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Synthesis and Structure of the "Dialuminyne" $Na_2[Ar'AlAlAr']$ and $Na_2[(Ar''Al)_3]$: Al–Al Bonding in Al_2Na_2 and Al_3Na_2 Clusters**

*Robert J. Wright, Marcin Brynda, and Philip P. Power**

The synthesis of R_2AlAlR_2 ($R = CH(SiMe_3)_2$) by Uhl in 1988 marked a key development for compounds with Group 13 metal–metal bonds because it was the first example of a stable molecule with an Al–Al bond to be structurally characterized.[1] In the early 1990s it was shown that this compound and its gallium congeners, as well as related aryl-substituted derivatives, could be reduced to afford anions of the type $[R_2MMR_2]^-$ ($M = Al$ or Ga, $R = CH(SiMe_3)_2$[2–4] or C_6H_2-2,4,6-iPr$_3$[5,6]), which had M–M bonds of formal order 1.5 owing to occupation of a π orbital by a single electron. Later work expanded these initial results to several other classes of Group 13 compounds with metal–metal multiple bonds,[7] including most notably the "digallyne" $Na_2[Ar^*GaGaAr^*]$ (**1**; $Ar^* = C_6H_3$-2,6-(C_6H_2-2,4,6-iPr$_3$)$_2$)[8] of Robinson and coworkers, the bonding of which has attracted considerable debate.[9] This compound has a *trans*-bent, planar C-Ga-Ga-C array, a short Ga–Ga bond length of about 2.32 Å, and a formal Ga–Ga triple bond (by analogy with alkynes). The only related Group 13 element derivative of this type is the closely related compound $Na_2[Ar'GaGaAr']$ (**2**; $Ar' = C_6H_3$-2,6-(C_6H_3-2,6-iPr$_2$)$_2$), which has very similar structural parameters to those of **1** but whose flanking aryl rings do not carry a *para*-iPr substituent.[10,11]

Since 2000, however, work on the isoelectronic neutral Group 14 element derivatives RM′M′R (M′ = Si,[12–14] Ge,[15,16] Sn,[17] Pb;[18] R = bulky organic or silyl group) has progressed to the extent that stable homonuclear species for each member of the series have now been isolated and structurally characterized. In addition, a series of related neutral Group 13 metal Ar′MMAr′ derivatives (M = Ga,[10,11] In,[19] Tl[20]) has been reported. These results prompted us to attempt a similar advance for the heavier Group 13 element alkyne analogues, especially in the case of aluminum, which is of key importance as the first metal of the p-block elements.[21] We now describe the synthesis and characterization of the first "dialuminyne" species $Na_2[Ar'AlAlAr']$ (**3**) and the "cyclotrialuminene" $Na_2[(AlAr'')_3]$ (**4**; $Ar'' = C_6H_3$-2,6-(C_6H_2-2,4,6-Me_3)$_2$).

Compounds **3** and **4** were synthesized by reduction of solutions of $Ar'AlI_2$ (**5**) and $Ar''AlI_2$ (**8**) in diethyl ether with excess sodium [Eq. (1)]. The reduction of **5** initially leads to **6**,

$$\begin{gathered}\underset{\mathbf{5}}{2\,\mathrm{Ar'AlI_2}} \xrightarrow[-2\,\mathrm{NaI}]{2\,\mathrm{Na}} \underset{\mathbf{6}}{\mathrm{I(Ar')AlAl(Ar')I}} \xrightarrow[-2\,\mathrm{NaI}]{2\,\mathrm{Na}} \underset{\mathbf{7}}{\mathrm{Ar'AlAlAr'}} \xrightarrow{2\,\mathrm{Na}} \underset{\mathbf{3}}{\mathrm{Na_2[Ar'AlAlAr']}} \\ \underset{\mathbf{8}}{3\,\mathrm{Ar''AlI_2}} \xrightarrow[-6\,\mathrm{NaI}]{8\,\mathrm{Na}} \underset{\mathbf{4}}{\mathrm{Na_2[(AlAr'')_3]}}\end{gathered} \tag{1}$$

thence to **7**,[22] which affords **3** upon further reduction. Compound **3** was isolated in about 20% yield as deep red, almost black crystals, while **4** was isolated in about 25% yield as red-orange crystals. The clusters were characterized by ^1H and ^{13}C NMR spectroscopy, UV/Vis spectroscopy, and X-ray crystallography.[23]

X-ray crystallographic analysis of **3** (Figure 1) revealed a centrosymmetric Al_2Na_2 core with Al–Al and Al–Na separations of 2.428(1) and 3.152(1) Å, respectively. The aluminum atoms are bound to the Ar′ substituents through the *ipso* carbon atoms (C(1) and C(1A)) of the central aryl ring, as well as to the sodium atoms (Na(1) and Na(1A)), which are further complexed in an η^6 fashion to the flanking aryl rings of Ar′ (centroid–Na 2.656(2) and 2.637(2) Å; C–Na 2.881(2)–3.084(2) Å). The C(1)-Al(1)-Al(1A)-C(1A) array has a *trans*-bent structure (C(1)-Al(1)-Al(1A) dihedral: 131.71(7)°) with local C_{2h} symmetry.

The structure of **4** is characterized by a triangular Al_3 core (Figure 2, Al–Al 2.5202(2) Å) with a crystallographically required three-fold axis of symmetry. Each aluminum atom has distorted trigonal-planar geometry and is bound to two aluminum atoms and to an Ar″ ligand through the *ipso* carbon atom of the central aryl ring. This ring is orientated perpendicularly to the Al_3C_3 core array. The two Na atoms are located above and below the centroid of the Al_3 core, and are also coordinated to the flanking mesityl rings of the terphenyl ligand (centroid–Na 3.177(2) Å, Na–Al 3.285(2) Å). The Al-Al-C bond angles differ by about 15°, such that the extension of the C–Al vector does not pass through the centroid of the Al_3 triangle.

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[*] Dr. R. J. Wright, Dr. M. Brynda, Prof. P. P. Power
Department of Chemistry
University of California
One Shields Avenue, Davis, CA 95616 (USA)
Fax: (+1) 530-752-8995
E-mail: pppower@ucdavis.edu

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

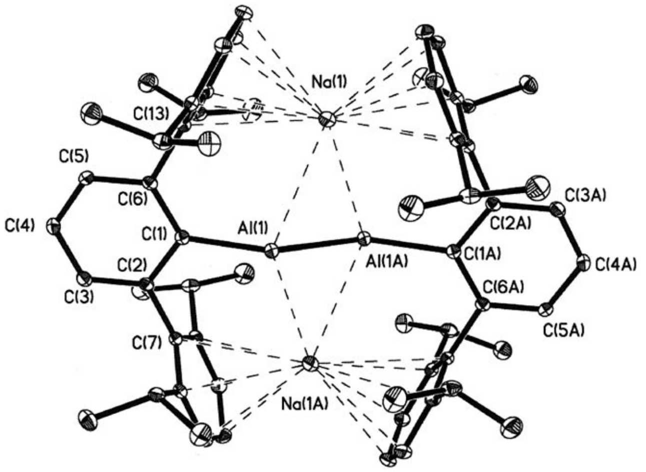

Figure 1. Thermal ellipsoid plot (30% probability) of **3** without H atoms. Selected bond lengths [Å] and angles [deg]: Al(1)-Al(1A) 2.428(1), Al(1)-C(1) 2.043(2), Al(1)-Na(1A) 3.152(1), Na-C_{ring} 2.881(2)–3.084(2) [av. 2.991(2)], Dipp(centroid)-Na(1) 2.656(2), Dipp(centroid)-Na(1A) 2.637(2); C(1)-Al(1)-Al(1A) 131.71(7), Na(1)-Al(1)-Na(1A) 134.58(2), Al(1A)-Al(1)-Na(1) 67.65(3), Al(1A)-Al(1)-Na(1A) 66.93(3), C(1)-Al(1)-Na(1) 104.71(6), C(1)-Al(1)-Na(1A) 105.07(6), Al(1)-C(1)-C(2) 121.9(1), Al(1)-C(1)-C(6) 122.2(1), C(1)-C(2)-C(7) 120.7(2), C(1)-C(6)-C(13) 120.8(2). Dipp = C_6H_3-2,6-*i*Pr_2.

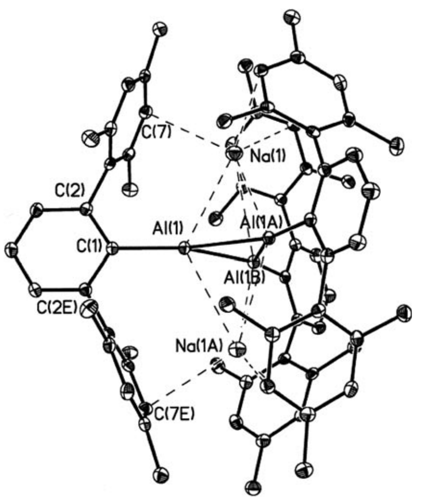

Figure 2. Thermal ellipsoid plot (30% probability) of **4** without H atoms. Selected bond lengths [Å] and angles [deg]: Al(1)-Al(1A) 2.520(2), Al(1)-C(1) 2.021(3), Al(1)-Na(1) 3.285(2), Na(1)-C(7) 3.066(2), Na-C_{ring} 3.066(2)–3.808(2) [av. 3.459(2)], Mes(centroid)-Na(1A) 3.177(2); A1(1)-Al(1A)-Al(1B) 60.0, Al(1A)-Na(1)-Al(1B) 45.12(3), C(1)-Al(1)-Al(1A) 142.8(1), C(1)-Al(1)-Al(1B) 157.2(1). Dihedral angle between Al_3 plane and Na(1)-Al_3(centroid)-Na(1 A) plane: 90.0. Mes = C_6H_2-2,4,6-Me_3.

The structure of **3** may be compared with those of the recently reported "disilyne" R′SiSiR′[14] (R′ = Si{CH($SiMe_3$)$_2$}$_2$*i*Pr; Si–Si 2.319(2) Å, Si-Si-Si 137.44(4)°) and the "digallynes" **1** (Ga–Ga 2.319(2) Å, C-Ga-Ga ca. 131°) and **2** (Ga–Ga 2.347(1) Å, C-Ga-Ga 130.7(1)°). The Al–Al bond length in **3** (2.428(1) Å) is considerably longer than the Si–Si or Ga–Ga bond lengths although the bending angle at Al is within 1° of those in **1** and **2** and is only 5.7° smaller than that of the "disilyne". The longer Al–Al bond length is a result of the larger radius of Al (1.3 Å) versus that of Si (1.17 Å) or Ga (1.25 Å). The dianionic nature of $[Ar'AlAlAr']^{2-}$ versus the neutral "disilyne" is also a factor in the large disparity in bond length. Nonetheless, the Al–Al bond length in **3** is much shorter than those in the Al–Al single-bonded compounds R_2AlAlR_2 (R = CH($SiMe_3$)$_2$; Al–Al 2.660(3) Å)[1] and $R'_2AlAlR'_2$ (R′ = C_6H_2-2,4,6-*i*Pr_3; Al–Al 2.647(3) Å)[6] although it is only about 0.04 Å shorter than the Al–Al bond length in the one-electron-reduction product Li(tmeda)$_2$[$R'_2AlAlR'_2$] (2.470(2) Å), which has a formal bond order of 1.5.[6]

The Al–Al bond lengths in **3** may also be affected by sodium–aryl interactions. Calculations by the groups of Nagase,[24] Cotton and Cowley have suggested that this is the case for the "digallynes".[25] More recent high-level calculations by Frenking and co-workers have demonstrated the importance of the Na–Ga interactions.[26] This work has shown that the Ga–Ga bond order in the model species Na_2[PhGaGaPh] is about half that of $[PhGaGaPh]^{2-}$. Unfortunately, computational data on model compounds for **3** feature only separated anions with simple ligands such as H[27,28] or Me[28] and do not take Na–aryl interactions into consideration. The calculated geometries of the organosubstituted (Me or Ph) model compounds all afforded planar *trans*-bent structures similar to that found experimentally with Al–Al bond lengths in the range 2.50–2.52 Å and Al-Al-C bond angles in the range 120–127°.[28] The longer calculated Al–Al distances support the view that some of the shortening (0.07–0.09 Å) of the Al–Al bond is indeed a result of the effect of the sodium atoms. The Al–Al bond order, calculated by the method of Mayer,[29] for the simplest planar *trans*-bent model $[HAlAlH]^{2-}$ is 2.51.[28] DFT calculations at the B3LYP/6-31g* level[30] on the model species Li_2[HAlAlH], followed by Wiberg bond-order calculations,[31] resulted in an Al–Al bond order of 1.35. Calculations at the same level of theory on the entire molecule of **3** afforded an Al–Al bond order of 1.13, while the same calculations on the gallium analogue **2** afforded a value of 1.39. Finally, we note that the Al–Al bond length in **3** is about 0.20 Å larger than that recently predicted from the sum of the triple-bond radii of aluminum (2.22 Å).[32]

Kohn–Sham frontier-orbital surfaces for the model compound Na_2[ArAlAlAr] (Ar = C_6H_3-2,6-Ph_2) were generated from the DFT calculations by using crystallographic coordinates of **3** (Figure 3).[33] The HOMO is clearly the out-of-plane π bond, and the HOMO−1 can be designated as n_-[34] (this type of orbital has also been called a slipped π bond),[35] although calculations on related gallium and germanium species indicate that such an orbital is essentially nonbonding in its effect.[36] The HOMO−2 features σ bonding between the metal centers and from the metal centers to the ligand carbon atoms. These calculations also shed light on the UV/Vis spectrum of **3**, which features three orbitally allowed absorbances at 354, 456, and 600 nm. Two of these absorbances are likely attributable to transitions from the HOMO (a_u) and the HOMO−1 (b_u) to the LUMO (a_g) while the highest-energy transition may involve the HOMO and the LUMO + 1 (a_g) levels.

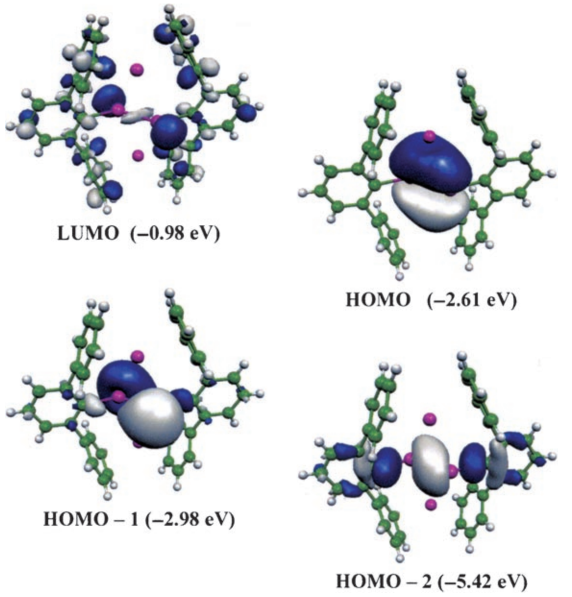

Figure 3. Selected Kohn–Sham orbital representations for the model species $Na_2[ArAlAlAr]$ ($Ar = C_6H_3$-2,6-Ph_2).

Compound **4**, the "cycloaluminene", is isoelectronic to the recently reported cyclotrisilenylium ion $[Si_3R_2R']^+$ ($R = SitBu_3$, $R' = SiMe_2tBu$) published by Sekiguchi and co-workers[37] and the previously described gallium salts $M_2[(GaAr'')_3]$ (**9**, M = Na[38]; **10**, M = K[39]) of Robinson and co-workers. The structure of **4** bears a resemblance to that of **9** except that the Al–Al bond length exceeds that of its gallium analogue **9** by about 0.08 Å and is about 0.30 Å larger than the Si–Si bond lengths in the cyclotrisilenylium ion $[Si_3R_2R']^+$. Kohn–Sham orbital representations were also generated for $Na_2[(AlAr)_3]$ (Figure 4; $Ar = C_6H_3$-2,6-Ph_2) and showed that the HOMO−2 is a π orbital delocalized over the three metal centers while the HOMO and HOMO−1 are Al–Al σ-bonding orbitals.

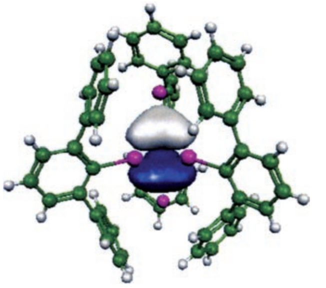

Figure 4. Kohn–Sham orbital representation for the delocalized HOMO−2 of $Na_2[(AlAr)_3]$ ($Ar = C_6H_3$-2,6-Ph_2).

The presence of a delocalized 2π orbital suggests that **4** is aromatic. Work on the related gallium species **9** and **10** has shown that they possess delocalized π systems, and nucleus-independent chemical shift (NICS) calculations confirmed their metalloaromaticity.[40] NICS calculations have not been undertaken on **4**, and attempts to obtain a ^{27}Al NMR spectrum which might provide further insight into the aromaticity of **4** failed.

The formal M–M bond order in **4** is 1.33; however, the calculated Wiberg bond order in the geometry-optimized model species $Na_2[(AlMe)_3]$ is 0.72 while a value of 0.88 was obtained for calculations (B3LYP/6-31g*) on the entire molecule of **4**. The lower bond orders are likely a result of the distorted localized geometry (C_{3h} instead of D_{3h}) caused by lone-pair character at the Al centers and polar–covalent Na–Al interactions. The Na–Al bond orders in $Na_2[(AlMe)_3]$ are calculated to be 0.34 and are indicative of incomplete electron transfer to the Al_3 ring. Clearly, the sodium atoms play an important role in the structure of the complex, and, like **3**, it should be viewed not as a separated dianion but as a Na/Al cluster.

In conclusion, the first "dialuminyne" $Na_2[Ar'AlAlAr']$ (**3**) and the "cycloaluminene" $Na_2[(AlAr'')_3]$ (**4**) have been synthesized. Compound **3** features an Al–Al bond with multiple-bond character (Wiberg bond order of 1.13). However, this value is substantially lower than the formal value of three, as a result of the *trans*-bent C-Al-Al-C core, which implies the presence of nonbonding lone-pair density at the Al centers (see HOMO−1). Theoretical calculations on the cyclic compound **4** showed that the HOMO−2 is a delocalized π bond. However, the Al–Al σ bonding is somewhat weakened by the lone-pair character at the metal centers, which results in a lower Al–Al bond order. Apparently, the Al–Al bonds in **3** and **4** are also weakened by Na–aryl interactions. Future work will be focused on the isolation of the neutral Ar′AlAlAr′ and $(Ar''Al)_3$ species and other heavier element analogues of **3** and **4**.

Experimental Section

All manipulations were carried out under anhydrous and anaerobic conditions.

3: $Ar'AlI_2$ (2.20 g, 3.25 mmol), Na (0.299 g, 13.0 mmol), and Et_2O (125 mL) were added to a Schlenk vessel (150 mL). The mixture was stirred for five days and gave a deep red-black solution. The solution was filtered by filter cannula, and concentration under reduced pressure to about 15 mL afforded dark red, almost black crystals of **3**. The mother liquor was carefully removed, and **3** was dried in a vacuum. Yield: 0.298 g, 20 %; m.p. 275–278 °C. X-ray quality crystals ($0.1 \times 0.1 \times 0.1$ mm^3) of **3** were obtained upon slow cooling of solutions of **3** in Et_2O. ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 1.029$ (d, 24 H, *o*-$CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 1.470 (d, 24 H, *o*-$CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 2.964 (sept, 8 H, *o*-$CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 6.960 (d, 6 H, *m*-C_6H_3), 7.124 (s, 12 H, *m*-Dipp), 7.189 ppm (t, 3 H, *p*-C_6H_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 25 °C): $\delta = 23.66$ ($CH(CH_3)_2$), 25.66 ($CH(CH_3)_2$), 30.92 ($CH(CH_3)_2$), 123.75 (*m*-Dipp), 127.48 (*p*-C_6H_3), 128.97 (*m*-C_6H_3), 129.21 (*p*-Dipp), 141.93 (*i*-Dipp), 147.04 (*o*-Dipp), 147.14 ppm (*o*-C_6H_3); UV/Vis (hexanes): λ_{max} [nm] (ε in mol^{-1} L cm^{-1}): 354 (25 600), 456 (16 800), 600 (12 400).

4: $Ar''AlI_2$ (3.2 g, 5.39 mmol), Na (0.51 g, 22 mmol), and Et_2O (70 mL) were added to a Schlenk vessel (150 mL). The mixture was stirred for three days to give a red solution. The solution was filtered by filter cannula and concentrated to about 30 mL. Upon addition of dry degassed hexane (ca. 15 mL) and overnight storage at about −20 °C, **4** precipitated as a red solid. The powder (0.486 g, 25 % yield) was isolated and dissolved in benzene (300 mL), and storage at about 10 °C resulted in small, red hexagonal crystals of X-ray quality. M.p.

183–185 °C; ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 2.255$ (s, 36 H, *o*-Me), 2.372 (s, 18 H, *p*-Me), 6.695 (d, 6 H, *m*-C_6H_3), 7.124 ppm (t, 3 H, *p*-C_6H_3); ^{13}C{^{1}H} NMR: (75.5 MHz, C_6D_6, 25 °C): $\delta = 21.92$ (*p*-Me), 22.12 (*o*-Me), 100.30, 125.91, 127.40, 134.39, 138.17 ppm; UV/Vis (hexanes) λ_{max} [nm] (ε in mol^{-1} L cm^{-1}): 280 (9000), 296 (10 000), 330 (13 000), 380 (16 000).

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[1] W. Uhl, *Z. Naturforsch. B* **1988**, *43*, 1113.

[2] C. Pluta, K. R. Pörschke, C. Krueger, K. Hildenbrand, *Angew. Chem.* **1993**, *105*, 451; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 388.

[3] W. Uhl, A. Vester, W. Kaim, J. Poppe, *J. Organomet. Chem.* **1993**, *454*, 9.

[4] W. Uhl, U. Schütz, W. Kaim, E. Waldhör, *J. Organomet. Chem.* **1995**, *501*, 79.

[5] X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon, P. P. Power, *Angew. Chem.* **1993**, *105*, 761; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 717.

[6] R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon, P. P. Power, *Inorg. Chem.* **1993**, *32*, 2983.

[7] a) P. P. Power, *Struct. Bonding (Berlin)* **2002**, *103*, 57; b) A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 3682; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532; c) H. W. Roesky, *Inorg. Chem.* **2004**, *43*, 7284; d) H. W. Roesky, S. S. Kumar, *Chem. Commun.* **2005**, *32*, 4027.

[8] J. Su, X.-W. Li, R. C. Crittendon, G. H. Robinson, *J. Am. Chem. Soc.* **1997**, *119*, 5471.

[9] R. A. Dagani, *Chem. Eng. News* **1998**, *76*(11), 31.

[10] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667.

[11] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *Angew. Chem.* **2002**, *114*, 2966; *Angew. Chem. Int. Ed.* **2002**, *41*, 2842.

[12] N. Wiberg, T. Blank, K. Amelunxen, H. Nöth, H. Schnöckel, E. Baum, A. Purath, D. Fenske, *Eur. J. Inorg. Chem.* **2002**, 341.

[13] N. Wiberg, S. K. Vasisht, G. Fischer, P. Mayer, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823.

[14] A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science* **2004**, *305*, 1755.

[15] M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem.* **2002**, *114*, 1863; *Angew. Chem. Int. Ed.* **2002**, *41*, 1785.

[16] Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase, N. Tokitoh, *J. Am. Chem. Soc.* **2006**, *128*, 1023.

[17] A. D. Phillips, R. J. Wright, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 5930.

[18] L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524.

[19] R. J. Wright, A. D. Phillips, N. J. Hardman, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 8538.

[20] R. J. Wright, A. D. Phillips, S. Hino, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 4794.

[21] The first stable low-valent organo-Al(I) compounds (or lower-oxidation-state species) $K_2[Al_{12}i Bu_{12}]$ and $[\{Al(\eta^5\text{-}C_5Me_5)\}_4]$ were characterized in 1991: W. Hiller, K. W. Klinkhammer, W. Uhl, J. Wagner, *Angew. Chem.* **1991**, *103*, 182; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 179; C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem.* **1991**, *103*, 594; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 564.

[22] R. J. Wright, A. D. Phillips, P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 11 626.

[23] Crystallographic data for **3** and **4** ($T = 90$ K with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation): **3**: monoclinic, space group $P2_1/n$, $a = 11.493(1)$, $b = 18.148(1)$, $c = 13.478(1)$ Å, $\beta = 100.167(1)°$, $Z = 2$, $R1 = 0.0518$ for 6554 ($I > 2\sigma(I)$) data; **4**: hexagonal, space group $P6_3/m$, $a = 13.9787(4)$, $b = 13.9787(4)$, $c = 20.266(1)$, $Z = 2$, $R1 = 0.0494$ for 2140 ($I > 2\sigma(I)$) data. CCDC-606648 (**3**) and CCDC-606647 (**4**) 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.

[24] N. Takagi, M. W. Schmidt, S. Nagase, *Organometallics* **2001**, *20*, 1646.

[25] F. A. Cotton, A. H. Cowley, X. Feng, *J. Am. Chem. Soc.* **1998**, *120*, 1795.

[26] R. Ponec, G. Yuzhakov, X. Gironés, G. Frenking, *Organometallics* **2004**, *23*, 1790.

[27] H. J. Schnöckel, H.-J. Himmel, *Chem. Eur. J.* **2002**, *8*, 2397.

[28] A. J. Bridgeman, L. R. Ireland, *Polyhedron* **2001**, *20*, 2841.

[29] I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270.

[30] Gaussian 03 (Revision A.01): M. J. Frisch et al., see Supporting Information for full reference.

[31] S. I. Gorelsky, AOMix Rev. 5.44, http://www.obbligato.com/software/aomix/.

[32] P. Pyykkö, S Riedel, M. Patzschke, *Chem. Eur. J.* **2005**, *11*, 3511.

[33] P. Flukiger, H. P. Luthi, S. Portmann, J. Weber, MOLEKEL 4.3, Swiss Center for Scientific Computing, Manno, Switzerland, **2000–2002**.

[34] n designates a lone pair orbital. The subscripts + and − refer to its symmetry (+) or antisymmetry (−) with respect to inversion.

[35] K. W. Klinkhammer, *Angew. Chem.* **1997**, *109*, 2387; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2320.

[36] T. L. Allen, W. H. Fink, P. P. Power, *J. Chem. Soc. Dalton Trans.* **2000**, 407.

[37] M. Ichinohe, M. Igarashi, K. Sanuki, A. Sekiguchi, *J. Am. Chem. Soc.* **2005**, *127*, 9978.

[38] X.-W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **1995**, *117*, 7578.

[39] X.-W. Li, Y. Xie, P. R. Schreiner, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer, G. H. Robinson, *Organometallics* **1996**, *15*, 3798.

[40] Y. Xie, P. R. Schreiner, H. F. Schaefer III, X.-W. Li, G. H. Robinson, *J. Am. Chem. Soc.* **1996**, *118*, 10 635.