Angewandte Chemie

DOI: 10.1002/anie.200901064

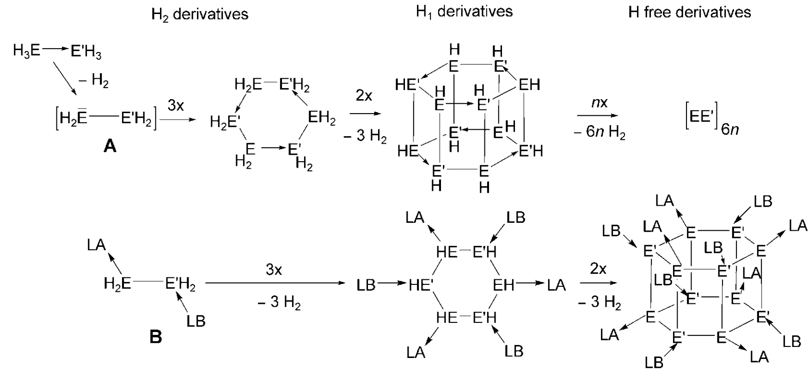
P–Al Compounds

Controlled Oligomerization of Lewis Acid/Base-Stabilized Phosphanylalanes**

*Michael Bodensteiner, Ulf Vogel, Alexey Y. Timoshkin, and Manfred Scheer**

Dedicated to Professor Michael Veith on the occasion of his 65th birthday

Compounds of Group 13/15 elements play an important role in the design of semiconducting materials and layers[1] as well as of unique inorganic polymers.[2] More recently N/B systems became of interest for hydrogen-storage purposes.[3] In contrast, the well-known P/B compounds[4,5] have not been considered for such objectives until Stephan et al. discovered the first reversible, metal-free hydrogen activation in such systems.[6] Furthermore, it has been found experimentally[7] and by theoretical calculations[8] that frustrated Lewis acid/base pairs of phosphanes (PR_3) and boranes (BR'_3) can be used for a concerted H_2 activation under mild conditions. What role can the parent compounds play in this context? Ammonia-borane $H_3N \rightarrow BH_3$ is an air and water stable adduct, which is, owing to its high hydrogen content, an interesting material for hydrogen storage.[9] In contrast, the parent pair of the heavier homologue, $H_3P \rightarrow BH_3$, is very labile even at low temperatures and dissociates.[10] However, Denis et al. described dehydrocondensation of both components (H_3P and BH_3) at higher temperatures (90 °C) catalyzed by $B(C_6F_5)_3$ to give a polymer of the presumed composition $[H_2P\text{-}BH_2]_n$.[11] It is ambiguous if a monomeric phosphinoborane is an intermediate of such a reaction (Scheme 1). On the other hand, a defined synthetic approach to compounds of the general formulae $H_2E\text{-}E'H_2$ (**A**) does not exist, even by matrix isolation techniques.[12]



Scheme 1. Schematic comparison of the H_2-elimination processes by a trimerization reaction starting from unprotected (not yet existing) as well as from Lewis acid/base-stabilized Group 13/15 compounds. E = P, As; E′ = B, Al, Ga; LA = Lewis acid, LB = Lewis base.

Recently we succeeded in the stabilization of these monomers by blocking the donor and acceptor positions by Lewis acids (LA) and Lewis bases (LB). In this way we have been able to synthesize the first stabilized parent compounds of the phosphanylalanes and phosphanylgallanes[13] as well as the corresponding arsanylboranes and phosphanylboranes.[14,15] Whereas arsanylboranes and phosphanylboranes of type **B** (Scheme 1) show no tendency to eliminate H_2, the phosphanylalanes and phosphanylgallanes loose H_2 extremely easily, for example by dissolving them in solvents more polar than hydrocarbons which results in mixtures of oligomers and polymers. In general, H_2 elimination processes of LA/LB-stabilized pentelyltrielanes **B** will always differ from those of unprotected (not yet existing) monomers **A** as Scheme 1 illustrates for a trimerization process. For unstabilized compounds **A**, the final product will probably be the binary Group 13/15 material and only the use of organic substituents at the Group 15 as well as the Group 13 elements can formally stop this process[16] as has been demonstrated for example, by the Driess group for CH_4 elimination reactions starting from ($i$$Pr_3Si$)$PH_2$ and Me_3Al.[17] Such organically substituted trimers[18] and hexagons[19] have also been obtained by synthetic routes other than H_2 eliminations. In contrast, because of the blocked donor/acceptor functions, the H_2 elimination of the LA/LB-stabilized pentelyltrielanes **B** (Scheme 1) would proceed through the exclusive formation of σ bonds[20] and no additional donor–acceptor bonds.[21] A following trimerization process gives the *cyclo*-trimer and subsequently the hexagonal prism as the entirely H-free final product (Scheme 1). This fundamentally different approach led to the challenge to control H_2 elimination in the LA/LB-stabilized pentelyltrielanes **B**. We now report that by tuning the reaction parameters such as temperature, solvent, con-

---

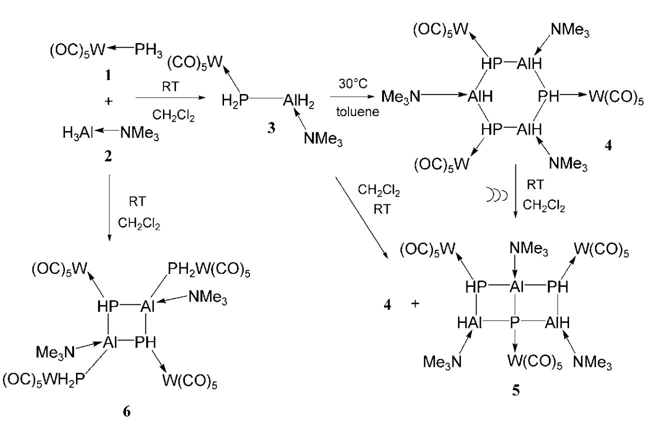
[*] M. Bodensteiner, Dr. U. Vogel, Prof. Dr. M. Scheer
Institut für Anorganische Chemie
Universität Regensburg, 93040 Regensburg (Germany)
Fax: (+49) 941-943-4439
E-mail: manfred.scheer@chemie.uni-regensburg.de
Dr. A. Y. Timoshkin
Department of Chemistry, St. Petersburg State University
University pr. 26, Old Peterhoff, 198504 Old Peterhoff,
St. Petersburg (Russia)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting information for this article (full experimental and spectroscopic data as well as the details of the DFT calculations) is available on the WWW under http://dx.doi.org/10.1002/anie.200901064.

centration, and catalysts, a straightforward synthesis to novel Group 13/15 oligomers is found. Thus, the first oligomers showing no additional donor–acceptor bonds within the framework are obtained.

In our initial synthetic approach for $[\{(CO)_5W\}H_2PAlH_2{\cdot}NMe_3]$ (**3**)[13] *n*-pentane was used as the solvent to stop the reaction between $[W(CO)_5PH_3]$ (**1**) and $H_3Al{\cdot}NMe_3$ (**2**). The pure product was obtained in yields of about 45 %. We have now found a high-yield synthesis of **3** (>80 %) by combining the starting materials in CH_2Cl_2 at room temperature. After the initial gas evolution ceases the solution must be quickly cooled to −28 °C to protect the product **3** from a subsequent H_2 elimination reaction. Dissolving **3** in toluene and stirring at 30 °C for one hour gives yellow crystals of the *cyclo*-trimer **4** as the only isolable product. Compound **4** is also formed by stirring **3** in CH_2Cl_2 at room temperature (Scheme 2). In this solvent additional dark yellow crystals of the ladder compound **5** are isolated as byproduct. To demonstrate that the *cyclo*-trimer **4** is a possible source of the ladder compound **5** by formal intramolecular H_2 elimination, **4** was treated with ultrasound in CH_2Cl_2. This approach resulted in a considerable conversion of the *cyclo*-trimer into the ladder derivative **5** (Scheme 2).



Scheme 2. Solvent-dependent reaction pathways of H_2 elimination (room temperature, ca. 22 °C).

Metal-catalyzed dehydrocoupling is a general method to obtain, for example, oligophosphanylboranes $[HRP\text{-}BH_2]_n$ ($n = 3$, 4; R = Ph) as Manners et al. have demonstrated.[22] For such P/B systems the active Rh^I catalysts usually work at elevated temperatures. Our initial attempts to introduce Rh^I catalysts for example, $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ (cod = cyclooctadiene) to oligomerize the monomers **B** of LA/LB-stabilized phosphanylalanes have been unsuccessful. For this class of compounds the H_2 elimination occurs at low to ambient temperatures at which the catalyst is still inactive. In contrast by using $[\{(cod)Rh(\mu\text{-}Cl)\}_2]$ as the catalyst at 30 °C in CH_2Cl_2, the reaction between the starting materials **1** and **2** results in **4** and **5**. Besides these products a third component is isolated in low yields, which is identified as **6**. A straightforward synthesis of this compound in moderate yields is achieved by using a 2:1 stoichiometry of **1** and **2** in CH_2Cl_2 (Scheme 2).

The products are characterized by mass spectrometry as well as by IR and Raman spectroscopy. Additionally, despite the low solubility, it was possible to record the ^1H and ^{31}P NMR spectra, in which all signals are found to be broad because of coupling to the ^{27}Al nucleus. The ^{31}P NMR spectrum of **4** shows three doublets, of which two overlap at $\delta = -328.5$ ($^1J(P,H) = 242$ Hz) and −328.2 ppm ($^1J(P,H) = 238$ Hz). The third signal occurs at $\delta = -317.4$ ppm ($^1J(P,H) = 223$ Hz). The ^{31}P NMR spectrum of **5** shows two doublets at $\delta = -289.4$ ($^1J(P,H) = 227$ Hz) and −267.6 ppm ($^1J(P,H) = 234$ Hz) for the phosphorus atoms carrying hydrogen substituents and a singlet at $\delta = -312.3$ ppm for the phosphorus atom bound to all three aluminum atoms. In the ^{31}P NMR spectrum of **6**, a triplet is observed at $\delta = -234.6$ ppm ($^1J(P,H) = 287$ Hz) for the exocyclic phosphorus atoms. Furthermore, a doublet is detected at $\delta = -287.6$ ppm ($^1J(P,H) = 229$ Hz) for the phosphorus atoms within the ring. The ^{31}P NMR signals are shifted upfield compared to coordinatively-bound compounds such as $Me_3Al{\leftarrow}P(H)(SiMe_3)_2$ ($\delta = -201.8$ ppm), and the P-H coupling constants in **4**–**6** are smaller than those reported for $Me_3Al{\leftarrow}P(H)(SiMe_3)_2$ (263 Hz).[23] Moreover, P-H functionalized frameworks of phosphanylalanes containing a mixture of donor–acceptor and σ bonds show a similar behavior with values in between, for example, for $[(R_2Al)_8(R'(H)P)_8]$ a chemical shift of $\delta = -242$ ppm and a P-H coupling constant of 256 is found.[24]

An X-ray structural analysis of **4** shows a distorted six-membered Al_3P_3 ring in boat conformation (Figure 1).[25] The atoms P1 and P2 are coordinated by $W(CO)_5$ units in an equatorial position and at P3 the $W(CO)_5$ unit is in an axial position. The amine bases at the atoms Al1 and Al2 adopt equatorial positions and at Al3 an axial position. Interestingly, for the parent compound, $Al_3P_3H_6$, the C_{3v} symmetric chair conformation is predicted to be about 16 kJ mol^{-1} more stable than the C_s symmetric boat conformer.[26] In contrast, the calculated energies for the isomers of **4** differ by less than 7 kJ mol^{-1}, with a structure corresponding to the experimentally observed conformer being the most stable.[27] The influence of the steric bulk of the LA and the LB dictates

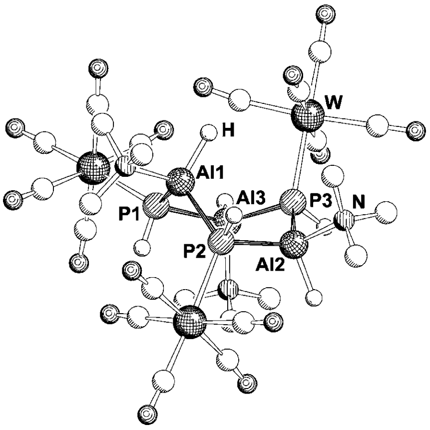


Figure 1. Molecular structure of **4** (hydrogen atoms at the methyl groups are omitted for clarity).[27]

which conformer of **4** is formed. All the bond angles in **4** within the ring are almost equal (110.60(6)-112.63(6)°) except for the Al1-P2-Al2 angle, which is compressed to 103.88(6)°. This fact is a consequence of the arrangement of the large $W(CO)_5$ units and leads to distortion of the ring.

Compound **4** is the first example of a LA/LB-stabilized phosphanylalane oligomer forming exclusive σ bonds[20,21] between the Group 15 and 13 elements. This fact is clearly revealed in the Al–P bond lengths (2.362(2)–2.383(2) Å) which are shorter than for example, in the comparable H-containing trimer $[\{Me_2AlP(H)Si\mathit{i}Pr_3\}_3]$ (2.453(2) Å)[17] in which additional donor–acceptor bonds are present. Consequently the Al–P bond lengths in **4** are in good agreement with a σ bond as in comparable monomers like for example, $[(Me_3Si)_2PAlMe_2{\cdot}dmap]$ (2.379(1) Å; dmap = 4-dimethylaminopyridine).[28] However, they are longer than those in $[(Mes^*AlPPh)_3]$ (2.323(3)–2.336(3) Å; Mes* = 2,4,6-tri(*tert*-butyl)phenyl) in which, in addition to the σ bond, a weak π interaction is expected.[29]

The X-ray structural analysis of **5** shows a distorted Al_3P_3 ladder core (Figure 2).[25] Unlike the *cyclo*-trimer **4**, the central atoms of **5**, Al3 and P2, bind to each other, which is a result of the H_2 elimination. Of 10 isomers considered for the ladder compound **5** the structure corresponding to the one found experimentally is the most stable; the maximal energy difference between the isomers is 29 kJ mol^{-1}.[27] For the parent (LA/LB-free) $Al_3P_3H_4$ ladder, the maximal difference between conformers is 25 kJ mol^{-1}, with the C_s symmetric structure with *cis*-orientation of P lone pairs being the most stable. The structures of the most stable parent (LA/LB-free) and LA/LB-stabilized ladder **5** do not match. Thus, the influence of the steric bulk of the LA and LB dictates which ladder conformer is formed as well.

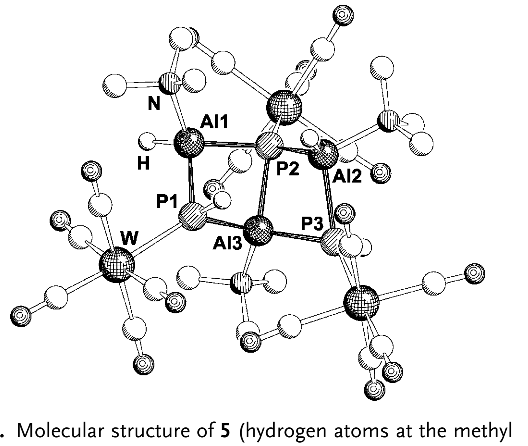


Figure 2. Molecular structure of **5** (hydrogen atoms at the methyl groups are omitted for clarity).[27]

The P–Al bond lengths of **5** (2.332(3)–2.394(3) Å) correspond to single bonds and are in good agreement with those in **4**. In contrast to the six-membered ring structure in **4** most of the angles are strongly bent to values below 100° (97.67(9)–76.83(8)°) as a result of the two four-membered ring substructures (Al1-P1-Al3-P2 and Al2-P2-Al3-P3). Other four membered Al_2P_2 rings such as $(Ph_2PAl\mathit{i}Bu_2)_2$,[30] also show small angles (Al-P-Al 93.8(1) and P-Al-P 86.2(1)°), but the differences within the corresponding ring systems are smaller owing to the longer Al–P bond lengths (2.475(1) Å) caused by the mixture of donor–acceptor and σ-bonding interactions. The range of bond lengths and angles are in good agreement with those reported for an eight-membered ladder compound $(ClAlPR)_4{\cdot}Et_2O$ (R = $Si\mathit{i}Pr_3$ and $SiMe\mathit{i}Pr_2$) (2.280(1)–2.427(1) Å and 78.51(5)–121.76°), but in this compound donor–acceptor bonding as well as the electron-withdrawing influence of the chlorine substituents is proposed.[31]

The X-ray structural analysis of **6** shows a planar Al_2P_2 four-membered ring with two additional exocyclic $\{(CO)_5W\}PH_2$ fragments at both the aluminum atoms (Figure 3).[25] The substituents at the ring have an all-*trans* configuration.

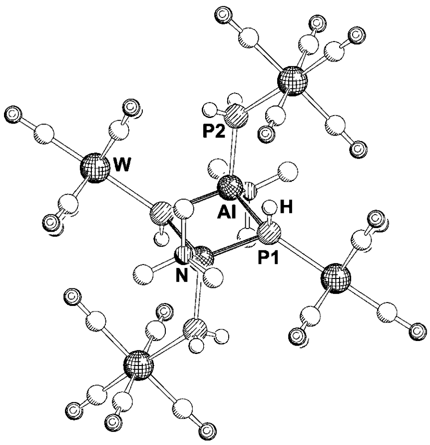
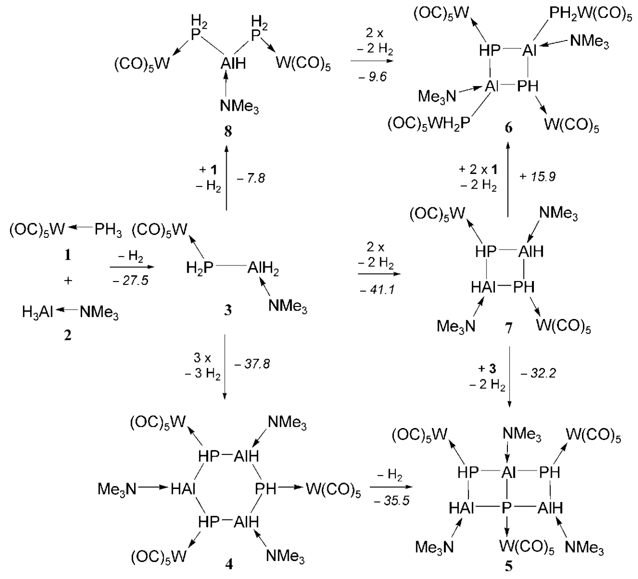


Figure 3. Molecular structure of **6** (hydrogen atoms at the methyl groups are omitted for clarity).[27]

The *endo*- and exocyclic Al–P bond lengths (2.368(6) and 2.375(5) Å) correspond to those in **4** and **5**. The angles within the ring (P-Al-P 98.86(17)°, Al-P-Al 81.14(17)°) are comparable to the four-membered ring substructures in **5**. Other Al_2P_2 rings, such as $[\{(Me_3Si)_2PAlMe_2\}_2]$, have angles closer to 90° (P-Al-P 89.4(3) and Al-P-Al 90.60(5)°) owing to longer Al–P bonds (2.460 Å) as a result of donor–acceptor bonding contributions.[32]

As mentioned above, the ladder compound **5** is formed together with the *cyclo*-trimer **4** from the monomer **3** in CH_2Cl_2. Experiments showed that direct H_2 elimination from **4** leads to **5**. Theoretical studies using density functional theory (DFT) calculations[33] for corresponding gas-phase reactions support this pathway with a Gibbs energy of $\Delta G^{\circ}_{298} = -35.5$ kJ mol^{-1} (Scheme 3). A second pathway for the formation of **5** is proposed in which two units of **3** form a four-membered ring $[(\{(CO)_5W\}HPAlH{\cdot}NMe_3)_2]$ (**7**) that adds a third molecule of **3** to give the ladder molecule **5**. The computations show the formation of the dimer **7** ($\Delta G^{\circ}_{298} = -41.1$ kJ mol^{-1}) is in thermodynamic competition with the generation of the trimerization product **4** ($\Delta G^{\circ}_{298} = -37.8$ kJ mol^{-1}). Intramolecular H_2 elimination of **4** to give **5** is only slightly more exergonic (-35.5 kJ mol^{-1}) than addition of the monomer **3** to the dimer **7** ($\Delta G^{\circ}_{298} =$



Scheme 3. Reaction pathways and calculated Gibb's energies [kJ mol^{-1}] of H_2 eliminations at B3LYP/6-31G*(ECP on W) level of theory.[33]

−32.2 kJ mol^{-1}). In fact, abortion of the reaction of **3** in CH_2Cl_2 to form **4** after a short reaction time led to ^{31}P NMR spectroscopic evidence for a possible intermediate **7**.[27] Yet, attempts to isolate **7** failed to date. Another question is the formation mechanism of the four-membered ring product **6**. Two pathways are possible (Scheme 3). Two equivalents of the PH_3 complex **1** could add to **7** resulting in **6**. Alternatively another molecule of **1** could add to the monomer **3** and the thus-formed compound [({(CO)$_5$W}PH$_2$)$_2$AlH·NMe$_3$] (**8**) gives **6** by subsequent H_2 elimination. As the computations show, the first path (**3**→**7**→**6**) includes the thermodynamically unfavorable step **7**→**6** ($\Delta G^{\circ}_{298} = +15.9$ kJ mol^{-1}), whereas the alternative pathway (**3**→**8**→**6**) includes only favorable steps: the formation of an intermediate **8** from **3** ($\Delta G^{\circ}_{298} = -7.8$ kJ mol^{-1}) with a subsequent dimerization of **8** under H_2 elimination to **6** ($\Delta G^{\circ}_{298} = -9.6$ kJ mol^{-1}). In agreement with these assumptions the ^{31}P NMR spectrum of the crude reaction mixture indicates a possible compound **8**.[27] Note also that decomposition of **3** with production of solid Al and **6** is also a thermodynamically allowed process that leads to the formation of **6**.[27]

The results presented show that Lewis acid/base-stabilized parent compounds of the phosphanylalanes can be synthesized in high yields. In comparison to unstabilized Group 13/15 compounds, this new class of Group 13/15 compounds undergoes a novel and fundamentally different dehydrogenation process. For the first time a controlled H_2 elimination is afforded by fine tuning the temperature and solvent conditions to obtain the *cyclo*-trimer **4**, from which a subsequent H_2 elimination is induced to produce the ladder compound **5**. Thus, the first compounds showing no additionally donor–acceptor bonds within the framework are synthesized. Comprehensive DFT calculations on different reaction pathways indicate the competition between the dimerization and trimerization reactions as well as the role of stoichiometry of the starting materials for the formation of the desired products.

Received: February 24, 2009

Keywords: aluminum · H_2 elimination · Lewis acids · Lewis bases · phosphorus

---

[1] a) R. A. Fischer, J. Weiß, *Angew. Chem.* **1999**, *111*, 3002–3022; *Angew. Chem. Int. Ed.* **1999**, *38*, 2830–2850; b) R. L. Wells, W. L. Gladfelter, *J. Cluster Sci.* **1997**, *8*, 217–238; c) J. D. Masuda, A. J. Hoshkin, T. W. Graham, C. Beddic, M. C. Fermin, N. Etkin, D. W. Stephan, *Chem. Eur. J.* **2006**, *12*, 8696–8707.

[2] a) A. Y. Timoshkin, *Coord. Chem. Rev.* **2005**, *249*, 2094–2131; b) B. Neumüller, E. Iravani, *Coord. Chem. Rev.* **2004**, *248*, 817–834; c) T. J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* **2006**, *12*, 8634–8648; d) A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem.* **2008**, *120*, 6308–6311; *Angew. Chem. Int. Ed.* **2008**, *47*, 6212–6215.

[3] a) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845; b) F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant, D. A. Dixon, *Angew. Chem.* **2007**, *119*, 760–763; *Angew. Chem. Int. Ed.* **2007**, *46*, 746–749; c) T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118; V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo, B. Rieger, *Angew. Chem.* **2008**, *120*, 6090–6092; *Angew. Chem. Int. Ed.* **2008**, *47*, 6001–6003.

[4] a) R. T. Paine, H. Nöth, *Chem. Rev.* **1995**, *95*, 343–379; b) H. Nöth, S. Staude, M. Thomann, R. T. Paine, *Chem. Ber.* **1993**, *126*, 611–618; c) T. Chen, J. Jackson, S. A. Jasper, E. N. Duesler, H. Nöth, R. T. Paine, *J. Organomet. Chem.* **1999**, *582*, 25–31; d) K. Knabel, T. M. Klapötke, H. Nöth, R. T. Paine, *Eur. J. Inorg. Chem.* **2005**, 1099–1108; e) K. Knabel, H. Nöth, R. T. Paine, *Z. Naturforsch. B* **2006**, *61*, 265–274.

[5] a) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463–3504; b) D. C. Pestana, P. P. Power, *J. Am. Chem. Soc.* **1991**, *113*, 8426–8437.

[6] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[7] a) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881; b) A. L. Kenward, W. E. Piers, *Angew. Chem.* **2008**, *120*, 38–42; *Angew. Chem. Int. Ed.* **2008**, *47*, 38–41.

[8] a) Y. Guo, S. Li, *Inorg. Chem.* **2008**, *47*, 6212–6219; b) T. A. Rokob, A. Hamza, A. Stirling, T. Soós, I. Pápai, *Angew. Chem.* **2008**, *120*, 2469–2472; *Angew. Chem. Int. Ed.* **2008**, *47*, 2435–2438.

[9] a) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626; b) W. J. Shaw, J. C. Linehan, N. K. Szymczak, D. J. Heldebrandt, C. Yonker, D. M. Camaioni, R. T. Baker, T. Autrey, *Angew. Chem.* **2008**, *120*, 7603–7606; *Angew. Chem. Int. Ed.* **2008**, *47*, 7493–7496.

[10] H. Schmidbaur, T. Wimmer, J. Lachmann, G. Müller, *Chem. Ber.* **1991**, *124*, 275–278.

[11] J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec, A.-C. Gaumonz, *Chem. Commun.* **2003**, 54–55.

[12] Only theoretical calculations give insight into the bonding situation of such monomers, see: a) T. L. Allen, W. H. Fink, *Inorg. Chem.* **1992**, *31*, 1703–1705; b) T. L. Allen, A. C. Scheiner, H. F. Schaefer III, *Inorg. Chem.* **1990**, *29*, 1930–1936; c) M. B. Coolidge, W. T. Borden, *J. Am. Chem. Soc.* **1990**, *112*, 1704–1706; d) H.-J. Himmel, *Dalton Trans.* **2003**, 3639–3649; e) H.-J. Himmel, *Eur. J. Inorg. Chem.* **2003**, 2153–2163.

[13] U. Vogel, A. Y. Timoshkin, M. Scheer, *Angew. Chem.* **2001**, *113*, 4541–4544; *Angew. Chem. Int. Ed.* **2001**, *40*, 4409–4412.

[14] U. Vogel, P. Hoemensch, K.-Ch. Schwan, A. Y. Timoshkin, M. Scheer, *Chem. Eur. J.* **2003**, *9*, 515–519.

[15] K.-Ch. Schwan, A. Y. Timoshkin, M. Zabel, M. Scheer, *Chem. Eur. J.* **2006**, *12*, 4900–4908.

[16] Reviews: a) S. Schulz, *Adv. Organomet. Chem.* **2003**, *49*, 225–317; b) B. Neumüller, E. Iravani, *Coord. Chem. Rev.* **2004**, *248*, 817–834.

[17] M. Driess, S. Kuntz, C. Monsé, K. Merz, *Chem. Eur. J.* **2000**, *6*, 4343–4347.

[18] a) J. F. Janik, E. N. Duesler, W. F. McNamara, M. Westerhausen, R. T. Paine, *Organometallics* **1989**, *8*, 506–514; b) K. Knabel, I. Krossing, H. Nöth, H. Schwenk-Kircher, M. Schmidt-Amelunxen, T. Seifert, *Eur. J. Inorg. Chem.* **1998**, 1095–1114; c) J. F. Janik, R. L. Wells, P. S. White, *Inorg. Chem.* **1998**, *37*, 3561–3566.

[19] C. von Hänisch, F. Weigend, *Z. Anorg. Allg. Chem.* **2002**, *628*, 389–393.

[20] In terms of two-center two-electron bonds in which one electron is coming from each bonding partner.

[21] Formally, σ bonds can also be formed by delivering two electrons from a lone pair into a vacant orbital in case of a donor–acceptor bond. However, this situation results in a greater diversity and complexity in the aggregations of Group 13/15 compounds.

[22] a) H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, I. Manners, *Angew. Chem.* **1999**, *111*, 3540–3543; *Angew. Chem. Int. Ed.* **1999**, *38*, 3321–3323; b) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678.

[23] L. K. Krannich, C. L. Watkins, S. J. Schauer, C. H. Lake, *Organometallics* **1996**, *15*, 3980–3984.

[24] C. von Hänisch, S. Stahl, *Angew. Chem.* **2006**, *118*, 2360–2363; *Angew. Chem. Int. Ed.* **2006**, *45*, 2302–2305.

[25] The crystal structure analysis for **6** is performed on a STOE-IPDS diffractometer using $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), whereas those for **4** and **5** are processed on an Oxford Diffraction Gemini R Ultra CCD diffractometer using $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). The structures are solved with the programs SIR-97[34] (**4**, **5**) and SHELXS-97[35a] (**6**); full-matrix-least-squares refinement on F^2 in SHELXL-97[35b] is performed with anisotropic displacements for all non-H atoms. Hydrogen atoms at the non-C atoms in **4** and **5** are located by difference Fourier syntheses and refined isotropically. The remaining ones are located in idealized positions and refined isotropically according to the riding model. **4**: $C_{24}H_{33}Al_3N_3O_{15}P_3W_3\cdot CH_2Cl_2$, $M_r = 1413.83$, crystal dimensions $0.12 \times 0.10 \times 0.07$ mm^3, monoclinic, space group $P2_1/n$ (No. 14), $a = 10.1237(1)$, $b = 22.2498(2)$, $c = 20.3792(2)$ Å, $\beta = 91.524(1)°$, $V = 4588.80(8)$ Å^3, $Z = 4$, $T = 123.0(1)$ K, $2\theta_{max} = 133.32°$, $\rho_{calcd} = 2.046$ g cm^{-3}, $\mu = 16.739$ mm^{-1}, 18307 reflections collected, 7767 unique reflections ($R_{int} = 0.0251$), 514 parameters, $R_1 = 0.0256$, $wR_2 = 0.0592$, residual electron density $-0.877/1.018$. **5**: $C_{24}H_{31}Al_3N_3O_{15}P_3W_3$, $M_r = 1326.89$, crystal dimensions $0.15 \times 0.10 \times 0.08$ mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 20.2444(3)$, $b = 9.7129(1)$, $c = 21.6887(3)$ Å, $\beta = 98.811(1)°$, $V = 4214.36(10)$ Å^3, $Z = 4$, $T = 123(1)$ K, $2\theta_{max} = 132.82°$, $\rho_{calcd} = 2.091$ g cm^{-3}, $\mu = 17.033$ mm^{-1}, 17243 reflections collected, 7105 unique reflections ($R_{int} = 0.0342$), 481 parameters, $R_1 = 0.0396$, $wR_2 = 0.0982$, residual electron density $-2.805/3.700$. **6**: $C_{26}H_{24}Al_2N_2O_{20}P_4W_4\cdot CH_2Cl_2$, $M_r = 1682.60$, crystal dimensions $0.30 \times 0.10 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.177(2)$, $b = 11.881(2)$, $c = 12.418(3)$ Å, $\alpha = 62.87(3)$, $\beta = 66.86(3)$, $\gamma = 87.02(3)°$, $V = 1333.1(7)$ Å^3, $Z = 1$, $T = 200(1)$ K, $2\theta_{max} = 51.92°$, $\rho_{calcd} = 2.096$ g cm^{-3}, $\mu = 8.917$ mm^{-1}, 9380 reflections collected, 4841 unique reflections ($R_{int} = 0.0355$), 283 parameters, $R_1 = 0.0397$, $wR_2 = 0.1062$, residual electron density $-1.606/1.930$. CCDC 720618 (**4**), 720619 (**5**) and 720620 (**6**) 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.

[26] A. Y. Timoshkin, G. Frenking, *Inorg. Chem.* **2003**, *42*, 60–69.

[27] See the Supporting Information.

[28] F. Thomas, S. Schulz, M. Nieger, *Eur. J. Inorg. Chem.* **2001**, 161–166.

[29] R. J. Wehmschulte, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 791–797.

[30] S. A. Sangokoya, W. T. Pennington, G. H. Robinson, D. C. Hrncir, *J. Organomet. Chem.* **1990**, *385*, 23–31.

[31] C. von Hänisch, F. Weigend, *Z. Anorg. Allg. Chem.* **2002**, *628*, 389–393.

[32] E. Hey-Hawkins, M. F. Lappert, J. L. Atwood, S. G. Bott, *J. Chem. Soc. Dalton Trans.* **1991**, 939–948.

[33] DFT calculations are performed by using the standard Gaussian 03 program suite (M. J. Frisch, et al. *Gaussian 03 (Revision D.01)*: Gaussian, Inc., Wallingford CT, **2004**) B3LYP functional (A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–793) is used together with standard 6-31G* basis set. Effective core potential basis set of Hay and Wadt (P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310) is used for W atoms. All structures are fully optimized and correspond to the minima on their respective potential energy surfaces.

[34] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[35] a) G. M. Sheldrick, *SHELXS-97*, Universität Göttingen, **1997**; b) G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, **1997**.