

$2\theta_{\max} = 41^\circ$, 57352 reflections collected, 11223 independent reflections ($R_{\text{int}} = 0.070$), 9132 observed reflections with $I > 2\sigma(I)$, 733 parameters, max residual electron density $0.78 \times 10^{-6} \text{ e}^- \text{ pm}^{-3}$, $R_1 = 0.055$, $wR_2 = 0.143$. Nb, Cu, Se, Cl, P refined anisotropically. **2**: monoclinic, space group $C2/c$ (no. 15), $Z = 4$, $T = 190 \text{ K}$, $a = 1806.3(4)$, $b = 1300.4(3)$, $c = 2209.4(4) \text{ pm}$, $\beta = 92.73(3)^\circ$, $V = 5183.8(18) \times 10^6 \text{ pm}^3$, $\mu(\text{MoK}\alpha) = 65.16 \text{ cm}^{-1}$, $2\theta_{\max} = 40^\circ$, 3536 reflections collected, 1654 independent reflections ($R_{\text{int}} = 0.103$), 1183 observed reflections with $I > 2\sigma(I)$, 139 parameters, max residual electron density $0.69 \times 10^{-6} \text{ e}^- \text{ pm}^{-3}$, $R_1 = 0.113$, $wR_2 = 0.256$. Nb, Cu, Se, P refined anisotropically. **3**: orthorhombic, space group $Pnma$ (no. 62), $Z = 4$, $T = 190 \text{ K}$, $a = 2092.5(4)$, $b = 3235.5(7)$, $c = 1228.9(3) \text{ pm}$, $V = 8320(3) \times 10^6 \text{ pm}^3$, $\mu(\text{MoK}\alpha) = 22.20 \text{ cm}^{-1}$, $2\theta_{\max} = 43^\circ$, 11702 reflections collected, 3621 independent reflections ($R_{\text{int}} = 0.035$), 3146 observed reflections with $I > 2\sigma(I)$, 278 parameters, max residual electron density $0.83 \times 10^{-6} \text{ e}^- \text{ pm}^{-3}$, $R_1 = 0.057$, $wR_2 = 0.153$. Nb, Cu, S, Cl, P refined anisotropically. **4**: triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, $T = 180 \text{ K}$, $a = 1348.9(8)$, $b = 1532.1(8)$, $c = 1782.7(9) \text{ pm}$, $\alpha = 104.33(3)$, $\beta = 105.41(3)$, $\gamma = 100.05(3)^\circ$, $V = 3325(3) \times 10^6 \text{ pm}^3$, $\mu(\text{MoK}\alpha) = 56.17 \text{ cm}^{-1}$, $2\theta_{\max} = 42^\circ$, 4338 reflections collected, 3629 independent reflections ($R_{\text{int}} = 0.082$), 3366 observed reflections with $I > 2\sigma(I)$, 352 parameters, max residual electron density $1.12 \times 10^{-6} \text{ e}^- \text{ pm}^{-3}$, $R_1 = 0.064$, $wR_2 = 0.169$. Nb, Cu, Te, Cl, P refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-165897–165900 (**1–4**, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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P_5X_2^+ ($\text{X} = \text{Br}, \text{I}$), a Phosphorus-Rich Binary P–X Cation with a C_{2v} -Symmetric P_5 Cage**

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Dedicated to Jack Passmore

Our knowledge on simple cations with a polyphosphorus skeleton is still very limited owing to the poor capability of the phosphorus atom to bear positive charge. With mass spectrometric methods naked polyphosphorus cations up to P_{89}^+ [1, 2] and binary P–X cations ($\text{X} = \text{halogen}$) were shown to exist in the gas phase.[3] Their structures have been elucidated by

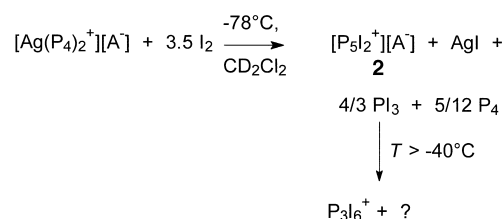
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quantum-chemical methods.[4, 5] In the solid state only the PX_4^+ ($\text{X} = \text{F} - \text{I}$)[6] and P_2I_5^+ ions[7, 8] are known—in contrast to numerous polyphosphorus(Zintl)-anion structures.[9] Classical weakly basic counteranions only led to decomposition.[10] Recently we reported on nonoxidizing, weakly coordinating anions of the type $\text{Al}(\text{OR})_4^-$ ($\text{OR} = \text{polyfluorinated aliphatic alkoxide}$).[11, 12] These anions stabilize binary Ag–P cations, such as D_{2h} -symmetric $\text{Ag}(\text{P}_4)_2^+$, **1**+. [13, 14] The reaction of $[\text{1}^+][\text{A}^-]$ ($\text{A}^- = \text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$) with X_2 ($\text{X} = \text{Br}, \text{I}$) provided evidence for the intermediate formation of the elusive P_5^+ ion but finally only led to the first subvalent binary P–X cation, the C_2 -symmetric P_3I_6^+ ion with a P_3 backbone.[15]

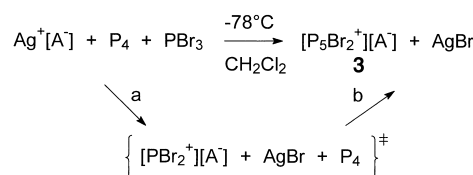
Herein we reinvestigate this reaction by using low-temperature in situ NMR spectroscopy: Reaction of $[\text{Ag}(\text{P}_4)_2^+][\text{A}^-]$ in CD_2Cl_2 with 3.5 equivalents of I_2 at -78°C revealed one major product in the in situ ^{31}P NMR spectrum at -78°C (see Supporting Information): $[\text{P}_5\text{I}_2^+][\text{A}^-]$ (**2**) (Scheme 1). A



Scheme 1. Reaction pathway for the formation and subsequent decomposition of the P_5I_2^+ ion.

scaled-up preparation verified these conclusions (mass balance, Raman spectrum of **2**, PI_3 and P_4 formation). The reaction mixture reacted according to Scheme 1 already at -40°C to give P_3I_6^+ and other yet unidentified species.[15] The formation and decomposition of P_5I_2^+ possibly proceed as follows: it is known that P_4 reacts with iodine to immediately give PI_3 (and only then to give P_2I_4).[16] The PI_3 reacted with the polarizing silver cation of $\text{Ag}^+[\text{A}^-]$ to give AgI and PI_2^+ . This “carbenoid”[5] cation inserted into one P–P bond of the P_4 tetrahedron leading to the formation of P_5I_2^+ . Upon warming the sample, the excess PI_3 and P_4 react to give P_2I_4 (Raman), which at about -40°C becomes slightly soluble and then reacts with P_5I_2^+ to form P_3I_6^+ and P_4 . The latter reaction in CH_2Cl_2 is exergonic by 26 kJ mol^{-1} (COSMO[17, 18] solvation model and MP2/TZVPP[26–29]).

To confirm the PI_2^+ insertion hypothesis, we reacted P_4 , PBr_3 , and $\text{Ag}^+[\text{A}^-]$ according to Scheme 2 at -78°C . Indeed, in situ ^{31}P NMR spectroscopy at -80°C showed that $[\text{P}_5\text{Br}_2^+][\text{A}^-]$ (**3**) was the only P-containing product visible after a reaction time of 10 days at this temperature. This confirms the insertion mechanism proposed in the steps a and



Scheme 2. Reaction pathway for the formation of the P_5Br_2^+ ion: The intermediate PBr_2^+ ion (a) inserts into the P–P bond of the P_4 cage (b).

b in Scheme 2, and is also in agreement with the MP2/TZVPP^[26–29] calculated free energy of this reaction in CH₂Cl₂ (COSMO^[17] model: $\Delta_r G(\text{step b, CH}_2\text{Cl}_2) = -111 \text{ kJ mol}^{-1}$).^[18] A scaled-up preparation gave temperature-, air-, and moisture-sensitive crystalline **3** in almost quantitative yield. However, solid **3** is stable for at least two months at -30°C . The structure of the C_{2v}-symmetric P₅ cage was deduced from the ³¹P NMR spectrum of the P₅X₂⁺ ions^[19–21] (X = Br, I; see Figure 1 for P₅Br₂⁺ spectrum).

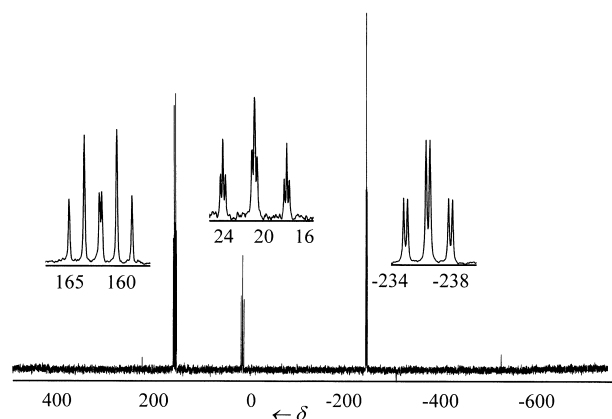


Figure 1. ³¹P NMR spectrum of **3** in CD₂Cl₂ at 203 K.

The P₅Br₂⁺ ion is rigid at 298 K according to the ³¹P NMR spectrum. The crystal structure determination^[22] of a colorless

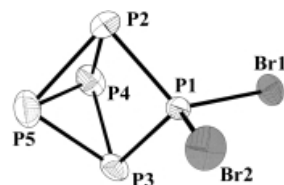


Figure 2. The structure of the P₅Br₂⁺ ion in **3** at 200 K (25% ellipsoids).

monoclinic block of **3** confirmed the presence of the almost C_{2v}-symmetric P₅Br₂⁺ ion (Figure 2) and the intact Al[OC(CF₃)₃]₄⁻ ion (see Supporting Information).^[23] This P₅ cage is unprecedented and is not found as part of the many polyphosphides or organopolyphosphanes known to

Table 1. Structural parameters of the P₅X₂⁺ ions (X = Br (**3**), I (**2**)).^[a]

Parameter	3 , Exp. ^[b]	3 , MP2 ^[c]	3 , MPW1PW91 ^[d]	2 , MP2 ^[c]
P–X	2.140(3)	2.163	2.164	2.383
P1–P2,3	2.156(7)	2.167	2.171	2.181
P2,3–P4,5	2.239(8)	2.259	2.239	2.254
P4–P5	2.211(8)	2.222	2.194	2.229
X–P–X	106.4(2)	105.8	106.1	108.5
P2,3–P1–X	114.7(3)	114.6	115.0	114.2
P2–P1–P3	91.4(3)	92.6	90.9	90.9
P4,5–P2,3–P1	83.0(3)	82.0	83.1	83.1

[a] Distances in Å, bond angles in °. [b] Salt **3** averaged according to C_{2v} symmetry. [c] TZVPP basis set. [d] 6-311G(2df) basis set.

date.^[24, 25] The P–P bond lengths in the P₅Br₂⁺ ion (2.150(7)–2.262(8) Å) are close to the values found in P₄ (2.21 Å) or Ag(P₄)₂⁺ (2.15–2.32 Å),^[13] and the P–Br distances lie in the normal range. Ab initio MP2/TZVPP^[26–29] and HF-DFT MPW1PW91/6-311G(2df)^[30–32] calculations reproduced the solid-state geometry of P₅Br₂⁺ within 0.024 Å and 1.2°. P₅Br₂⁺ is a true minimum at both levels of theory; calculated and experimental structural parameters are compared in Table 1. For comparison the P₅I₂⁺ geometry calculated at the MP2/TZVPP level of theory is also included.

The Mulliken (NBO) charges calculated at the HF-DFT level of theory show that the unipositive charge of the P₅Br₂⁺ ion is delocalized over the P₅ cage. A partial charge of +0.27 (+0.47) was assigned to P1, +0.16 (+0.15) to P2,3, and +0.14 (+0.13) to P4,5, while the more electronegative atoms Br1,2 remain nearly uncharged (+0.06 or –0.02, respectively). Raman spectroscopy showed that also the bulk material is pure **2** and **3**. Observed and calculated vibrational frequencies of **2** and **3** are collected^[30] in Table 2. A total of 10 (**2**) and 13 (**3**) of the 15 expected vibrational bands of the cations were observed and all bands of the P₅ cage are strongly mixed. The symmetric breathing mode of the P₅ cage (A₁, **2**: 541, **3**: 553 cm⁻¹) is slightly weakened compared to the A₁ mode of P₄ (600 cm⁻¹) but higher in energy than the P–P vibrations of red phosphorus (highest energy band at 461 cm⁻¹).^[33]

Table 2. Experimental and nonscaled calculated vibrational frequencies ν [s⁻¹] of **2** and **3**.

2 , ν_{exp} (Int. [%])	2 , ν_{calcd} ^[a]	Symmetry	3 , ν_{exp} (Int. [%])	3 , ν_{calcd} (Int. [%]) ^[b]	Symmetry	Assignment for 3
796 (21)			797 (34)			Al–O (cf. 798 for Ag(P ₄) ₂ [A]) ^[13]
745 (20)			747 (29)			Al–O (cf. 746 for Ag(P ₄) ₂ [A]) ^[13]
541 (32)	544	A ₁	553 (71)	571 (100)	A ₁	ν_s ; “breathing mode” of the P ₅ cage
within A ₁ at 541?	537	B ₁	534 (20)	557 (7)	B ₁	ν_{as} ; P2–P1–P3
502 (20)	505	A ₁	523 (51)	538 (27)	A ₁	ν_s ; P ₅ cage
within B ₁ at 448?	450	B ₂	504 (11)	486 (4)	B ₂	ν_{as} ; P2,3,1 and Br1,2
448 (10)	444	B ₁	443 (20)	465 (10)	B ₁	ν_{as} ; P2,3,4,5
385 (30)	390	B ₁	387 (31)	409 (35)	B ₂	ν_{as} ; P ₅ cage
359 (sh)	357	A ₂	375 (77)	383 (34)	A ₁	ν_s ; P2,3,4,5
354 (80)	350	A ₁	361 (37)	382 (17)	A ₂	ν_{as} ; P2,3,4,5
329 (70)	314	A ₁	331 (29)	344 (12)	A ₁	ν_s ; P ₅ cage
318 (sh)			321 (24)			anion (cf. 322 for Ag(P ₄) ₂ [A]) ^[13]
234 (4)			234 (8)			anion (cf. 234 for Ag(P ₄) ₂ [A]) ^[13]
under A ₁ at 168?	170	B ₁	203 (100)	203 (35)	A ₁	ν_s ; PBr ₂ unit
168 (100)	169	A ₁	191 (37)	191 (11)	B ₂	ν_{as} ; PBr ₂ unit
126 (4)	132	B ₂	150 (20)	148 (5)	B ₁	P2–P1–P3 bend
87 (4)	86	A ₁	120 (9)	115 (10)	A ₁	PBr ₂ bend
n.o. ^[c]	79	A ₂	n.b. ^[c]	84 (3)	A ₂	cage deformation
n.o. ^[c]	56	B ₁	n.b. ^[c]	60 (2)	B ₂	cage deformation

[a] MP2/TZVPP frequencies. [b] MPW1PW91/6-311G(2df) frequencies. [c] n.o. = Not observed.

The very weakly basic $\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$ ion stabilizes, in **1** and **2**, the first binary phosphorus-rich P–X cation (X = halogen, H, organyl) and shows that this class of cations is accessible if a suitable weakly basic and nonoxidizing counterion is provided. In the course of this reaction PX_2^+ ions (X = Br, I), which are isoelectronic to silylene SiX_2 and an interesting class of compounds in their own right, were formed as intermediates and may be used in further reactions with other simple inorganic or organic substrates.

Experimental Section

All manipulations were performed using grease-free Schlenk or dry box techniques and a dinitrogen or argon atmosphere. All apparatus were closed by Young valves and the solvents were rigorously dried over P_2O_5 and degassed prior to use and stored under N_2 on molecular sieves (4 Å). Yellow phosphorus was sublimed prior to use. Full details are disclosed in the Supporting Information.

In situ synthesis of **2**: $\text{Ag}(\text{P}_4)_2^+[\text{A}^-]$ (0.151 g, 0.114 mmol) was weighed into an NMR tube connected to a valve. I_2 (0.101 g, 0.399 mmol) was sublimed onto the solid at 77 K after which CD_2Cl_2 (0.9 mL) was condensed onto the mixture. The NMR tube was sealed and then placed in a dry ice/2-propanol bath and activated with ultrasound at -78°C for about 10 min. The initial ^{31}P NMR spectra were run 30 min later and the ^{13}C and ^{27}Al NMR spectra after storage at -80°C one week later (no decomposition visible in the ^{31}P NMR spectrum). ^{13}C NMR (63 MHz, CD_2Cl_2 , -90°C): $\delta = 122.4$ (q, $J(\text{C},\text{F}) = 290.1$ Hz; CF_3); ^{27}Al NMR (78 MHz, CD_2Cl_2 , -90°C): $\delta = 39.5$ (s, $\nu_{1/2} = 27$ Hz); ^{31}P NMR (101 MHz, CD_2Cl_2 , -90°C): $\delta = 168.2$ (dt, $^1J(\text{P}_2,3,\text{P}1) = 278.5$ Hz, $^1J(\text{P}_2,3, \text{P}4,5) = 152.6$ Hz, 2P), -89.0 (tt, $^1J(\text{P}1,\text{P}2,3) = 278.5$ Hz, $^2J(\text{P}1, \text{P}4,5) = 26.7$ Hz, 1P), -193.9 (td, $^1J(\text{P}4,5, \text{P}2,3) = 152.6$ Hz, $^2J(\text{P}4,5, \text{P}1) = 26.7$ Hz, 2P). Upon warming the sample to -40°C , the P_3I_2^+ signals vanish quickly and, apart from other unassigned signals of lower intensity, those of P_3I_6^+ appear as the major P-containing peaks ^{31}P NMR (-80°C): $\delta = 89.2$ (d, $^1J(\text{P},\text{P}) = 385.5$ Hz, 2P), -4.6 (t, $^1J(\text{P},\text{P}) = 385.5$ Hz, 1P).

Synthesis of **2**: $\text{Ag}(\text{P}_4)_2^+[\text{A}^-]$ (1.020 g, 0.765 mmol) was weighed into a two bulb vessel incorporating a sintered glass frit and stopped by Young valves. I_2 (0.697 g, 2.746 mmol) was sublimed onto the solid at 77 K after which CH_2Cl_2 (5 mL) was condensed onto the mixture. The apparatus was placed in a dry ice/2-propanol bath until the solvent had thawed and was then stored in a -80°C freezer and heavily shaken every 30 minutes for about one minute ($10 \times$). After four days at -80°C the yellow solution over yellow-orange precipitate was filtered at -80°C . All volatiles were then quickly removed at about 0°C (expected weight of the material: 1.717 g, found: 1.737 g) and the apparatus immediately transferred into a glove box. Soluble yellow **2** (0.963 g, 0.700 mmol), expected: 1.052 g; yield: 92%) and insoluble material (0.611 g; expected: 0.665 g) were isolated, while 0.140 g were not accessible within the flask (total: 0.963 g + 0.611 g + 0.140 g = 1.714 g; expected: 1.717 g). Raman spectra of **2** (Table 2) and the insoluble material (P_4 , PI_3 , and traces of P_2I_4) were recorded immediately after the sample preparation. A ^{31}P NMR sample of yellow **2** in CD_2Cl_2 gave the same spectrum as the one observed in the in situ reaction described above.

Synthesis of **3**: $\text{Ag}^+(\text{CH}_2\text{Cl}_2)[\text{A}^-]$ (0.848 g, 0.731 mmol) was weighed into a two-bulb glass vessel incorporating a fine sintered glass frit and two Young valves. P_4 (0.086 g, 0.694 mmol) was added to the solid. PBr_3 (0.188 g, 0.066 mL, 0.695 mmol) was added to it at 77 K and CH_2Cl_2 (ca. 10 mL) was condensed onto the mixture and allowed to stir at -78°C for 8 h. For completion of the reaction the vessel was stored in a -80°C freezer for 10 days and occasionally heavily shaken. After filtration from the insoluble AgBr a clear colorless solution was obtained. The volume of the solvent was quickly reduced to about 1 mL at 0°C . Salt **3** crystallized as colorless blocks almost quantitatively from the cooled concentrated filtrate (-30°C). Yield: 0.752 g (85%). ^{13}C NMR (63 MHz, CD_2Cl_2 , -70°C): $\delta = 121.5$ (q, $J(\text{C},\text{F}) = 292.0$ Hz; CF_3); ^{27}Al NMR (78 MHz, CD_2Cl_2 , -70°C): $\delta = 38.7$ (s, $\nu_{1/2} = 12$ Hz); ^{31}P NMR (101 MHz, CD_2Cl_2 , -80°C): $\delta = 162.0$ (dt, $^1J(\text{P}_2,3, \text{P}1) = 320.9$ Hz, $^1J(\text{P}_2,3, \text{P}4,5) = 148.7$ Hz, 2P), 20.0 (tt, $^1J(\text{P}1,$

$\text{P}2,3) = 320.9$ Hz, $^2J(\text{P}1, \text{P}4,5) = 25.8$ Hz, 1P), -237.1 (td, $^1J(\text{P}4,5, \text{P}2,3) = 148.7$ Hz, $^2J(\text{P}4,5, \text{P}1) = 25.8$ Hz, 2P).

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[22] Crystal structure determination of **3**: IPDS (Stoe), graphite-mono-chromated MoK_α radiation, $T = 200(2)$ K, unit cell determination: 5000 reflections, corrections: Lorentz, polarization, and numerical absorption correction, $\mu = 2.61 \text{ cm}^{-1}$, direct methods with SHELXS-97, refinement against F^2 with SHELXL-97. Space group: $P2/m$, $Z = 2$, $a = 13.536(3)$, $b = 9.554(2)$, $c = 14.508(3)$ Å, $\beta = 90.15(3)^\circ$, $V = 1876.2(6)$ Å³, $\rho_{\text{calcd}} = 2.269 \text{ g cm}^{-3}$, $2\theta_{\text{max}} = 52^\circ$, reflections: 14525 collected, 3469 unique, 2323 observed (4σ), 322 parameters, 48 SADI restraints (to fix the anion), $R_1 = 0.0957$, wR_2 (all data) = 0.2823, GooF = 1.082. Upon further cooling a phase transition occurred and all of the 10 tested crystals cracked even when cooled very slowly. Therefore, the rotation of the 12 CF_3 groups could not be frozen out and the agreement factor remained relatively high. Moreover the P_3Br_2^+ ion occupies two different positions with a 50% occupation each (see Supporting Information). Crystallographic data (excluding

structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167142. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

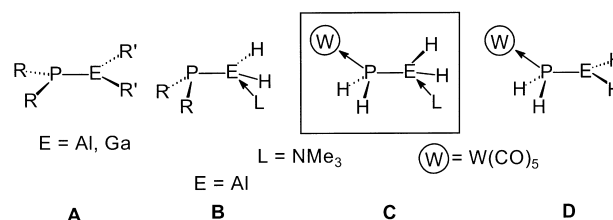
- [23] The solid-state arrangement of **3** is derived from a distorted CsCl packing in which the almost spherical $\text{Al}(\text{OR})_4^-$ ions form a cubic primitive lattice in which the cubic interstices are occupied by the P_3Br_2^+ ion.
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Lewis Acid/Base Stabilized Phosphanylalane and -gallane**

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*Dedicated to Professor Max Herberhold
in occasion of his 65th birthday*

Bulky substituents at the main group atoms are necessary for the synthesis of monomeric phosphanylalanes and -gallanes of the type **A**.^[1] In contrast to the strong π bonding in B–N, B–P, and B–As derivatives, only very weak π interactions combined with an increase of ionic bond con-



tributions is supposed for the heavier Group 13 elements.^[1] Thus, the lone pair of electrons at the heavier Group 15 element and the presence of an adjacent empty orbital at the Group 13 element leads to a head-to-tail dimerization or trimerization if the substituents are not sufficiently bulky. These compounds are mainly synthesized by salt elimination reactions;^[1] however, it was shown recently that the cleavage of cyclic oligomers $[\text{R}_2\text{PER}'_2]_n$ ($\text{E} = \text{P}, \text{As}$; $\text{R} = \text{Me}$; $\text{R}' = \text{SiMe}_3$; $n = 2, 3$) by a Lewis base, such as 4-(dimethylamino)pyridine (DMAP), leads to monomeric complexes.^[2] To our knowledge, the parent compounds $[\text{H}_2\text{E}(\text{PH}_2)]$ ($\text{E} = \text{Al}, \text{Ga}$) have not yet been synthesized or even detected in matrix isolation experiments,^[3a] but ab initio calculations have been carried out for both compounds.^[3, 4] It has been suggested that they play important roles in the formation of aluminum phosphide and gallium phosphide semiconductors starting from PH_3 and EH_3 , respectively, by chemical vapor deposition (CVD) processes.^[5] In 1993 Cowley and Jones reported the synthesis of monomeric base-stabilized phosphanyl- and arsanylalanes of type **B** by a metathetical reaction.^[6] In **B** the P atom still contains bulky mesityl substituents, whereas the AlH_2 moiety was stabilized by a Lewis base.

Our interest in this field concerns the synthesis of unsubstituted^[7] oligomers and polymers of mixed ligands of elements of Group 13 and 15. By using our general concept of the stabilization of unstable moieties by fixation of the phosphorus lone pair of electrons by metal carbonyl complexes,^[8] we report herein on the first synthesis of Lewis acid/base stabilized phosphanylalane and -gallane of type **C**.

According to our density functional theory (DFT) calculations^[9a] (Table 1), the additional coordination of a Lewis base, such as NMe_3 , at $[\text{H}_2\text{AlPH}_2]$ stabilizes the resulting adduct by 108 kJ mol^{-1} . The additional coordination of a Lewis acid such as $[\text{W}(\text{CO})_5]$ leads to a further increase of stabilization by 154 kJ mol^{-1} . On the other hand, if $[\text{H}_2\text{AlPH}_2]$ is only coordinated by the Lewis acid $[\text{W}(\text{CO})_5]$ (compound **D**) the stabilization energy is only -135 kJ mol^{-1} . $[\text{H}_2\text{AlPH}_2\{\text{W}(\text{CO})_5\}]$ (**D**) tends to display an intramolecular $(\text{O})\text{C}\cdots\text{Al}$ interaction that stabilizes the unsaturated Al center. Therefore, for steric as well as thermodynamic reasons, it seems to be essential for the molecule $[\text{H}_2\text{AlPH}_2]$ to possess both Lewis base and acid stabilization, as realized in a molecule of type **C**; the stabilization energy of -262 kJ mol^{-1} is higher than the dimerization energy of $[\text{H}_2\text{AlPH}_2]$ (-147 kJ mol^{-1} ; Table 1). Furthermore, it is interesting that the Gibbs energies of H_2 elimination reactions between unprotected AlH_3 and PH_3 [reaction (9)] and between their donor–acceptor complexes [reaction (7)] are similar and, therefore, the presence of the used protecting groups does not change the thermodynamics of the elimina-

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