][GaCl_4]$ are known.[18] During the last years, our group showed the potential of E_n ligand complexes as precursors for electrophilic functionalizations.[19] A recent report of an easy access to the mixed pnictogen complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-EE')]$ (E, E' = P, As, Sb, Bi)[20] in a one-pot reaction opened new possibilities for the synthesis of numerous subsequent compounds. Herein, their reactivity towards suitable group 14 electrophiles is reported. The resulting products can formally be considered as unprecedented heavier inorganic diazonium analogs (Scheme 1d). Furthermore, the subsequent reactions of these compounds with N-heterocyclic carbenes (NHCs) have been studied yielding novel asymmetrically substituted diphosphenes.

Results and Discussion

When $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-PE)]$ (E = P (**A**), As (**B**)) are reacted with the carbenium ion precursor $[Mes-N_2][BArF_{20}]$ ($[BArF_{20}]^- = [B(C_6F_5)_4]^-$) at 70 °C in o-DFB (1,2-difluorobenzene), an immediate colour change from orange (**A**) or red (**B**) to dark red can be observed. After workup, $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-EPMes)][BArF_{20}]$ (E = P (**1a**), As (**1b**)) were isolated in 63% (**1a**) and 72% (**1b**) yield, respectively (Scheme 2). The reaction of $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-PSb)]$ (**C**) with $[Mes-N_2][BArF_{20}]$, leads in-
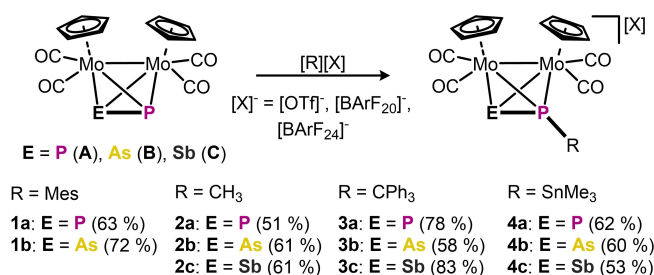
Scheme 2. Synthesis of **1**–**4** starting from **A**, **B** or **C**. **1a**–**1b**: [Mes-N₂][BArF₂₀], in o-DFB at 70 °C for 2 h; **2a**–**2b**: [Me][OTf], in o-DFB at 70 °C for 2 h; **2c**: [Me][OTf], K[BArF₂₀] in o-DFB at r.t. for 2 h; **3a**–**3c**: [Ph₃C][BArF₂₀], in CH₂Cl₂ at r.t. for 3 h; **3a**–**3c**: Me₃SnBr, Tl[BArF₂₄], in o-DFB at r.t. for 2 h.

stead to the formation of the oxidized product $[\{CpMo(CO)_2\}_4(\mu_4,\eta^{2:2:2:2}-SbPPSb)]^{2+}$, even at low temperatures (−80 °C).[20] Since alkyl-substituted diazonium salts can hardly be considered for organic syntheses due to their extreme thermal instability, our interest focused to the introduction of sp^3-hybridized substituents, since additional stabilization via the two $\{CpMo(CO)_2\}$ units was anticipated. The reaction of $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-PE)]$ (E = P (**A**), As (**B**)) with MeOTf in o-DFB at 70 °C for 2 h yielded $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-EPMe)][OTf]$ (E = P (**2a**, 51%), As (**2b**, 61%)) (Scheme 2). For the synthesis of $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-SbPMe)][BArF_{20}]$ (**2c**), an anion exchange with an additional equivalent K[BArF₂₀] added to the crude reaction solution of $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-SbPMe)][OTf]$ at r.t. was needed in order to increase the solubility and create suitable crystallization conditions (61% yield). **A**–**C** react with [Ph₃C][BArF₂₀], containing the sterically more demanding $[Ph_3C]^+$ cation in CH_2Cl_2 to yield $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-EPCPh_3)][BArF_{20}]$ (E = P (**3a**, 78%), As (**3b**, 58%), Sb (**3c**, 83%)) (Scheme 2). In contrast to organic diazonium salts, compounds **1**–**3** are stable in boiling o-DFB, presumably due to the stabilization by the transition-metals. In order to demonstrate the generality of this reaction method and to expand the scope of inorganic diazonium homologs, readily available Sn-electrophiles were chosen as potential substrates. Stannylations of polypnictogen complexes are so far limited to anionic E_n complexes. Cummins reported the formation of the stannyltriphosphirene complex $[(\eta^2-Ph_3SnP_3)Nb(ODipp)_3]$ upon reaction of the anionic complex $Na[(\eta^3-P_3)Nb(ODipp)_3]$ with Ph₃SnCl.[21] Moreover, Ruiz reported the functionalization of Li-$[\{CpMo(CO)\}_2(\mu-PCy_2)(\mu,\eta^{2:2}-P_2)]$ with Ph₃SnCl.[22] To the best of our knowledge, cationic polypnictogen complexes formed from tin electrophiles are not known so far. Hence, reactions of **A**–**C** with "[Me₃Sn][BArF₂₄]", in situ generated by the reaction of Tl[BArF₂₄] ($[BArF_{24}]^- = [B\{C_6H_3(CF_3)_2\}_4]^-$) with Me₃SnBr in o-DFB, were performed. A colour change to dark red and the formation of a white precipitate (TlBr) are observed over the course of 2 h. Compounds $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}-EPSnMe_3)][BArF_{24}]$ (E = P (**4a**, 62%), As (**4b**, 60%), Sb (**4c**, 53%)) were obtained after filtration from TlBr and layering a concentrated solution in o-DFB with n-hexane (Scheme 2).

Compounds **1**–**4** were crystallized from concentrated solutions in o-DFB or CH₂Cl₂ layered with n-pentane or n-hexane

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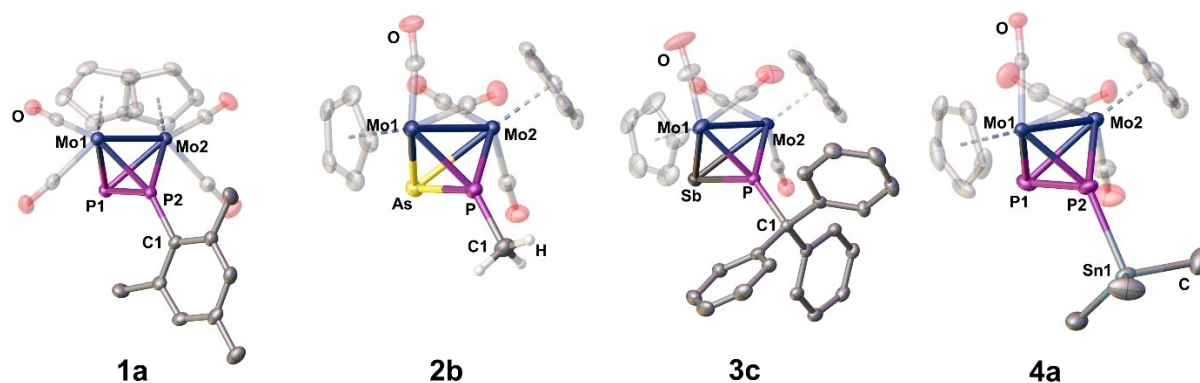European Chemical
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Figure 1. Molecular structures of the cations in **1a**, **2b**, **3c** and **4a** in the solid state: Structural models for the cations in **1b**, **2a**, **2c**, **3a**, **3b**, **4b** and **4c** as well as a list of selected parameters (bond lengths and angles) for all compounds are summarized in the Supporting Information.

(Figure 1). The central core in **1a**–**1b**, **2a**–**2c**, **3a**-**3c** and **4a**–**4c** consists of an [**E-P**-R]$^+$ chain (E = P, As, Sb) which is coordinated to two {CpMo(CO)$_2$} units. The interpnictogen bonds E–P (**1a**: 2.080(1) Å, **1b**: 2.196(2) Å, **2a**: 2.083(1) Å, **2b**: 2.196(1) Å, **2c**: 2.379(2) Å, **3a**: 2.091(2) Å, **3b**: 2.209(1) Å, **3c**: 2.406(1) Å, **4a**: 2.105(2) Å, **4b**: 2.223(1) Å, **4c**: 2.426(1) Å) do not deviate significantly from the reported starting materials (**A**: 2.079(2) Å,[23] **B**: 2.232(2) Å,[24] **C**: 2.470(2) Å[24]) or related compounds[22,25] indicating that the bond formation occurs almost exclusively via the lone-pair of the P atom. The bond lengths of the newly formed P–C bonds in **1a** (1.829(3) Å), **1b** (1.821(4) Å) as well as in **2a**–**2c** (1.807(5)-1.824(4) Å) are in the range of single bonds (1.86 Å),[26] whereas those in **3a**–**3c** are slightly elongated (1.932(2)-1.940(2) Å) presumably due to the steric demand of the [Ph$_3$C]$^+$ substituent. As expected, the P–Sn bond lengths of compounds **4a**–**4c** (2.541(1)-2.562(1) Å) are within the range of a P–Sn single bond (2.51 Å) as well.[26] To elaborate the behaviour of the obtained diazonium homologs in solution, NMR spectroscopic investigations were carried out. In general, the ^{31}P NMR chemical shifts within one cation (R = Mes, CH$_3$, CPh$_3$, SnMe$_3$) are comparably downfield shifted going from P to Sb, respectively. The ^{31}P{^{1}H} NMR spectra of compounds **1a** and **2a** reveal an AX spin system with a $^1J_{P-P}$ coupling constant of 484 Hz and 481 Hz for **1a** and **2a**, respectively. The corresponding ^{31}P NMR spectra display considerably broadened signals as a consequence of the unresolved $^2J_{P-H}$ coupling to the hydrogen atoms of the Mes or the Me substituent. The ^{31}P{^{1}H} NMR spectrum of **3a** shows two broad resonances at −133.3 ppm (P1) and 20.9 ppm (P2), sharpening upon cooling resulting in two doublets ($^1J_{P-P}$ = 490 Hz), proving the structural integrity of **3a** in solution (see Supporting Information). In contrast, **4a** reveals one singlet at −117.8 ppm in the ^{31}P NMR spectrum, probably due to the fast exchange of the Me$_3$Sn moiety between the two P atoms. This dynamic process could not be resolved even at −80 °C (see Supporting Information).

The compounds **1b**, **2b**, **2c**, **3b**, **3c**, **4b** and **4c** that bear only one P atom show a singlet in the respective ^{31}P NMR spectrum. The ^{119}Sn{^{1}H} NMR spectra for **4a–c** exhibit a broad signal at 185.1 ppm (**4a**), 174.8 ppm (**4b**) and 162.8 ppm (**4c**), respectively.

In order to estimate the reaction behavior towards nucleophiles, DFT calculations were performed on the model system **2a**. Although the frontier molecular orbitals of **2a** are relatively delocalized, the main contributions from the unsubstituted P atom are nevertheless easily identified (see Supporting Information). Furthermore, NBO analysis provides a clearer picture (Figure 2, NBO 103 and 107 correspond to the lowest unoccupied molecular orbitals of **2a**) and reveals the p(P) character within the P1-Mo bonds hinting towards a P1-centered reactivity (according to Figure 1) of **2a** towards nucleophiles (see below).

Thus, **2a** was chosen as model substrate for investigating its reactivity towards neutral nucleophiles. Reactions of **2a** with the N-heterocyclic carbenes (NHCs) IDipp[27] (1,3-bis-(2,6-diisopropylphenyl)imidazoline-2-ylidene), I^{i}Pr$_2$Me$_2$[28] (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) and IMe$_4$[28] (1,3,4,5-tetramethylimidazol-2-ylidene) as neutral nucleophiles were carried out. The reactions at −80 °C led to an immediate color change to yellow-brownish. The respective ^{31}P NMR spectra of the crude reaction products showed full conversion and revealed the formation of two isomers *sync*-[{CpMo(CO)$_2$}(μ,η$^{2:1}$-P(NHC)PMe){CpMo(CO)$_2$}][OTf] (**5a** (NHC=IDipp), **6a** (NHC = I^{i}Pr$_2$Me$_2$), **7a** (NHC = IMe$_4$)) and *gauche*-[{CpMo(CO)$_2$}(μ,η$^{2:1}$-P-(NHC)PMe){CpMo(CO)$_2$}][OTf] (**5b** (NHC = IDipp), **6b** (NHC = I^{i}Pr$_2$Me$_2$), **7b** (NHC = IMe$_4$)) isolated in moderate yields (51–
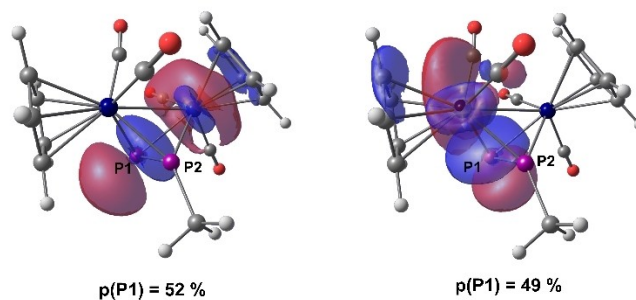

p(P1) = 52 %   p(P1) = 49 %

Figure 2. Natural bond orbitals (NBOs) 103 (left) and 107 (right) corresponding to the lowest unoccupied molecular orbitals within **2a** calculated at the wB97XD/def2tzvpp level of theory.

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67%), whose ratio depends on the steric bulk of the NHC used (Scheme 3a). The amount of the minor isomer *gauche*-[{CpMo(CO)$_2$}$_2$($\mu,\eta^{2:1}$-P(NHC)PMe){CpMo(CO)$_2$}] [OTf] (**5b** (NHC = IDipp), **6b** (NHC = I^{i}Pr$_2$Me$_2$), **7b** (NHC = IMe$_4$)) rises by decreasing the steric bulk of the NHC (see below). The ratio of the isomers determined by the integrals in the ^{31}P NMR spectrum (**5a/5b** 1/0.03; **6a/6b** 1/0.40; **7a/7b** 1/0.63) correlate with the buried volume of the respective NHC (see Supporting Information).[29] Attempts to influence the ratio of the isomers by changing the reaction conditions such as temperature (−80 °C to 60 °C) or reaction time (2 h to 7 days) were unsuccessful and resulted in the same isomer ratios. Interestingly, compounds **5–7** display new asymmetrically substituted diphosphenes stabilized by transition metal units.

In 2008, Robinson reported the synthesis of symmetrically substituted P$_2$ dumbbells containing different NHCs.[30] Only a few years later, Bertrand oxidized the same compound with [Fc][OTf] (Fc = ferrocenium).[31] Moreover, the groups of Macdonald and Weigand reported the generation of symmetrically substituted diphosphenes coordinated to transition metal units.[32] Besides these examples of symmetrically substituted derivatives, the only asymmetrically substituted diphosphenes reported so far were synthesized by Grützmacher and Weigand et al. independently.[33] To the best of our knowledge, diphosphenes bearing at least one alkyl substituent as in **5–7** are not known to date. Compounds **5a** and **6a** crystallize from concentrated solutions in *o*-DFB or THF layered with *n*-hexane or *n*-pentane, whereas, for **7a**, a counterion exchange with [TEF]$^-$ is needed in order to obtain good quality single crystals. Compounds **5a–7a** (Scheme 3b and 3c) reveal P-C^{Me} (1.817(2)-1.828(4) Å) and P-C^{NHC} (1.848(2)-1.868(2) Å) bond lengths which are within the range of P–C single bonds (1.81 Å).[26] Moreover, the P–P bond lengths (2.128(1)-2.134(1) Å) are slightly elon-
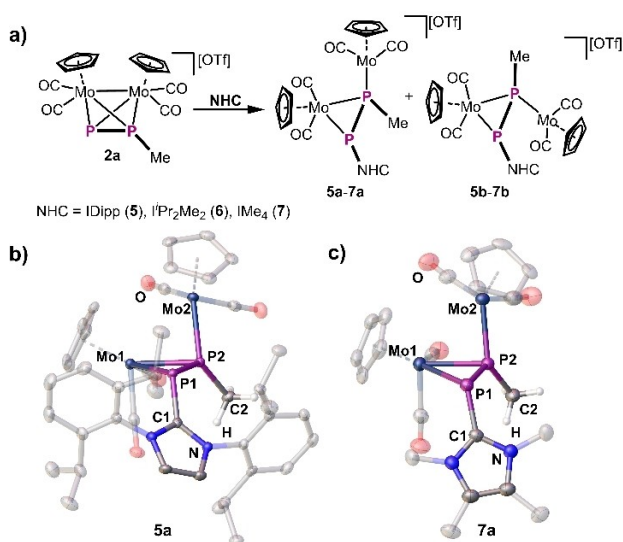
gated compared to **2a** (2.083(1) Å) and between P–P single and double bonds, but close to double bonds.[26] Interestingly, the solid-state structure of **5a** indicates a semi-bridging CO ligand. Indeed, in its ATR-IR spectrum, one of the CO stretches is slightly shifted to lower wavenumbers (ν(CO) = 1846 cm^{-1}). The ^{31}P{^{1}H} NMR spectra of **5–7** show two sets of doublets in the ranges of −120 to 100 ppm and 165 to 175 ppm with coupling constants between 499 Hz (**7**) and 548 Hz (**5**). In the ^{31}P NMR spectra, the lowfield shifted signals split additionally into a quartet due to the $^2J_{P-H}$ coupling to the CH$_3$ group. While single crystals of the minor isomers **5b**, **6b** and **7b** could not be obtained, DFT calculations show that they are present as *gauche*-isomers (with respect to the orientation of the Me group and the imidazolyl substituent around the central P–P bond, see Supporting Information). However, compared to the *sync*-isomers (**6a**: 34 kJ/mol, **7a**: 34 kJ/mol), these isomers are too high in energy to simply arise from the interconversion with the respective *sync*-isomers. ^{31}P NMR studies show that the two isomers, once formed, do not interconvert (see above). This strongly points towards kinetic reasons being responsible for the formation of these isomers within these nucleophilic functionalization reactions.

Conclusions

In summary, a general pathway for the synthesis of a broad library of diazonium homologs [{CpMo(CO)$_2$}$_2$($\mu,\eta^{2:2}$-EPR)][X] (E = P, As, Sb; R = Mes, Me, CPh$_3$, SnMe$_3$, [X]$^-$ = [OTf]$^-$, [BArF$_{20}$]$^-$, [BArF$_{24}$]$^-$) (**1a–4c**) of the heavier group 15 elements was presented. The central structural motif of these novel compounds consists of an [E-P-R]$^+$ chain which arises from the formal addition of the respective group 14 electrophile to the phosphorus lone pair, stabilized by two 15 VE [CpMo(CO)$_2$] units and thus can formally be considered as heavier diazonium analogs. The influence of the pnictogen atoms and the respective electrophiles was studied to reveal a dynamic behavior in solution for [CPh$_3$]$^+$ and [SnMe$_3$]$^+$. The fast exchange between the respective pnictogen atoms was monitored by variable temperature ^{31}P{^{1}H} NMR spectroscopy and is accompanied by P–R bond elongation in the solid-state. An underlying NBO analysis elucidated the potential of the model substrate [{CpMo(CO)$_2$}$_2$($\mu,\eta^{2:2}$-P$_2$Me)][OTf] (**2a**) for further nucleophilic modifications. Indeed, upon reaction with NHCs, the unprecedented asymmetrically substituted diphosphenes **5a–7a** and **5b–7b** were accessible representing *sync* and *gauche* isomers, the ratio of which depends on the size of the respective carbene.

Scheme 3. a) Synthesis of cationic diphosphenes **5–7** starting from **2a**; **5**: IDipp, in *o*-DFB at r.t. for 30 min; **6**: I^{i}Pr$_2$Me$_2$, in THF at −80 °C for 1 h; **7**: IMe$_4$, in THF at −80 °C for 2 h; b) and c) Molecular structures of **5a** and **7a** in the solid state. Structural models for the cations in **6a** as well as a list of selected parameters (bond lengths and angles) for all compounds are summarized in the Supporting Information.

Supporting Information

Experimental procedures for the synthesis of all compounds, analytical data, quantum chemical calculations and X-ray crystallographic details are summarized in the Supporting Information. The authors have cited additional references within the Supporting Information (Ref. [34–49]).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

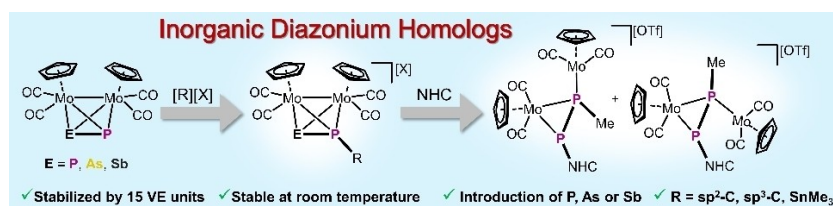The data that support the findings of this study are available in the supplementary material of this article.

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RESEARCH ARTICLE

Inorganic Diazonium Homologs

E = P, As, Sb

✓ Stabilized by 15 VE units   ✓ Stable at room temperature   ✓ Introduction of P, As or Sb   ✓ R = sp²-C, sp³-C, SnMe₃

Reactions of the mixed dipnictogen complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-PE})]$ (E=P, As, Sb) with carbon- and tin-based electrophiles led to the formation of novel [EPR]⁺ chains stabilized by two [CpMo(CO)₂] units, which can formally be considered as heavier diazonium homologs. Reactivity studies on these unique entities with different NHCs showed the formation of novel, asymmetrically substituted diphosphenes.

L. Zimmermann, C. Riesinger, Dr. G. Balázs, Prof. Dr. M. Scheer*

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Synthesis and Reactivity of Hetero-Pnictogen Diazonium Analogs Stabilized by Transition Metal Units