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$Al_4(P^tBu_2)_6$ − a Derivative of Al_4H_6 − and Other Al_4 Species: A Challenge for Bonding Interpretation between Zintl Ions and Metalloid Clusters

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Abstract: The highly energetic molecule Al_4H_6, with its distorted tetrahedral structure, was recently characterized via mass spectrometry and photoelectron spectroscopy investigations (Li, X.; et al. *Science* **2007**, *315*, 356). Here we present the preparation and structural investigation of the first analogous Al_4R_6 cluster compound. In order to understand the bonding in this kind of Al_4 molecule, density functional theory and second-order Møller−Plesset perturbation theory calculations were performed. The results obtained are discussed in comparison with bonding in other Al_4 moieties, especially the aromatic bonding behavior in the dianionic planar Al_4^{2-} species (Li, X.; et al. *Science* **2001**, *291*, 859). Finally, on the basis of the results obtained for Al_4 species, a more general problem is discussed: the difference in bonding between Zintl ions and metalloid clusters.

Introduction

Via mass spectrometry and photoelectron spectroscopy (PES) experiments, we have recently demonstrated that Al_4H_6 (**1**) is a stable molecule in the gas phase.[1,2] These experimental findings have been confirmed with the help of quantum-chemical calculations showing that this hydride may be described as a closo Wade-analogue species via $Al_4H_4^{2-}$ and subsequent addition of two protons. These results raised the question of whether it would be possible to synthesize on a preparative scale an Al_4R_6 species with an unusual average oxidation number of 1.5 for the aluminum atoms. As far as we know, there is hardly another example of a successful synthesis of a molecule or a substituted analogue of remarkable interest with respect to bonding that has previously been detected in the diluted gas phase. The C_{60} story may be the most exciting example,[3] but the gas-phase and solid-state investigations were not performed collaboratively.[4]

Here we describe such a new type of molecule, $Al_4R'_6$ ($R' = P^tBu_2$) (**2**), together with its analogues $Al_4R'_5X$ [X = Br (**2a**), Cl (**2b**)]. These results are compared with those for other Al_4-containing molecules, such as $Al_4Br_4 \cdot 4L$ ($L = NEt_3$) (**3**),[9−11] $Al_4Cp^*_4$ (**4**),[6,11−19] and the spectroscopically detected anion Al_4^{2-} (**5**).[20] This Al_4^{2-} species, which exhibits a prototypical bonding situation for the crystalline compound $Ga_4R''_4{}^{2-} \cdot 2Na(THF)^+$ ($R'' = Si^tBu_4$) (**6**),[21] has been carefully highlighted by Boldyrev and co-workers[20] with respect to its aromatic bonding as a planar four-membered-ring molecule.

Experimental Section

All of the reactions were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques. The compound LiP^tBu_2 was prepared from HP^tBu_2 and ^tBuLi in pentane.[22]

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Synthesis of $Al_4(P^tBu_2)_6$ (2). A 0.4 M solution of AlBr (10 mmol) in 3:1 toluene/Et_2O (25 mL) was warmed from 77 K to room temperature for 10 min. After the solution was cooled to −78 °C and stirred for 30 min, a suspension of LiP^tBu_2 (1.45 g, 10.3 mmol) in 20 mL of toluene was added dropwise. After the mixture was warmed to room temperature and the solvent removed in vacuo, a dark-brown pentane-soluble residue was obtained. The dark-brown solution was separated from solid LiBr. After a week, brown crystals of **2** were obtained in almost quantitative yield. NMR results: The ^1H and ^{31}P NMR spectra of **2** with broad signals at 1.54 and 39.9 ppm are caused by dynamic behavior.[23]

Synthesis of $Al_4Br(P^tBu_2)_5$ (2a). To a suspension of LiP^tBu_2 (0.77 g, 5.1 mmol) in 10 mL of toluene was added a 0.21 M solution of AlBr (4.2 mmol) in 3:1 toluene/Et_2O (20 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature under stirring. A dark-brown solution was obtained. Removal of the solvent in vacuo yielded a dark residue that was extracted with pentane, giving a dark-blue pentane solution. After 1 day, blue crystals of **2a** were obtained (∼400 mg, 0.123 mmol). $^{31}P\{^1H\}$ NMR (toluene-d_8, ppm): 43.2 (t), 41.8 (t), 35.3 (d), 33.4 (d), 32.3 (d), $^2J_{P-P} = 57$ Hz for all signals.

Synthesis of $Al_4Cl(P^tBu_2)_5$ (2b). A 0.39 M solution of AlCl (3.9 mmol) in 3:1 toluene/Et_2O (10 mL) was stored at 60 °C for 25 min and then added to solid LiP^tBu_2 (620 mg, 4.1 mmol). After the resulting mixture was stirred overnight, the solvent was removed in vacuo, and the residue was dissolved in pentane. After filtration, a few brown crystals of **2b** (120 mg, 0.13 mmol) were obtained out of pentane.

Synthesis of $Ga_3(P^tBu_2)_5$ (7). A 0.27 M solution of GaBr (2.7 mmol) in 4:1 toluene/THF (10 mL) was heated from −78 to −10 °C within 3 h. Afterward, LiP^tBu_2 (502.1 mg, 3.3 mmol) dissolved in 40 mL of toluene and 3 mL of THF was added to the GaBr solution. The solution was brought to room temperature, stirred for another 8 h, filtered, and stored under reduced pressure at 70 °C. The solvent was removed in vacuo, and the residue was dissolved in pentane. After 2 weeks at 7 °C, compound **7** crystallized from this pentane extract in the form of small yellow quadratic plates. When LiP^iPr_2 was used, the dimeric phosphorus-bridged species $Ga_6(P^iPr_2)_{10}$ (**8**) was obtained in the same way (Scheme 4).[24]

Quantum-Chemical Calculations. Quantum-chemical calculations were carried out with the TURBOMOLE program package. The model compounds were investigated with density functional theory (DFT) calculations (BP86[25,26]) and ab initio molecular orbital (MO) calculations (MP2[27,28]). The structure of each calculated compound was optimized in the highest possible point-group symmetry. Vibrational frequencies were calculated with AOFORCE[29] at the BP86/def-SV(P) and MP2/def-SV(P) levels to verify the nature of the obtained minima. Both the MP2 and DFT calculations were carried out within the resolution of identity (RI) approximation.[28] The orbital energy values were calculated at the MP2/def2-QZVPP level.[30] The programs MOLDEN (version 3.7)[31] and POV-Ray (version 3.6) were used to plot the structures of the orbitals.

Results

AlBr molecules generated at ∼1200 K were trapped together with a 3:1 toluene/Et_2O mixture at 77 K.[6,32] Annealing to ∼200 K produced a dark-brown solution that was metastable against disproportionation to solid Al and dissolved $AlBr_3$. Afterward, solid LiP^tBu_2 was added to the solution, which was subsequently allowed to reach room temperature. After removal of solid LiBr and evaporation of the solvent, a dark-blue solution in pentane was obtained, from which blue crystals of $Al_4Br(P^tBu_2)_5$ (**2a**) could be isolated. $Al_4Cl(P^tBu)_5$ (**2b**) was obtained in a similar way. In a slightly different procedure (using a longer reaction time in the original toluene/ether solution), the fully substituted $Al_4R'_6$ compound $Al_4(P^tBu_2)_6$ (**2**) was obtained from a dark-brown pentane solution. The results of X-ray structure analyses of **2**, **2a**, and **2b** [33,34] are presented in Figure 1 and collected in Table 1. In contrast to Al_4H_6 (**1**), which is only slightly distorted from a tetrahedral shape (the calculated lengths of the unbridged and H-bridged Al−Al bonds in **1** are 264 and 263 pm, respectively), **2** with its bulky substituents exhibits longer Al−Al bonds: 281 (nonbridging) and 312 pm (bridging). The unsymmetrically partially substituted species **2a** and **2b** are much more distorted, exhibiting shorter Al−Al bonds to those Al atoms

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(23) Ongoing experimental and theoretical investigations will be subject of a separate publication.

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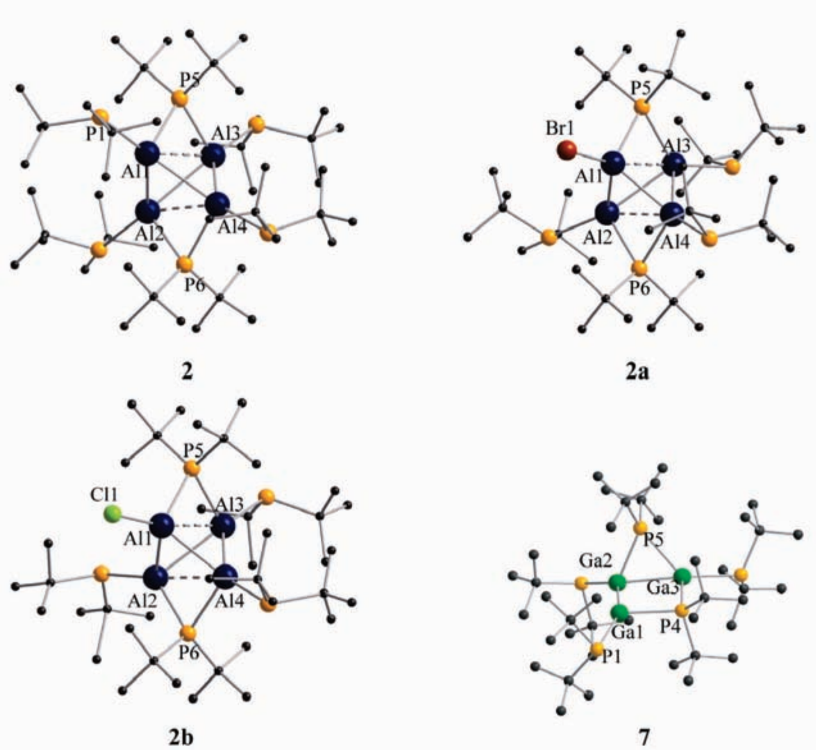
(33) Crystallographic data and refinement parameters for **2**: empirical formula, $C_{48}H_{108}Al_4P_6$; fw = 979.08; $T = 150(2)$ K; $\lambda = 0.71073$ Å; cryst syst, monoclinic; space group, $P2_1/c$; $a = 21.1040(14)$ Å, $b = 12.4808(8)$ Å, $c = 23.3842(15)$ Å, $\beta = 96.406(5)°$; $V = 6120.8(7)$ Å^3; $Z = 4$; $D_{calcd} = 1.062$ Mg/m^3; abs coeff = 0.261 mm^{-1}; $F(000) = 2152$; cryst size = 0.09 × 0.32 × 0.32 mm^3; θ range for data collection, 1.75 to 25.05°; index ranges, $-25 \le h \le 25, -14 \le k \le 14, -27 \le l \le 27$; reflns collected, 38587; independent reflns, 10760 ($R_{int} = 0.0779$); refinement method, full-matrix least-squares on F^2; data/restraints/params, 10760/0/554; GOF on $F^2 = 0.827$; R1 $[I > 2\sigma(I)] = 0.0386$, wR2 $[I > 2\sigma(I)] = 0.0746$; R1 (all data) = 0.0796, wR2 (all data) = 0.0828; max diff. peak/hole, 0.457/−0.371 e Å^{-3}. For **2a**: empirical formula, $C_{40}H_{90}Al_4BrP_5$; fw = 913.80; $T = 150(2)$ K; $\lambda = 0.71073$ Å; cryst syst, orthorhombic; space group, *Pbca*; $a = 11.8724(3)$ Å, $b = 22.19085)$ Å, $c = 39.4936(13)$ Å; $V = 10404.9(5)$ Å^3; $Z = 8$; $D_{calcd} = 1.167$ Mg/m^3; abs coeff = 1.037 mm^{-1}; $F(000) = 3936$; cryst size = 0.18 × 0.28 × 0.20 mm^3; θ range for data collection, 1.91 to 25.00°; index ranges, $-12 \le h \le 14, -26 \le k \le 23, -46 \le l \le 46$; reflns collected, 42929; independent reflns, 8840 ($R_{int} = 0.0641$); refinement method, full-matrix least-squares on F^2; data/restraints/params, 8840/0/437; GOF on $F^2 = 1.059$; R1 $[I > 2\sigma(I)] = 0.0447$, wR2 $[I > 2\sigma(I)] = 0.1093$; R1 (all data) = 0.0563, wR2 (all data) = 0.1163; max diff. peak/hole, 0.676/−0.720 e Å^{-3}. For **7**: empirical formula, $C_{40}H_{90}Ga_3P_5$; fw = 935.13; $T = 150(2)$ K; $\lambda = 0.71073$ Å; cryst syst, triclinic; space group, $P\bar{1}$; $a = 11.666(2)$ Å, $b = 12.902(3)$ Å, $c = 18.331(4)$ Å, $\alpha = 90.96(3)°$, $\beta = 106.39(3)°$, $\gamma = 99.60(3)°$; $V = 2604.0(9)$ Å^3; $Z = 2$; $D_{calcd} = 1.193$ Mg/m^3; abs coeff = 1.718 mm^{-1}; $F(000) = 996$; cryst size = 0.18 × 0.28 × 0.19 mm^3; θ range for data collection, 2.04 to 25.92°; index ranges, $-14 \le h \le 14, -15 \le k \le 15, -22 \le l \le 22$; reflns collected, 20582; independent reflns, 9424 ($R_{int} = 0.0456$); refinement method, full-matrix least-squares on F^2; data/restraints/params, 9424/0/433; GOF on $F^2 = 0.827$; R1 $[I > 2\sigma(I)] = 0.0321$, wR2 $[I > 2\sigma(I)] = 0.0681$; R1 (all data) = 0.0648, wR2 (all data) = 0.0743; max diff. peak/hole, 0.418/−0.533 e Å^{-3}. See: Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(34) The weak reflection intensity during the X-ray experiments on **2b** did not allow a proper structure determination. Therefore, only the following results are presented: space group, $P\bar{1}$; $a = 11.881$ Å, $b = 11.922$ Å, $c = 21.188$ Å, $\alpha = 83.18°$, $\beta = 84.28°$, $\gamma = 82.14°$; $V = 2941.1$ Å^3; $Z = 2$.



2 **2a** **2b** **7**

Figure 1. Structures of $Al_4(P^tBu_2)_6$ (**2**), $Al_4(P^tBu_2)_5Br$ (**2a**), $Al_4(P^tBu_2)_5Cl$ (**2b**), and $Ga_3(P^tBu_2)_5$ (**7**), with H atoms omitted. In **7**, d(Ga3−Ga2) = 2.5892 Å, d(Ga1−Ga2) = 2.5001 Å, d(Ga1−Ga3) = 3.4973(12) Å, and ∠(Ga3−P5−Ga2) = 62.671(10)°.

Table 1. Selected Distances and Angles in the Experimentally Detected and Calculated Structures of $Al_4(P^tBu_2)_6$ (**2**), $Al_4Br(P^tBu_2)_5$ (**2a**), and $Al_4Cl(P^tBu_2)_5$ (**2b**) Along with Calculated Structural Data for Al_4H_6 (**1**)[a]

	$Al_4(P^tBu_2)_6$ (**2**)		$Al_4Br(P^tBu_2)_5$ (**2a**)		$Al_4Cl(P^tBu_2)_5$ (**2b**)		Al_4H_6 (**1**)
	exptl	calcd (C_1)	exptl	calcd (C_1)	exptl[b]	calcd (C_1)	calcd (D_{2d})
			Distances (Å)				
Al1−Al2	2.7917(2)	2.874	2.6607(1)	2.691	2.68	2.688	2.642
Al1−Al3	3.1135(2)	3.176	2.9007(0)	2.957	2.94	2.950	2.628
Al1−Al4	2.8332(1)	2.872	2.6549(1)	2.698	2.65	2.691	2.642
Al2−Al3	2.8148(2)	2.873	2.7918(1)	2.853	2.79	2.849	2.642
Al2−Al4	3.1005(2)	3.177	3.0947(1)	3.172	3.11	3.173	2.642
Al3−Al4	2.8075(2)	2.875	2.7469(0)	2.819	2.79	2.819	2.628
Al1−X	–	–	2.3219(0)	2.357	2.16	2.189	–
Al1−H1	–	–	–	–	–	–	1.605
Al1−P1	2.4477(1)	2.505	–	–	–	–	–
Al1−P5	2.4109(1)	2.442	2.3765(0)	2.386	2.36	2.382	–
Al3−P5	2.4060(1)	2.441	2.4711(1)	2.474	2.43	2.475	–
Al1−H5	–	–	–	–	–	–	1.745
			Angles (deg)				
Al1−Al4−Al3	67.002(2)	67.089	64.931(1)	64.778	65.32	64.702	59.661
Al1−Al2−Al3	67.466(2)	67.090	64.229(1)	64.390	64.87	64.323	59.661
Al2−Al1−Al4	66.895(2)	67.121	71.208(1)	72.109	71.29	72.283	59.661
Al4−Al3−Al2	66.934(2)	67.097	67.930(1)	67.995	67.80	68.074	59.661
Al1−P5−Al3	80.536(2)	81.147	73.479(1)	74.944	75.66	74.792	–
Al2−P6−Al4	80.154(2)	81.178	80.113(1)	80.334	80.14	80.368	–
Al1−H5−Al3	–	–	–	–	–	–	97.832

[a] Calculated values were obtained at the bp86/def-sv(p) level of theory. The point-group symmetry used for each molecule is given in parentheses. [b] See ref 34.

that are directly connected to the halogen atoms. As expected for **2**, **2a**, and **2b**, the terminal Al−P bonds (240 pm) are slightly shorter than the bridging Al−P−Al bonds (246 pm).

Discussion

1. Formation. The formation of **2** with an oxidation number of 1.5 can formally be interpreted as a comproportionation reaction between Al_2R_4[35−37] and Al_2R_2[38] molecules; for each of these two species, examples in Al/Ga chemistry[12] have

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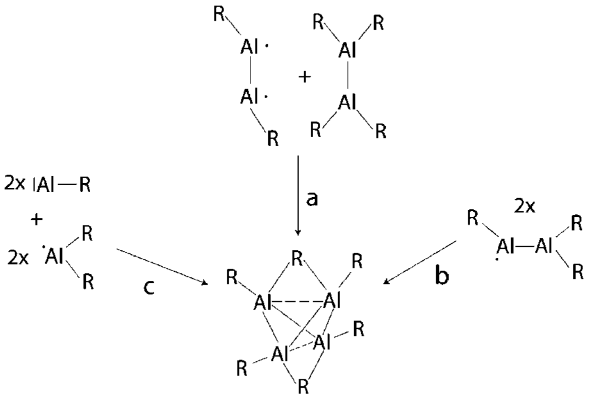
Scheme 1. Proposed Mechanisms for the Formation of **2** Based on Different Educts That Are Plausible on the Basis of Already Structurally Characterized Species



already been described (Scheme 1a). Instead of Al_2R_4 and Al_2R_2, the monomeric species AlR_2[39] and AlR[40] may be involved (Scheme 1c). However, more realistic is a reaction between two Al_2R_3 radicals,[36,41] each of which may be formed as the product of a reaction between AlR_2 and AlR molecules. It is likely that these Al_2R_3 radicals (Scheme 1b) may be present in the reaction solution during the disproportionation of AlR on the way to Al(s) and AlR_3, since the analogous Ga_2R_3 radical is already known in solution and as a crystalline compound.[36] Furthermore, an Al_2R_3 radical may be formed in solution by the removal of an R^- anion from the structurally determined radical anion $Al_2R_4^{-}$.[42−44] A further hint regarding reactions of radical species during this complex formation of **2** comes from the compound $Ga_3R'_5$ (**7**) ($R' = P^tBu_2$) (Figure 1).[45] From the above-mentioned arguments, one can conclude that compound **7** may be formed from the radical species Ga_2R_3[46] and GaR_2. However, the complete reaction from AlX (X = Cl, Br) solutions to the substituted cluster **2** is more complex, since besides the above-mentioned formation of Al−Al bonds, substitution reactions (X vs R) must also take place simultaneously (cf. **2a**, **2b**). To sum up, there are multiple plausible mechanisms based on already characterized species; however, to date there is no experimental evidence supporting one particular mechanism.

2. Bonding. The classical bonding of two Al_2R_3 radicals via one additional two-electron−two-center (2e2c) bond, resulting in three 2e2c bonds altogether, as shown in Scheme 1b, is not an adequate description of $Al_4R'_6$ molecules, since there are, with respect to the Al−Al distances, at least four nonbridged Al−Al bonds, i.e., in molecule **1** as well as in **2** (Figure 1), there are four nearly equal Al−Al bond lengths. Therefore, a more appropriate description of Al_4H_6 starts from the hypothetical species $Al_4H_4^{2-}$ (Scheme 2). This C_{2v}-shaped molecule (the Al_4 moiety is slightly distorted from planarity) with its four 2e2c Al−Al bonds and one occupied π orbital is energetically stabilized by 292.03 kJ mol^{-1} relative to the tetrahedral isomer. The relevant four orbitals for the Al−Al σ bonds are similar to those of planar (D_{4h}) Al_4^{2-},[47] which have a_{1g}, e_u, and b_{1g} symmetry (Figure 2).[20] The fifth orbital, representing the π bonding, has a_{2u} or a_1 symmetry for Al_4^{2-} or $Al_4H_4^{2-}$, respectively. If the Al_4^{2-} moiety is stabilized and electronically neutralized by two Li^+ cations, the result is a distorted octahedral molecule in which Al_4^{2-} units are still present.[20] In addition to this calculated structure of a naked Li_2Al_4 cluster, a crystalline compound also confirms this formation mechanism for the $Al_4H_4^{2-}$-analogous species $Ga_4R''_4{}^{2-}\cdot 2Na(THF)^+$ (**6**)[21] (see Scheme 4). In contrast, there is an additional but different stabilization if two H^+ ions approach an $Al_4H_4^{2-}$ moiety. A distortion via the diagonals of the square molecule results, generating Al_4H_6 as a D_{2d}-shaped molecule in which the H atoms are integrated into the bonding of the whole cluster (Figure 3).[1,2]

The high stability of Al_4H_6 is evident from the highly exothermic reaction of two H^+ with an $Al_4H_4^{2-}$ anion: even after subtraction of the Coulomb attractions, the value $\Delta E \approx -1500$ kJ mol^{-1} is obtained (Scheme 2). Altogether, 10 electrons in five MOs are responsible for the cluster bonding. There are two orbitals of lowest energy (a_1 at −12.288 eV and b_2 at −12.229 eV), which represent the Al−H−Al bridging bonds and the bonds within the H_2Al_4 framework (Figure 3). A small amount higher in energy is an a_1 orbital (at −11.343 eV) that stabilizes the Al_4 core. After a gap of ~3.1 eV come the two highest occupied orbitals (with e symmetry, at −8.238 eV), representing the four unbridged Al−Al bonds of the distorted tetrahedral Al_4 moiety. Therefore, as for Al_4^{2-} and $Al_4H_4^{2-}$, altogether there are five orbitals responsible for the bonding of the central H_2Al_4 core of the Al_4H_6 molecule.

In principle, analogous bonding is expected for $Al_4R'_6$ molecules. However, in the case of **2**, each of the R′ ligands is directly bonded to the Al_4 framework via a phosphorus atom, and therefore, special bridging Al−P−Al bonding can be expected. In order to make this similarity to bonding of Al_4H_6 more obvious, we looked at the model reaction of $Al_4H_4^{2-}$ with two PH_2^+ cations, each with one lone pair, to give $Al_4H_4(PH_2)_2$ (**2c**) (Figure 3, Scheme 2). For the whole **2c** molecule, there are, in contrast to Al_4H_6, two additional orbitals with four electrons involved. These e-symmetry orbitals (at −10.050 eV) are mainly bonding with respect to the Al−P−Al bridges. These orbitals separate the two highest MOs of e symmetry (at −7.803 eV) from the a_1 orbital (at −10.202 eV) that extends over the four Al atoms. The two lowest orbitals are, as expected, similar to those of the Al_4H_2 core of Al_4H_6 (b_2 at −12.450 eV and a_1 at −12.444 eV).

Therefore, altogether there are 10 electrons for the Al_4P_2 framework plus four additional bonding electrons from the two lone pairs of the PR_2^+ units. In contrast to the similarity of the MO schemes of Al_4H_6 and $Al_4H_4(PH_2)_2$, the reaction $Al_4H_6 + P_2H_4 \rightleftarrows Al_4(PH_2)_2H_4 + H_2$ convincingly shows the high stability of Al_4H_6 (Scheme 2). This reaction is exothermic in the reverse direction (toward Al_4H_6) by ~248 kJ mol^{-1}, even though the bond energy of the H_2 molecule is more than twice as high as the weak P−P bond of P_2H_4.[48]

In the sequence $Al_4H_6 \rightarrow Al_4H_4R'_2 \rightarrow Al_4R'_6$, the compound $Al_4H_2R'_4$ (**2d**) is missing.[49] In a molecule of the type **2d**, the

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(47) As expected, the hypothetic dianionic species Al_4^{2-} and $Al_4H_4^{2-}$ are unstable with respect to ejection of one electron or addition of cations (e.g., H^+, Li^+), and consequently, their HOMOs have positive energies.

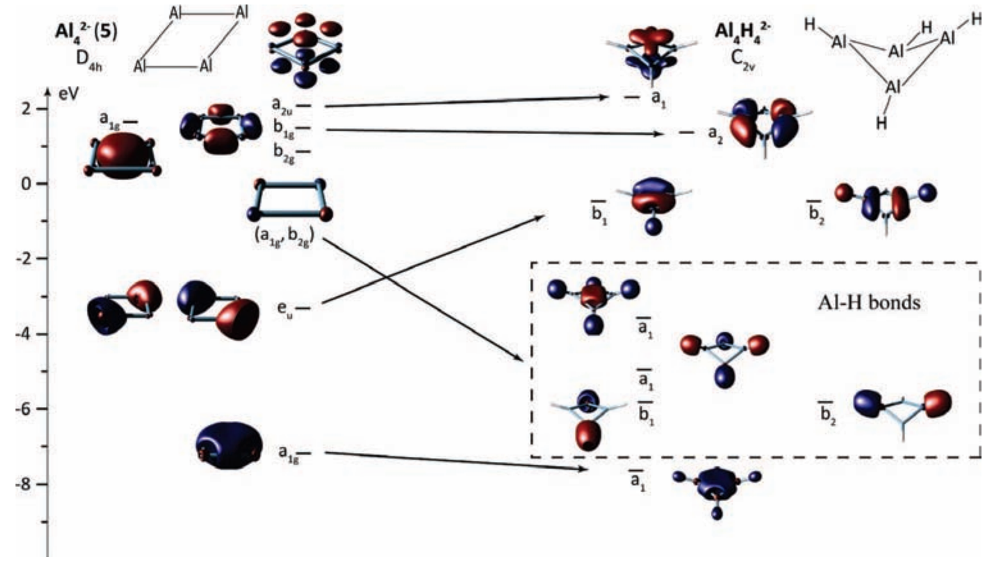
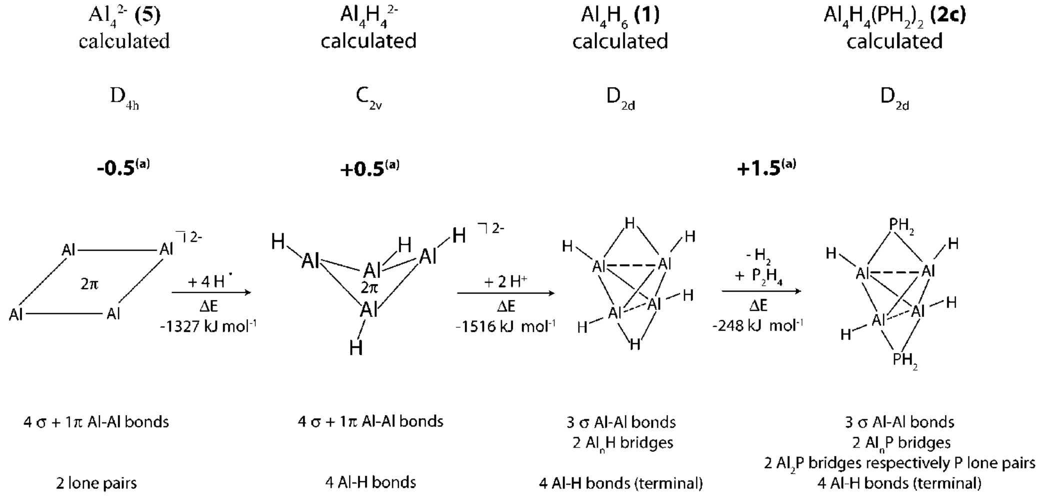


Figure 2. Pictures of MOs (see the text) of Al_4^{2-} (**5**) and $Al_4H_4^{2-}$, showing the HOMOs (a_{2u} and a_1, respectively) down to the fifth (HOMO−5, a_{1g}) and eighth (HOMO−8, a_1), respectively. The relation between the cluster bonding orbitals of **5** and $Al_4H_4^{2-}$ and that between the "lone pairs" of **5** and the localized Al−H bonds of $Al_4H_4^{2-}$ are shown.

Scheme 2. Energetic Relations and Relations with Respect to Number and Kind of Bonds in the Species Al_4^{2-} (**5**), $Al_4H_4^{2-}$, Al_4H_6 (**1**), and $Al_4H_4(PH_2)_2$ (**2c**)



[a] Average oxidation number.

four terminal hydrogen atoms in **1** are substituted by Cp^{Me4} ($=C_5Me_4H$). In order to compare the $Al_4R'_6$ species **2** with tetrahedral Al_4R_4 species[12] stabilized via their four MOs (t_2 and a_1), we investigated the reaction of Al_4R_4 ($R = C_5Me_4H$) with H_2 (Scheme 3).[49,50] The calculated reaction enthalpy is −14 kJ mol^{-1}. Via ^{27}Al NMR mass spectrometry, we monitored this reaction in a C_6D_6 solution under a H_2 pressure of ~2 bar. After 4 days, a new signal could be detected at −33.9 ppm, which is similar to the calculated one (−30.5 ppm). This observation is a strong hint of the formation of **2d**, since the calculation of ^{27}Al NMR shifts within a wide range (+300 to −300 ppm) is a very reliable method.[52,53]

Conclusion and Outlook

Though the field of low-valent Al and Ga compounds was unknown about 20 years ago, many compounds have been characterized during a short period.[6,18,37,54,55] However, the

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(48) The formation of the model cluster $Al_4H_4(PH_2)_2$ **2c** can also be described in an alternative way, in terms of PR_2^- ligands that in reality should be present in the reaction mixture starting from LiP^tBu_2. In a gedankenexperiment, we start with an $Al_4H_4^{2+}$ cation, in which six electrons form the cluster bonding. The reaction with two PR_2^- anions, each containing two lone pairs, generates two very low lying orbitals in which Al−P−Al and Al_4P_2 moieties are the prominent entities and two orbitals that are nonbonding, as in the above-mentioned description of **2c**. Thus, in this model we also have 10 electrons for the cluster bonding and four only weakly bonding electrons within the Al−P−Al bridges.

(49) Huber, M.; Schnöckel, H. *Inorg. Chim. Acta* **2008**, *361*, 457.

(50) The reaction between AlCp* and H_2 has been investigated under matrix conditions.[51]

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(52) This is also valid for the calculated and experimentally detected ^{27}Al NMR shifts of Al_4R_4' ($R' = C_5Me_4H$) (calcd 87.2 ppm; exptl 81.9 ppm).

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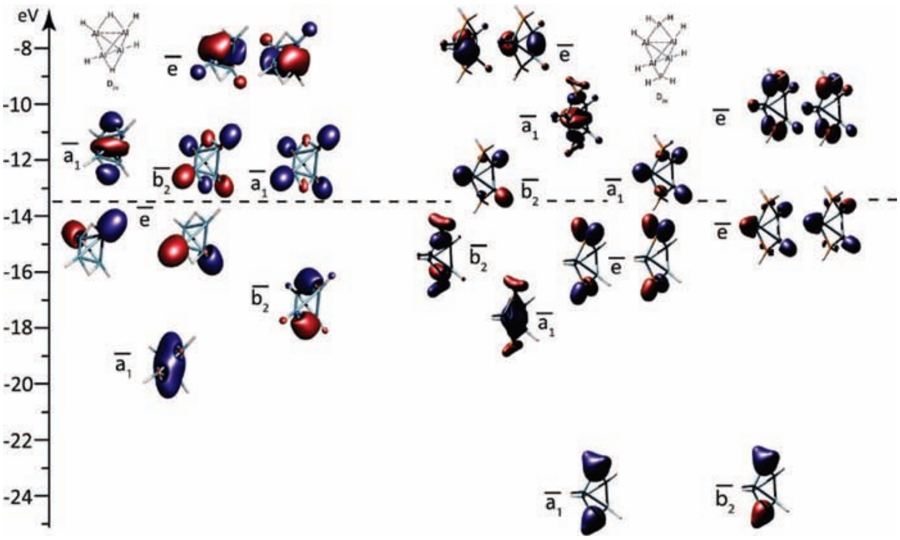
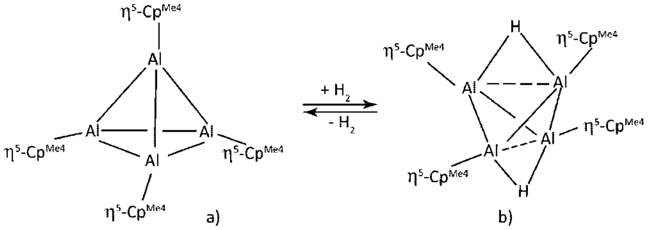


Figure 3. MO pictures (see the text) of Al_4H_6 (**1**) and $Al_4H_4(PH_2)_2$ (**2c**), showing the HOMOs (both with e symmetry) down to the HOMO−3 and HOMO−4 valence orbitals, respectively, of the cluster core. Below the dashed line are shown the localized orbitals representing the Al−H and P−H bonds.

Scheme 3. Equilibrium Reaction between Al_4R_4, H_2, and $Al_4R_4H_2$ in Solution



complexity of bonding variations within this novel class of subvalent organometallic and metalloid cluster compounds is already evident in the differences in bonding among small molecules of this type (e.g. those containing four metal atoms):
(a) The tetrahedral Al_4R_4 species are bonded via four delocalized Al_n MOs (a_1 and t_2).[6,12] The first example of an Al(I) compound of this type, which is now already a textbook example and exhibits a rich chemistry itself, was $Al_4Cp^*_4$.[56−58]
(b) The first crystalline Al(I) halide, $Al_4Br_4 \cdot 4L$ (L = ether), as a planar four-membered-ring molecule, exhibits classical 2e2c bonding.[6,9−11]
(c) Via PES, Al_4^{2-} and Al_4^{4-} cluster species[20,59,60] have been investigated as naked four-membered gas-phase clusters.[61] They were originally discussed as examples of aromatic and antiaromatic systems. In this contribution, Al_4^{2-} has been shown to be a suitable model to understand the bonding in **1**.

In the field of gallium chemistry there are also tetrahedral Ga_4R_4[12,62] species, and even a $Ga_4R_4^{2-}$ moiety in the compound $Ga_4R''_4 \cdot 2Na(THF)$ is known.[21] In order to complete the list of Ga_4 moieties known to date, one also has to mention the highly symmetrical $(GaRX)_4$ species[63] with an oxidation state of 2 for the Ga atoms (Scheme 4).

In order to finish this discussion and to include the stabilization via bonding to group 15 elements, one also has to mention some cagelike molecules containing Al−Al or Ga−Ga bonds as well as direct Al−P or Ga−P bonds. Most of them are not easy to describe with respect to their bonding, because different bonding models can be applied. Examples include the following (Scheme 4): $As_2(AlR)_3$[64] (Wade-type bonding?); $P_4(AlR)_6$[65] (an electron-deficient bonding situation); $P_4(GaR)_3$;[66] and $Ga_4(OR)_8$.[63]

Finally, the discussion of bonding in **1** and **2** initiates a first answer to a more general question: what is the difference between negatively charged naked metal atom clusters (so-called Zintl ions[67,68]) and the ligand-stabilized metalloid clusters M_nR_m (M = Al, Ga)?[5,18] The $Ga_4R''_4{}^{2-}$ cluster[21] (Ga oxidation state +0.5) and the hypothetical Zintl-like Al_4^{2-} species [20,59] (Al oxidation state −0.5) provide two experimentally detected simple examples to make visible the similarities and differences between the chemistries of the Zintl ions (mostly stabilized in ionic solids with an overall negative oxidation state of the metal atoms) and the metalloid clusters (exhibiting oxidation states between 0 and +1). The similarities seem plausible via the bonding descriptions of Al_4^{2-} and the hypothetical $Al_4H_4^{2-}$ presented in this contribution: In Figure 2, the MO sequence of $Al_4H_4^{2-}$ is visible, exhibiting MOs within the Al−Al bonds having shapes similar to those in Al_4^{2-}. However, the important difference between these two species is the high-energy position

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(61) With respect to the partially neutralized species containing alkaline cations (e.g., Al_4Li^-).
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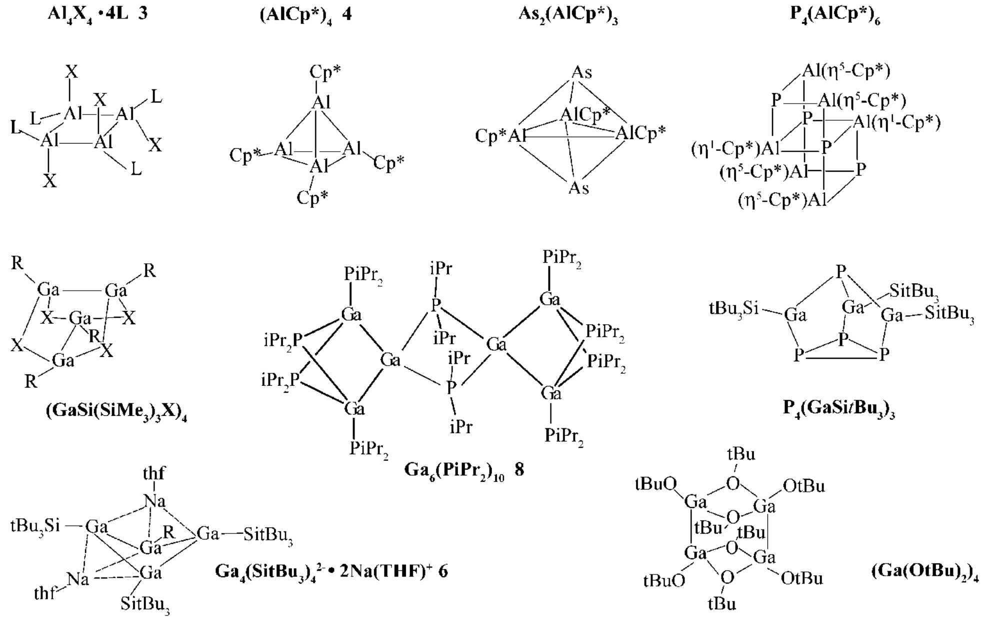
(68) Of the large number of publications in this field, see these two selections, which contain references to many other contributions: (a) Corbett, J. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 692. (b) Fässler, T. F.; Hoffmann, S. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 6242. (c) Sevov, S. C.; Goicoechea, J. M. *Organometallics* **2006**, *25*, 5678.

Scheme 4. Topological Arrangements in Some Al_n and Ga_n Cluster Compounds Mentioned in the Text



of the two additional lone pairs (a_{1g} and b_{2g}) for the Zintl ion Al_4^{2-} in contrast to the low-energy position of the four electrons localized in the four AlH bonds of $Al_4H_4^{2-}$. Therefore, it is not surprising that the calculated reaction of Al_4^{2-} with four H atoms is strongly exothermic ($\Delta E \approx -1300$ kJ mol^{-1}) (Scheme 2). Thus, though the negative oxidation numbers in Zintl-like metalloid clusters (e.g., -0.5 in Al_4^{2-}) and the slightly positive oxidation numbers in the molecular metalloid clusters protected by bulky ligands seem to be only a formal aspect, comparison of the MOs of Al_4^{2-} and hypothetical $Al_4H_4^{2-}$ and the energy relation between these species convincingly shows the higher stability of the ligand-protected clusters, which, in accordance with the presented bonding type, can be handled in solution, even with nonpolar solvents. In contrast, Zintl clusters have a high reduction potential, with a negative unprotected charge on the surface of the ions, causing a high reactivity (e.g., the strong association with positively charged species in any equilibrium solution). Thus, though there are similarities between Zintl ions and metalloid clusters with respect to bonding between the metal atoms, there are not only formal differences (oxidation number) but also differences in principle between the two kinds of metalloid clusters. Consequently, it seems to be a highly ambitious challenge for further investigations to stabilize "naked" pure Al_n^{x-} species such as the Al_4^{2-} anion and the prototypical jellium cluster Al_{13}^{-} [69] as salt-like compounds. Therefore, with support from the discussed stabilization via ligand bonding, the chance to observe isolated stabilized species increases in going from Al_4^{2-} to $Al_4H_4^{2-}/Al_4R_4^{2-}$ and finally to the Al_4H_6/Al_4R_6 molecules presented in this contribution (Scheme 2). Thus, another approach toward highly energetic species (other than use of PR_2) might be realizable first: the preparation of Al_4H_6 and its derivates (e.g., $Al_4H_4R_2$) stabilized by ligands that are less bulky than PR_2 units.

To summarize, bonding in the field of low-valent Al and Ga compounds is a very complex and diverse subject, even for species containing M_4 moieties. The unexpected stability islands for molecules like Al_4H_6 (**1**) and Al_4R_6 (**2**) provide further insight into novel bonding aspects of this experimentally nontrivial chemistry.

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Supporting Information Available: X-ray structural data for **2**, **2a**, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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