

Phosphine-Stabilized Pnictinidenes

Dominik Raiser,^[a] Klaus Eichele,^[a] Hartmut Schubert,^[a] and Lars Wesemann^{*[a]}

Abstract: The reaction of the intramolecular germylene-phosphine Lewis pair (*o*-PPh₂)C₆H₄GeAr* (1) with Group 15 element trichlorides ECl₃ (E=P, As, Sb) was investigated. After oxidative addition, the resulting compounds (*o*-PPh₂)C₆H₄(Ar*)Ge(E)Cl₂ (2: E=P, 3: E=As, 4: E=Sb) were reduced by using sodium metal or LiHBEt₃. The molecular structures of the phosphine-stabilized phosphinidene (*o*-PPh₂)C₆H₄(Ar*)Ge(Cl)P (5), arsinidene (*o*-PPh₂)C₆H₄(Ar*)Ge(Cl)As (6) and stibinidene (*o*-PPh₂)C₆H₄(Ar*)Ge(Cl)Sb (7) are presented; they feature a

two-coordinate low-valent Group 15 element. After chloride abstraction, a cyclic germaphosphene [(*o*-PPh₂)C₆H₄(Ar*)GeP][B(C₆H₃(CF₃)₂)₄] (8) was isolated. The ³¹P NMR data of the germaphosphene were compared with literature examples and analyzed by quantum chemical calculations. The phosphinidene was treated with [*i*Bu₂AlH]₂, and the product of an Al–H addition to the low-valent phosphorus atom (*o*-PPh₂)C₆H₄(Ar*)Ge(H)P(H)Al(C₄H₉)₂ (9) was characterized.

Introduction

The stabilization and chemistry of pnictogen-centered molecules which contain Group 15 elements with a low oxidation state and low coordination number has been an area of ongoing and considerable interest in chemical research for many decades.^[1] Due to their high reactivity phosphinidenes were investigated as Lewis base adducts^[1d,2] and coordinated at transition metals.^[3] In this context, phosphine adducts of phosphinidenes (phosphanylidene-σ⁴-phosphoranes) (A,^[4] B^[2] Figure 1) and carbene adducts of phosphinidenes^[2h] (C,^[2m] D,^[2k] E^[2j] Figure 1) are prominent derivatives featuring a broad chemistry.^[2h,i–n,5] In comparison to the extensively investigated chemistry of phosphinidenes studies on the higher homologues As^I (F,^[6] G,^[7] H,^[8] I^[9] Figure 1), Sb^I (J,^[10] K,^[11] L^[12] Figure 1) and Bi^I (M^[10,13]) are much less developed.^[14] A cyclic example of an arsanilidene-phosphorane F was obtained by a dehydrocoupling strategy.^[6] Chelating N,C ligands were also employed for stabilization of P^I, As^I, Sb^I and Bi^I species.^[15] The coordination chemistry of low-valent arsenic and antimony has been a very attractive field of research since their discovery.^[3b] Terminal as well as bridging coordination modes were found for a variety of transition metals.^[16]

We are currently investigating the chemistry of an intramolecular cyclic germylene-phosphine adduct 1.^[17] This low-valent germanium compound reacts through oxidative addition

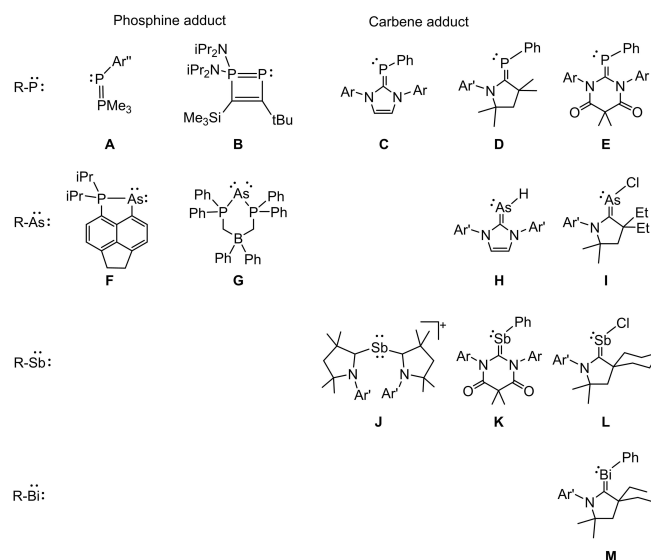


Figure 1. Selected pnictinidene molecules. (Ar=Mes, Ar'=Dipp, Ar''=2,6-Mes₂C₆H₃, Mes=2,4,6-trimethylphenyl).

with element halides of Groups 13 and 14: BX₃ (X=Cl, Br), PhBCl₂ and GeCl₂. After reduction of these addition products double bonds between Ge=B and Ge=Ge were characterized.^[17–18] In this manuscript we report on the addition of Group 15 halides PCl₃, AsCl₃ and SbCl₃ to the cyclic germylene-phosphine adduct. Furthermore, reduction of the oxidative addition products is presented.

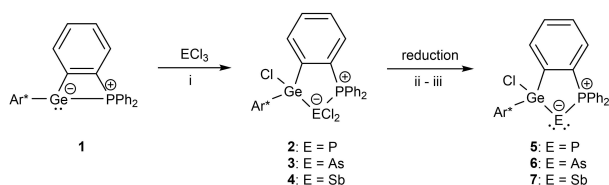
Results and Discussion

The germylene-phosphine adduct 1 was reacted in *n*-hexane with the element trichlorides of phosphorus, arsenic, and antimony (Scheme 1) to give the addition products 2–4 as colorless solids in good yield (2: 84%, 3: 86%, 4: 89%). In the case of BiCl₃ we were not able to isolate the reaction product.

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Scheme 1. Oxidative addition and reduction protocol. i) $-40\text{ }^{\circ}\text{C}$, *n*-hexane, PCl_3 (2), AsCl_3 (3), SbCl_3 (4); ii) 2 and 4, Na, RT, Et_2O /toluene; iii) 3, RT, THF, LiHBET_3 , $\text{Ar}^* = 2,6\text{-Tri}p_2\text{C}_6\text{H}_3$, $\text{Tri}p = 2,4,6\text{-triisopropylphenyl}$.

The chlorides 2–4 were characterized by elemental analysis, NMR spectroscopy and single crystal structure analysis. The molecular structure of the antimony dichloride 4 is presented in Figure 2. Details of the structure analyses and the molecular structures of 2 and 3 are presented in the Supporting Information. After oxidative addition of the trichlorides at the low-valent germanium atom the ECl_2 fragment reacts as an acceptor with the Ph_2P -phosphine moiety and forms a donor–acceptor interaction.

Compounds 2–4 exhibit a *trans* dichloride geometry with almost linear ECl_2 fragments. This type of donor–acceptor interaction and nearly linear ECl_2 geometry was presented for phosphorus, arsenic and antimony in peri-substituted acenaphthenes and P, C as well as P, P chelating ligands.^[6–7,14c,19] Selected distances found in 2, 3 and 4 are listed in Table 1. The P–Cl distances of 2.142(1) and 2.607(1) Å are short and very long in

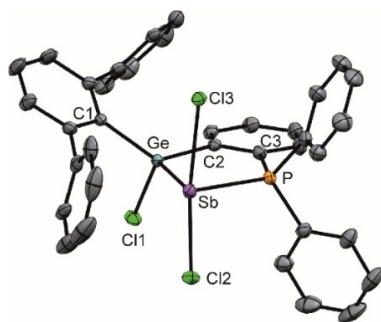


Figure 2. ORTEP of the molecular structure of 4. Ellipsoids are set at 50% probability. Hydrogen atoms and *iPr* groups are omitted for clarity. Compounds 2 and 3 show comparable molecular structures; their ORTEPs may be found in the Supporting Information.

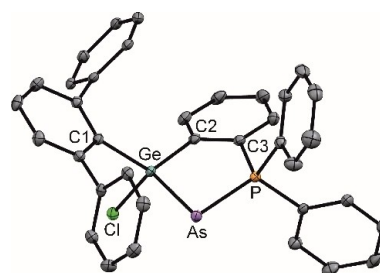


Figure 3. ORTEP of molecular structure of 6. Ellipsoids are set at 50% probability. Hydrogen atoms and *iPr* groups are omitted for clarity.

comparison to the values found in the literature for *trans* PCl_2 moieties [2.252(1)–2.501(1) Å].^[19a,c] The long distance points toward an ionic bond in compound 2. The P–P distance in the Cl_2P – PPH_2 moiety of 2.2225(8) Å is slightly shorter than bond lengths found in the literature for peri-substituted acenaphthene derivatives Cl_2P – PPr_2 [2.257(1) Å], Cl_2P – PPH_2 [2.268(2) Å].^[19a,c] The As–Cl and Sb–Cl as well as the E–P interatomic distances of 3 and 4 are comparable with values found for Cl_2E – PR_2 moieties exhibiting a seesaw geometry connected to phosphine donors (E=As, Sb).^[6–7,14c,19c,e] The Ge–E distances in molecules 2–4 are slightly shorter than comparable bond lengths of literature examples.^[20]

Reduction of compounds 2–4 was carried out using either sodium or a solution of LiHBET_3 in THF (Scheme 1). The germyl pnictinidenes 5–7 were isolated in moderate yield and analyzed by single crystal X-ray diffraction, elemental analyses, and NMR spectroscopy. The molecular structures of the arsinidene (6) and the stibinidene (7) are shown in Figures 3 and 4 and an ORTEP of the molecular structure of 5 may be found in the Supporting Information. The Ge–E bond lengths found in the reduction products 5–7 are shorter than the Ge–E bonds found in compounds 2–4 and are short for single bonds between the respective elements.^[20c,21] Furthermore, the E–P bond lengths of compounds 5–7 (Table 1) exhibit short interatomic distances of the reduced elements to phosphorus. The P–P distance in 5 of 2.103(1) Å can be compared with distances found in phosphine adducts of phosphinidenes N [2.1371(9), 2.1328(9) Å], P [2.148(5) Å] and Q [2.084(2) Å] (Figure 5)^[2f,o,4] and points toward partial double bond character.^[4,22] The ^{31}P NMR signal of the phosphinidene in 5 (Table 2, -244.3 ppm, $^1J_{\text{pp}} = 531$ Hz) was

Table 1. Selected interatomic distances [Å] and angles [deg] in compounds 2–7.

	E=P (2)	E=As (3)	E=Sb (4)	E=P (5)	E=As (6)	E=Sb (7)
Ge–E	2.346(1)	2.439(1)	2.614(1)	2.267(1)	2.361(1)	2.560(1)
E–P	2.223(1)	2.351(1)	2.577(1)	2.103(1)	2.369(1)	2.469(1)
E–Cl	2.142(1)	2.323(1)	2.504(1)		2.234(1)	
	2.607(1)	2.611(1)	2.652(1)		2.233(1)	
Cl–E–Cl	169.6(1)	167.5(1)	162.3(2)			
Ge–E–P	88.9(1)	76.8(2)	82.4(1)	90.1(2)	87.3(1)	82.2(1)
					87.2(1)	
Ge–E–Cl	67.2(1)	68.1(2)	68.0(1)			
	104.7(1)	102.3(2)	99.3(1)			

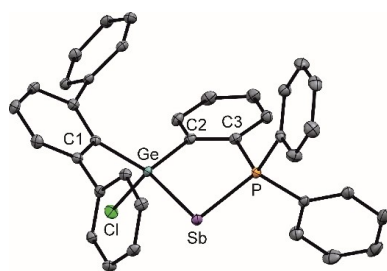


Figure 4. ORTEP of molecular structure of **7**. Ellipsoids are set at 50% probability. Hydrogen atoms and *iPr* groups are omitted for clarity.

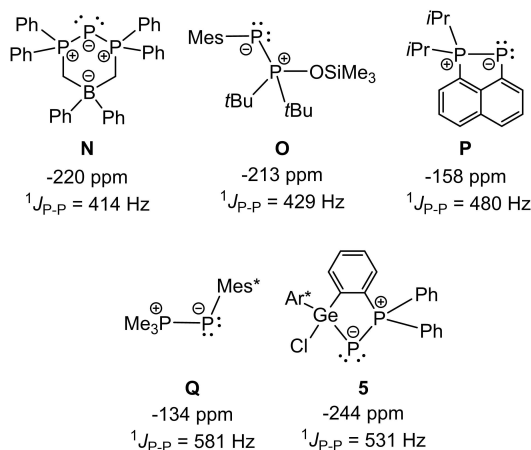


Figure 5. Selected phosphine adducts of phosphinidenes with ^{31}P NMR data of phosphinidene phosphorus. **N**,^[20] **O**,^[2d] **P**,^[2f] and **Q**^[23] (Mes = 2,4,6-Me₃C₆H₂, Mes* = 2,4,6-t-Bu₃C₆H₂).

	$\delta^{31}\text{P}(\text{PPh}_2)$	$\delta^{31}\text{P}(\text{P})$	$^1J_{\text{P} < \text{C} > \text{P}}$ (Hz)
2	54.7	-103.6	468.3
5	56.7	-244.3	531.0
8	56.9	-81.4	455.3

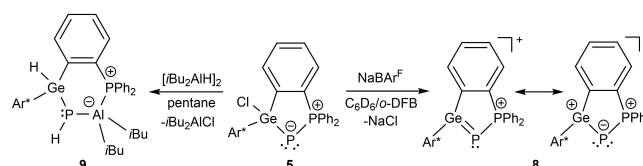
found at low frequencies indicating an ylid structure, with both lone pairs located at the phosphinidene phosphorus atom. In Figure 5 a selection of phosphinidenes exhibiting also a ^{31}P NMR signal at low frequencies is presented.

To analyze the P–P bond of **5** DFT calculations were carried out (see the Supporting Information for details).^[24] Based on a natural bond orbitals analysis (NBO),^[25] the phosphorus lone pairs of the phosphinidene phosphorus atom in **5** are localized on the P atom. Furthermore, the Wiberg bond index^[26] of the P–P bond of 1.1568 also points toward the ylid resonance structure of phosphinidene **5** (Figure 5, see the Supporting Information for NBOs).^[27]

In the case of the arsinidene the As–P bond length in **6** of 2.234(1) Å lies in the range of published phosphine adducts of arsinidenes [2.2082(5)–2.2710(7) Å].^[6–7,14a,21f,27] To the best of our knowledge, a phosphine adduct of a stibinidene has not been characterized by single crystal X-ray diffraction so far [Figure 5,

Table 1, 7 Sb–P 2.469(1) Å]. Tetrameric cations of type [(Me₃P)₄Sb₄]⁴⁺ exhibit slightly longer Sb–P bonds [2.552(2)–2.578(2) Å].^[28] Stabilized by transition metal coordination a stibinidene was characterized as a Ph₃P-adduct in [(Ph₃P)SbMe(W(CO)₅)₂] [Sb–P 2.594(6) Å].^[16a] Thus, with compound **7** a rare case for a phosphine adduct of a stibinidene was isolated.

The reduction products **5–7** were investigated toward chloride abstraction (Scheme 2). In all cases reactions with reagents like Na[B{C₆H₃–3,5-(CF₃)₂}]^[29] or Na[Al(OC(CF₃)₃)₄]^[30] have been carried out. Unfortunately, only in the case of the phosphorus compound **8** crystals suitable for X-ray diffraction were isolated. Based on ^{31}P NMR spectroscopy compounds **6** and **7** show formation of the desired cations upon reaction with the sodium salts of the WCA but the products could not be isolated. In Figure 6 an ORTEP of the cationic product of chloride abstraction is shown. The most striking feature in this molecular structure is the short Ge–P bond length of 2.163(2) Å, which is, together with the trigonal planar geometry around the Ge atom (sum of angles: 359.2°), a good indicator for a double bond between the Ge and P atoms. Examples for germaphosphenes were already published in the literature exhibiting a Ge=P bond length in the range of [2.138(3)–2.247(2) Å].^[15h,31] The electronic structure of **8** was also investigated using quantum chemical calculations (see the Supporting Information for details). The HOMO and LUMO of the cation of **8** are shown in the Supporting Information together with results of NRT (natural resonance theory)^[25] analysis. The Wiberg bond index of the Ge–P bond of 1.358 points toward a partial Ge–P double bond character in the cation of **8** (Scheme 2).



Scheme 2. Reactions of phosphinidene **5**: halide abstraction (right) and hydride substitution together with Al–H addition (left) (NaBAR^f = Na[B{C₆H₃–3,5-(CF₃)₂}]₄).

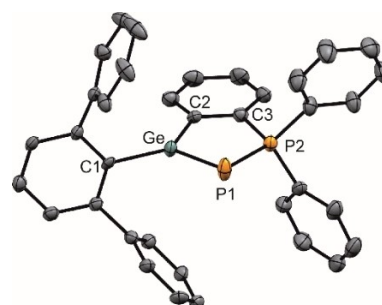


Figure 6. ORTEP of molecular structure of **8**. Ellipsoids are set at 50% probability. Hydrogen atoms and *iPr* groups are omitted for clarity. Interatomic distances [Å] and angles [deg]: Ge–P1 2.163(2), P1–P2 2.158(2), Ge–C1 1.921(5), Ge–C2 1.928(6), C1–Ge2–C2 117.6(2), C1–Ge–P1 132.5(2), C2–Ge–P1 109.1(2), Ge–P1–P2 88.3(1).

Whereas the phosphorus donor unit (Ph_2P) shows almost no change of the chemical shift upon transformation of **2** to **5** to **8** (Table 2), the Ge–P moiety of cationic germaphosphene **8** exhibits with a signal in the ^{31}P NMR spectrum at -81.4 ppm a shift of the Ge–P resonance in comparison to **5** of about 160 ppm to higher frequencies upon double bond formation. Remarkably, germaphosphenes synthesized by Sekiguchi and Escudié et al. exhibit ^{31}P NMR signals of the Ge=P unit at much higher frequencies: 416.3 ppm [$(t\text{Bu}_2\text{MeSi})_2\text{Ge}=\text{P}-\text{Mes}^*$ (**R**)]; 175 ppm [$[\text{Mes}_2\text{Ge}=\text{P}-\text{Mes}^*]$ ($\text{Mes}^* = 2,4,6-t\text{Bu}_3\text{C}_6\text{H}_2$)]^[31c] To rationalize the difference in the ^{31}P NMR chemical shift of **8** (-81.4 ppm) and **R** (416.3 ppm) quantum chemical calculations were carried out. Based on the optimized structures of the cation of **8** and germaphosphene **R'** (the optimized structure of **R'** from the original publication: [$(\text{Me}_3\text{Si})_2\text{Ge}=\text{P}-\text{Mes}$] ($\text{Mes} = 2,4,6-\text{Me}_3\text{C}_6\text{H}_2$ was used) the NMR shielding tensor for the respective phosphorus atoms was calculated using the ADF program package (see the Supporting Information for details).^[32] The calculated chemical shifts of the Ge–P phosphorus atoms in **8**: (P1 exp. -81.4 , calcd. -142 ppm, P2 exp. 56.9, calcd. 68.6 ppm) and **R'** (exp. 416.3, calcd. 370 ppm) exhibit for the phosphorus atoms of the Ge=P unit a relatively strong deviation from the experiment but the tendency of the chemical shift difference is convincing.^[32] On the other hand, the deviation between experiment and calculation for P2 in compound **8** of 12 ppm can be regarded as good agreement and an evaluation of the method. In the case of transition metal carbene complexes $[\text{M}=\text{C}]$ exhibiting high frequency ^{13}C NMR chemical shifts for the $\text{M}=\text{C}$ unit, the magnetic shielding tensor is dominated by the paramagnetic term.^[33] The largest paramagnetic contribution belongs to a magnetic dipole allowed coupling of the σ_{MC} and π_{MC}^* orbitals. With a small gap between these orbitals a large σ^{para} deshielding arises under the influence of the external magnetic field. Following the arguments published by Eisenstein et al.,^[33] the orientation of the principal components of the ^{31}P NMR magnetic shielding tensor of both molecules **8** and **R'** was analyzed using the results of the ADF calculations. In both molecules σ_{22} is close to parallel to the Ge–P bond and σ_{33} is directed perpendicular to the P–P–Ge (**8**) or C–P–Ge (**R'**) plane (see the Supporting Information). The direction of least shielding (σ_{11}) is located in-plane and perpendicular to the P–Ge bond. In this direction, the magnetic shielding exhibits a large difference between **R'** (-662 ppm) and **8** (225 ppm), switching from strong deshielding in **R'** to moderate shielding in **8**. The major deshielding contribution along this direction arises from the paramagnetic mixing between σ_{GeP} and π_{GeP}^* , which has a smaller gap in **R'** compared to **8**. In combination with increased shielding contributions to σ_{22} and σ_{33} in the cation **8**, the net result is a strongly deshielded phosphorus atom in **R'** in comparison to **8**.

To substitute the chloride substituent at the germanium atom of the phosphinidene-phosphorane **5** against a hydride addition of diisobutylaluminium hydride (Scheme 2) was carried out. However, compounds **6** and **7** have not been reacted with diisobutylaluminium hydride. Based on NMR spectroscopy and crystal structure analysis besides hydride substitution an addition of an aluminium hydride unit at the phosphinidene

phosphorus atom was observed (Figure 7). Because in reaction with half of an equivalent of $[\text{iBu}_2\text{AlH}]_2$ only mixtures were isolated, **5** was reacted with one equivalent of dimeric $[\text{iBu}_2\text{AlH}]_2$. A very small amount of colorless crystals of **9** were isolated from a hexane solution. However due to the high solubility of both compound **9** and the by-product iBu_2AlCl , the product was contaminated with the aluminium by-product. In the molecular structure of **9** two different Al–P bond lengths of 2.392(1) Å (HP–Al) and 2.503(1) Å (Al–PPh₂) were found. The longer bond is only slightly shorter than the Al–P bond length found in the adduct $\text{Me}_3\text{AlPPh}_3$ [2.535(1) Å] and the shorter bond is comparable with known Al–P single bonds.^[34] In the ^{27}Al NMR spectrum of **9** a broad signal [~ 4600 Hz] was found at 71.2 ppm which lies in the typical range of tetra coordinate aluminium compounds stabilized by phosphorus donor ligands.^[35] Two sets of signals in a ratio of 78:22 were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reflecting two diastereomers with respect to the *cis* and *trans* position of the Ge–H and P–H hydrogen atoms. Based on the $^1\text{H},^1\text{H}$ NOESY NMR spectra (Figures S31 and S32 in the Supporting Information) the major isomer was identified as the *cis* isomer. The signal for the Ph_2P unit of the major isomer was found at -18.1 ppm [minor isomer: -16.1 ppm] and the resonance of the P–H group at -282.9 ppm [minor isomer: -289.9 ppm]. These signals could be compared with ^{31}P NMR signals found for phosphanylaluminanes [$\text{Mes}^*(\text{Cl})\text{Al}-\text{P}(\text{H})\text{Mes}$ -133 ppm, $\text{Mes}^*\text{Al}(\text{P}(\text{H})\text{Mes})_2$ -120 ppm]^[34d] and adducts thereof [$\text{Bbp}(\text{Im}-\text{Me}_4)(\text{Br})\text{Al}-\text{P}(\text{H})\text{Mes}$ -157 ppm, $\text{Bbp}(\text{DBU})(\text{Br})\text{Al}-\text{P}(\text{H})\text{Mes}$ -152 ppm].^[34c] In the ^{31}P NMR spectrum of **9** for the P–H unit a doublet of doublets due to hydrogen coupling [$^1J_{\text{PH}} = 183.4$ Hz, $\text{GeH } ^3J_{\text{PH}} = 42.5$ Hz] was found (see the Supporting Information). For the minor isomer only coupling with the hydrogen atom at the phosphorus atom is resolved [$^1J_{\text{PH}} = 152.6$ Hz]. Based on $^{31}\text{P}\{^1\text{H}\}$ -EXSY NMR experiments slow exchange between the diastereomers of **9** was established. In the ^1H NMR spectrum the signal for the P–H unit was observed at -0.71 ppm ($^1J_{\text{PH}} = 152.3$ Hz) for the major isomer and at 0.10 ppm for the minor isomer. The signals of the

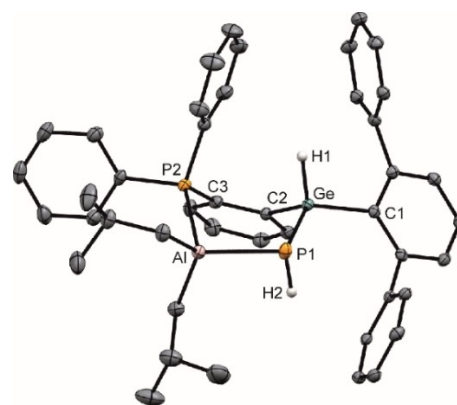


Figure 7. ORTEP of the molecular structure of **9**. Ellipsoids are set at 50% probability. Hydrogen atoms, except for PH and AlH and *i*Pr groups, are omitted for clarity. Interatomic distances [Å] and angles [deg]: Ge–C1 1.981(2), Ge–C2 1.985(2), Ge–P1 2.294(1), P1–Al 2.392(1), Al–P2 2.503(1), Ge–H1 1.39(2), P1–H2 1.26(3), C2–Ge–P1 114.3(1), Ge–P1–Al 100.3(1), P1–Al–P2 103.0(1), C3–P2–Al 106.8(1).

Ge–H unit for the two isomers were resolved at 4.29 ppm (major isomer, dd, $^2J_{\text{PH}}$ 44.4 Hz, $^3J_{\text{HH}}$ 11.6 Hz) and 4.20 ppm (minor isomer, t, $J=6.7$ Hz).

Conclusion

In a sequence of oxidative addition followed by reduction, a germylene-phosphine Lewis pair was treated with trichlorides of phosphorus, arsenic, and antimony. A phosphinidene, an arsinidene, and a stibinidene were stabilized in a germylene-phosphine chelating ligand and structurally characterized. After halide abstraction, a germaphosphene was isolated, and the ^{31}P NMR data of the germaphosphene were analyzed by using quantum chemical calculations. The product of an Al–H addition was found upon reaction of the phosphinidene with $[\text{iBu}_2\text{AlH}]_2$.

Experimental Section

All manipulations were carried out under argon by using standard Schlenk techniques or an MBraun Glovebox. Benzene, toluene, and tetrahydrofuran were distilled from sodium. Hexane and pentane were obtained from a MBRAUN solvent purification system and degassed by three times freeze pump thaw. $[\text{D}_6]$ benzene, $[\text{D}_6]$ toluene, and $[\text{D}_8]$ tetrahydrofuran were distilled from sodium and stored over molecular sieves. Terphenyl-Ge^{II} chloride (Ar^*GeCl) and **1** were prepared according to literature procedures.^[17–18,36] Furthermore, chemicals were purchased commercially and used as received. Elemental analysis was performed at the Institut für Anorganische Chemie, Universität Tübingen using a Vario MICRO EL analyser.

NMR spectra were recorded with either a Bruker Avance III HD 300 NanoBay spectrometer equipped with a 5 mm BBFO probe head and operating at 300.13 (^1H), 75.47 (^{13}C), 121.49 (^{31}P) and 96.29 (^{11}B) MHz, a Bruker Avancell+400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head and operating at 400.13 (^1H), 100.62 (^{13}C), 161.97 (^{31}P) MHz, a Bruker AVII+500 NMR spectrometer with a variable temperature set up and a 5 mm TBO probe head and operating at 500.13 (^1H), 125.76 (^{13}C), 202.47 (^{31}P) and 160.46 (^{11}B) MHz, a Bruker Avance III HDX 600 NMR spectrometer with a 5 mm Prodigy BBO cryo probe head operating at 600.13 (^1H), 150.90 (^{13}C), 242.94 (^{31}P) and 192.55 (^{11}B) MHz or a Bruker Avance III HDX 700 NMR spectrometer with a 5 mm Prodigy TCI cryo probe head operating at 700.29 (^1H), 176.10 (^{13}C) MHz. Chemical shifts are reported in δ values in ppm relative to external standard TMS (^1H , ^{13}C), 85% aqueous H_3PO_4 (^{31}P) and referenced in most cases on the residual proton signal of the solvent C_6D_6 (^1H 7.15 ppm; ^{13}C 128.0 ppm). ^{31}P , ^{11}B , ^1H and ^{13}C -spectra in $[\text{D}_6]$ toluene, $[\text{D}_6]$ benzene, $[\text{D}_8]$ tetrahydrofuran were referenced to the chemical shift of the solvent ^2H resonance frequency and $\Xi=25.145020\%$ for ^{13}C , $\Xi=40.480742\%$ for ^{31}P , $\Xi=32.083974\%$ ^{11}B .^[37] The multiplicity of the signals is abbreviated as s=singlet, d=doublet, t=triplet, quint=quintet, sept=septet and m=multiplet or unresolved. The proton and carbon signals were assigned by detailed analysis of ^1H , $^{13}\text{C}\{^1\text{H}\}$ or $^{13}\text{C}\{^1\text{H}\}$ UDEFT, $^1\text{H},^1\text{H}$ COSY, $^1\text{H},^{13}\text{C}$ HSQC, $^1\text{H},^{13}\text{C}$ HMBC and $^{13}\text{C}\{^1\text{H}\}$ DEPT 135 spectra. Selected 1D NMR spectra of the compounds and mixtures can be found in the Supporting Information, along with NMR data of the new compounds.

X-ray data were collected with a Bruker Smart APEX II diffractometer with graphite-monochromated $\text{Mo}_{\text{K}\alpha}$ radiation or a Bruker

APEX II Duo diffractometer with a Mo μS microfocus tube and TRIUMPH monochromator. The programs used were Bruker's APEX2 v2011.8-0, including SADABS for absorption correction, SAINT for data reduction and SHELXS for structure solution, as well as the WinGX suite of programs version 1.70.01 or the GUI ShelXle, including SHELXL for structure refinement.^[38]

DFT calculations of **5** and **8** were carried out using ORCA^[24] and the ADF^[32] program package was used for shielding calculations of **8** and **R'**. The NBO7 software was used to obtain natural bond orbitals.^[25]

Synthesis of compound (o-PPh₂)C₆H₄(Ar*)Ge(Cl)PCl₂ (2). In a Schlenk tube, (o-PPh₂)C₆H₄GeAr* (**1**) (50.0 mg, 61.3 μmol , 1.00 equiv) was dissolved in *n*-hexane (5 mL) and PCl_3 (5.35 μL , 61.3 μmol , 1.00 equiv) was added by a cannula to the solution. After stirring for 2 h the clear orange reaction mixture turned to a yellow suspension. The colorless product **1** was isolated by filtration and washed with cold *n*-hexane (1 mL, -40°C). More product **2** was obtained by crystallization from the concentrated *n*-hexane solution at -40°C (48.8 mg, 51.2 μmol , 84%). Colorless single crystals suitable for X-ray crystallography were obtained by slow evaporation of *n*-hexane to a concentrated toluene solution at room temperature. Anal. calcd. (%) for $\text{C}_{54}\text{H}_{63}\text{Cl}_3\text{GeP}_3$: C 68.06, H 6.66; found: C 68.17, H 6.99.

Synthesis of compound (o-PPh₂)C₆H₄(Ar*)Ge(Cl)AsCl₂ (3). (o-PPh₂)C₆H₄GeAr* (**1**) (100.0 mg, 123 μmol , 1.00 equiv) was dissolved in *n*-hexane (5 mL), and the solution was cooled to -40°C . AsCl_3 (10.3 μL , 123 μmol , 1.00 equiv) was added to the solution and the reaction was stirred for 1 h at -40°C . All volatiles were removed in vacuo at -40°C and the remaining colorless product **3** was washed with cold (-40°C) *n*-pentane (0.5 mL). The product **3** was obtained as a colorless powder (105 mg, 105 μmol , 86%). Colorless single crystals of **3** suitable for X-ray crystallography were obtained from a concentrated toluene solution at -40°C . Anal. calcd. (%) for $\text{C}_{54}\text{H}_{63}\text{Cl}_3\text{GePAs}$: C 65.06; H 6.37; found: C 65.21, H 6.03.

Synthesis of compound (o-PPh₂)C₆H₄(Ar*)Ge(Cl)SbCl₂ (4). SbCl_3 (14.0 mg, 61.3 μmol , 1.00 equiv) was dissolved in Et_2O (2 mL) and solution of (o-PPh₂)C₆H₄GeAr* (**1**) (50.0 mg, 61.3 μmol , 1.00 equiv) in Et_2O (3 mL) was added at -40°C . The reaction mixture was slowly allowed to reach room temperature and after a total reaction time of 3 h all volatiles were removed *in vacuo*. The remaining colorless product **4** was washed with cold (-40°C) *n*-pentane (0.5 mL). The product **4** was obtained as a colorless powder (56.6 mg, 54.2 μmol , 89%). Colorless single crystals suitable for X-ray crystallography were obtained by slow evaporation of *n*-hexane to a concentrated toluene solution at room temperature. Anal. calcd. (%) for $\text{C}_{54}\text{H}_{63}\text{Cl}_3\text{GePSb}$: C 62.14, H 6.08; found: C 62.54, H 6.49.

Synthesis of compound (o-PPh₂)C₆H₄(Ar*)Ge(Cl)P (5). Na-Sand (5.31 mg, 231 μmol , 2.20 equiv) and **2** (100 mg, 105 μmol , 1.00 equiv) were stirred in toluene (5 mL) for up to 5 days. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and as soon as no educt **2** was detected all volatiles were removed *in vacuo*. Product **5** was extracted with cold (-40°C) *n*-pentane (3 mL) and after removal of the solvent in vacuo obtained as a yellow powder (49.7 mg, 56.3 μmol , 54%). Yellow single crystals of **5** suitable for X-ray crystallography were obtained from a concentrated *n*-pentane solution at -40°C . Anal. calcd. (%) for $\text{C}_{54}\text{H}_{63}\text{ClGeP}_2$: C 73.53, H 7.20; found (%) : C 73.76, H 7.06.

Synthesis of compound (o-PPh₂)C₆H₄(Ar*)Ge(Cl)As (6). To a solution of **3** (117 mg, 117 μmol , 1.00 equiv) in THF (2 mL) a 1 mol/L THF solution of LiEt_3H (235 μL , 235 μmol , 2.00 equiv) was added at room temperature. The reaction mixture turned immediately orange and formation of H_2 was visible. After filtration and removal of all volatiles in vacuo product **6** was obtained as an orange

powder (yield 66.0 mg, 71.3 μmol , 61 %). Yellow single crystals of **6** suitable for X-ray crystallography were obtained from a concentrated *n*-pentane solution at -40°C . Anal. calcd. (%) for $\text{C}_{54}\text{H}_{63}\text{Cl}_3\text{GePA}_5$: C 65.06; H 6.37; found: C 65.21, H 6.03.

Synthesis of compound (o-PPh₂)C₆H₄(Ar*)Ge(Cl)Sb (7). Na-Sand (4.51 mg, 196 μmol , 2.20 equiv) and **4** (93.0 mg, 89.1 μmol , 1.00 equiv) were stirred in toluene (3 mL) for up to 2 days. The reaction was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and as soon as no educt **4** was detected all volatiles were removed *in vacuo*. Product **7** was extracted with cold (-40°C) *n*-pentane (3 mL) and after removal of the solvent *in vacuo* obtained as an orange powder (48.2 mg, 49.5 μmol , 56 %). Orange single crystals of **7** suitable for X-ray crystallography were obtained from a concentrated *n*-pentane solution at -40°C . Anal. calcd. (%) for $\text{C}_{54}\text{H}_{63}\text{ClGePSb}$: C 66.66; H 6.53; found: C 66.61, H 6.64.

Synthesis of compound [(o-PPh₂)C₆H₄(Ar*)GeP]⁺ [B(C₆H₃(CF₃)₂)₄]⁻ (8). A Young NMR tube was charged with **5** (30.0 mg, 34.0 μmol , 1.00 equiv) and Na[B(C₆H₃(CF₃)₂)₄] (30.8 mg, 34.0 μmol , 1.00 equiv). C₆D₆ (0.3 mL) and 1,2-difluorbenzene (0.05 mL) were added. The yellow color of the solution intensified. Toluene (0.5 mL) was added to the solution and product **8** was obtained as yellow crystals at -40°C (21.0 mg, 12.3 μmol , 36 %). Yellow single crystals of **8** suitable for X-ray crystallography were obtained from a concentrated toluene solution at room temperature. Notably in toluene first separation of an oil is visible before crystals of **8** are formed. Anal. calcd. (%) for C₆₈H₇₅BF₂GeP₂: C 60.41, H 4.42; found (%): C 60.46, H 5.11.

Synthesis of compound (o-PPh₂)C₆H₄(Ar*)Ge(H)P(H)Al(C₄H₉)₂ (9). To a solution of **5** (20.0 mg, 22.7 μmol , 1.00 equiv) in C₆D₆ (0.4 mL) a 1 mol/L *n*-hexane solution of DIBAL-H (8.08 μL , 45.3 μmol , 2.00 equiv) was added at room temperature. The reaction mixture turned to a light yellow. All volatiles were removed *in vacuo* and the product **9** was crystallized from a concentrated *n*-pentane solution (3–5 drops) at -40°C (9.8 mg, 9.6 μmol , 42 %). Colorless crystals of **9** suitable for X-ray crystallography were obtained from a concentrated *n*-hexane solution (3–5 drops) at -40°C . Due to the high solubility of **9** washing of the crystals could not be performed and removal of DIBAL-Cl was not quantitative. But DIBAL-Cl was not found in the molecular structure of **9**. Anal. calcd. (%) for C₆₂H₈₃AlGeP⁺ DIBAL-Cl: C 72.07; H 8.37; found: C 72.10, H 8.43.

Deposition Numbers 2091902 (for **7**), 2091903 (for **8**), 2091904 (for **2**), 2091905 (for **6**), 2091906 (for **4**), 2091907 (for **5**), 2091908 (for **3**), and 2091926 (for **9**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

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