Angewandte International Edition Chemie

VIP Organoaluminum Compounds Very Important Paper

DOI: 10.1002/anie.201304143

Syntheses and Structures of an "Alumole" and Its Dianion**

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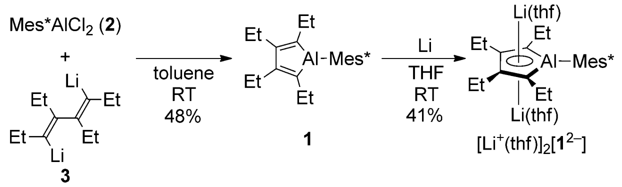
Dedicated to Professor Renji Okazaki on the occasion of his 76th birthday

Heteroles of electron-deficient group 13 elements are expected to have low-lying LUMOs owing to the orbital interactions between the empty p orbital of group 13 elements and the π* orbitals. For instance, boroles (boracyclopentadienes) exhibit various fascinating properties and reactivity,[1] including extremely high electrophilicity of the boron center; this electrophilicity has been exemplified by the generation of the corresponding 5π-radical anions[2] and 6π-dianions.[3] Such intriguing properties of boroles invoke the question of whether the aluminum analogues of boroles, that is, alumoles, would also possess peculiar characteristics derived from the conjugation involving the empty 3p(Al) orbital.[4,5] To date, only a few examples of alumole/Lewis base complexes have been structurally characterized.[6,7] The coordination of Lewis bases to the aluminum center may substantially affect the electronic structures, therefore the synthesis of Lewis base free alumoles has been desired to provide a basis for the elucidation of the intrinsic nature of alumoles.

Herein, we report the synthesis of stable alumole **1**, which is not coordinated to a Lewis base. Reduction of alumole **1** afforded the lithium salt of the alumole dianion $[Li^+(thf)]_2$-$[\mathbf{1}^{2-}]$. Structures of these alumole derivatives have been elucidated.

On the basis of the successful application of 2,4,6-$(tBu)_3C_6H_2$ (Mes*) group in the syntheses of stable galloles[8] and dibenzoboroles,[9] this bulky group was chosen as a substituent on the aluminum atom to protect the alumole from Lewis base attack. Treatment of Mes*$AlCl_2$ (**2**)[10] with 1,4-dilithiobutadiene (**3**)[11] in toluene afforded alumole **1** as a colorless solid (48%),[12] which is stable under an inert atmosphere (Scheme 1). Alumole **1** is readily hydrolyzed to give 4,5-diethyl-3,5-octadiene and Mes*H on exposure to air and moisture. Addition of THF or Et_2O to a C_6D_6 solution of **1** did not affect its ^1H NMR spectrum, thus suggesting that the aluminum center of **1** maintains a tri-coordinated structure in solution even in the presence of such coordinative solvents.



Scheme 1. Syntheses of alumole **1** and the lithium salt $[Li^+(thf)]_2[\mathbf{1}^{2-}]$ (Mes* = 2,4,6-$(tBu)_3C_6H_2$).

X-ray crystallographic analysis of **1** revealed its molecular structure.[13] In the unit cell two crystallographically independent molecules were found; the structure for one of the two molecules is shown in Figure 1a. The AlC_4 ring is completely planar as shown by the sum of the internal bond angles of 560° with the tri-coordinated aluminum atom

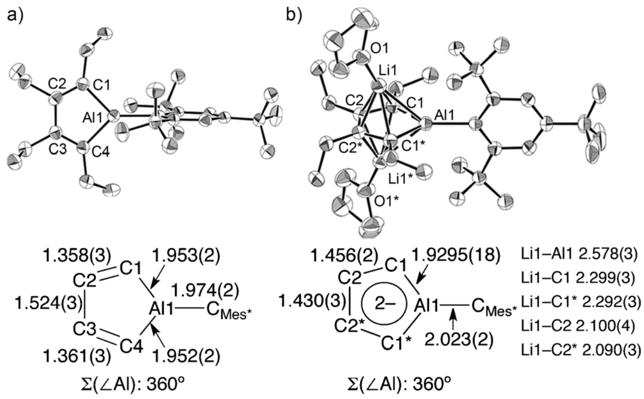


Figure 1. Molecular structures and selected bond lengths (Å) of a) **1** and b) $[Li^+(thf)]_2[\mathbf{1}^{2-}]$ (thermal ellipsoids are set at 50% probability level). Hydrogen atoms are omitted for clarity.

showing planar geometry (Σ(∠Al) = 360°). The butadiene moiety of the AlC_4 ring exhibits apparent bond alternation. The Al–C bond lengths in the AlC_4 ring are comparable to those of alkenylaluminum compounds (e.g., (*E*)-$[(Me_3Si)_2HC]_2$Al–CH=CH–$SiMe_3$: Al–C(alkene) = 1.951(5) Å).[14]

Treatment of **1** with an excess amount of lithium in THF afforded the lithium salt of the alumole dianion, $[Li^+(thf)]_2[\mathbf{1}^{2-}]$, as air- and moisture-sensitive orange crystals in 41% yield (Scheme 1).[15] The choice of reductant is crucial; treatment of **1** with Na, K, or KC_8 gave a complicated mixture and there was no evidence for the generation of the corresponding metal salts.

X-ray crystallographic analysis of $[Li^+(thf)]_2[\mathbf{1}^{2-}]$ revealed a C_2 symmetric structure with a C_2 axis passing through the

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[**] This work was partially supported by JSPS KAKENHI Grant (Nos. 22350017, 24550048, 24655028, and 24109013) and by the "Molecular Systems Research" project of RIKEN Advanced Science Institute. T.A. thanks to the Kyoto Technoscience Center for the financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201304143.

Al(1)–C_{Mes*} bond and the center of the AlC_4 ring.[13] The two lithium cations are located above and below the planar AlC_4 ring and bound to the AlC_4 ring in a η^5 fashion. The C–C bond lengths in the AlC_4 ring are nearly equal, and the Al–C bond lengths in the AlC_4 ring are slightly shortened compared with those in **1**.

In the ^{13}C NMR spectrum of **[Li$^+$(thf)]$_2$[1^{2-}]** in C_6D_6, the AlC_4-ring carbon atom resonances ($\delta(C_\alpha) = 102.6$ ppm, $\delta(C_\beta) = 112.6$ ppm) were shifted upfield to those of **1** ($\delta(C_\alpha) = 144.0$ ppm, $\delta(C_\beta) = 156.4$ ppm). The ^{7}Li NMR chemical shift of **[Li$^+$(thf)]$_2$[1^{2-}]** ($\delta = -6.0$ ppm) is in accordance with the calculated value ($\delta = -5.5$ ppm), thus indicating that the contact ion-pair structure of **[Li$^+$(thf)]$_2$[1^{2-}]** is retained in solution.

To elucidate the electronic structure of **1**, the molecular orbitals of parent alumole **4**, butadiene **5**, and dimethylalane **6** were computed (Figure 2). The structural parameters of the

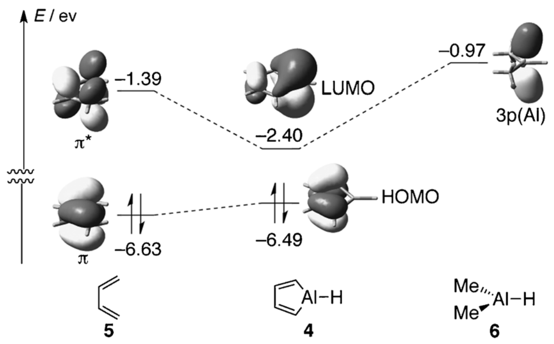


Figure 2. Frontier orbitals of parent alumole **4** and the corresponding orbital energies.

AlC_4 ring in **4** are in good agreement with those of **1**. The frontier orbitals of **4** can be explained by the interactions between the π/π* orbitals of **5** and the 3p(Al) orbital of **6**. The HOMO of **4** is seemingly similar to that of **5**. The π* orbital of **5** and the 3p(Al) orbital of **6** can be favorably overlapped, thus making the LUMO level of **4** lower than those of **5** and **6**. Such a lowered LUMO level should explain the high electron acceptability of **1**.

Structures of the dianions of parent alumole **4** were optimized (Figure 3). The planar form of Li-free dianion **4**$^{2-}$, having C_{2v} symmetry, was the transition state with one

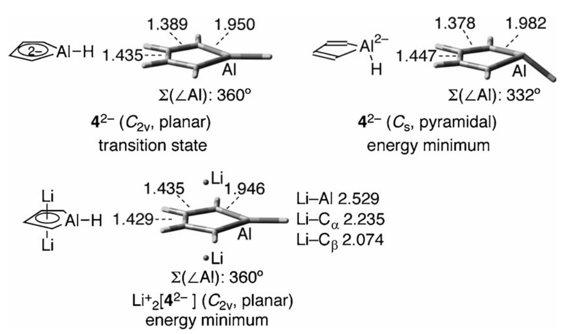


Figure 3. Optimized geometries and the selected bond lengths (Å) of the dianions of parent alumole **4**.

imaginary vibrational frequency. Alternatively, the pyramidal form ($\Sigma(\angle Al) = 332°$), having C_s symmetry, was the energy minimum. Even in the case of structural optimization of Li-free dianion **1**$^{2-}$, not the planar form but the pyramidal form ($\Sigma(\angle Al) = 332°$) was obtained as the equilibrium structure, thus indicating that the bulky substituent would not enforce the planar geometry of the alumole dianion. The pyramidal structures of Li-free alumole dianions **1**$^{2-}$ and **4**$^{2-}$ suggest that the negative charges are localized on the aluminum atoms.[16] On the other hand, the energy-minimum structure of the lithium salt of **4**$^{2-}$ exhibited a planar AlC_4 ring without C–C bond length alternation, as in the case of the experimentally observed structure of [Li$^+$(thf)]$_2$[**1**$^{2-}$]. The distances between the lithium cations and the AlC_4 ring atoms in Li$^+_2$[**4**$^{2-}$] are comparable to those observed in the crystal structure of [Li$^+$(thf)]$_2$[**1**$^{2-}$]. It can be concluded that coordination of two lithium cations on the alumole dianion with inverse sandwich geometry makes the alumole dianion planar.

The small negative nucleus-independent chemical shift (NICS(0)) values of the Li-free dianion **4**$^{2-}$ (planar form: $\delta = -5.10$ ppm, pyramidal form: $\delta = -3.10$ ppm) suggest that the AlC_4 ring in **4**$^{2-}$ is nearly nonaromatic. In contrast, lithium salt Li$^+_2$[**4**$^{2-}$] has a considerably negative NICS value ($\delta = -15.48$ ppm) at the center of the AlC_4 ring. Almost the same NICS value ($\delta = -15.01$ ppm) was calculated at the center of the AlC_4 ring in [Li$^+$(thf)]$_2$[**1**$^{2-}$]. Therefore, the coordination of the lithium cations should significantly influence not only the geometry but also the electronic states of the alumole dianions, thus indicating a *closo*-cluster description for the bonding of the lithium salt [Li$^+$(thf)]$_2$[**1**$^{2-}$].[17] This bonding picture is of interest from the viewpoint of spherical aromaticity.

In summary, we have synthesized a Lewis base free alumole and its dianion. The AlC_4 ring of the alumole exhibits bond alternation. Reduction of the alumole with lithium afforded the lithium salt of the alumole dianion. DFT calculations revealed that the 3p(Al)-π* conjugation effectively lowers the LUMO energy level of the alumole. Coordination of two lithium cations to the alumole dianion is a key factor to keep the planar AlC_4 ring structure. Further investigation of the bonding situation and properties of the lithium salt of the alumole dianion is currently underway.

Experimental Section

General experimental: Solvents were purified by the Ultimate Solvent System, Glass Contour Company (*n*-hexane and toluene)[18] and by distillation from a potassium mirror (THF and C_6D_6). NMR spectra were measured on a Bruker Avance-600 or a JEOL AL-300 spectrometer. Chemical shifts (δ) are reported in ppm and are referenced against solvent signals (^{1}H, ^{13}C) or external standards ($Al(NO_3)_3/D_2O$ (^{27}Al) or LiBr/D_2O (^{7}Li)). Mass spectra were recorded on a Bruker micrOTOF mass spectrometer equipped with an AMR DART-SVP ion source using He as an ionization gas. Melting points were determined on a Yanaco micro melting point apparatus and uncorrected. Elemental analyses were performed at the microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

Synthesis of alumole **1**: Mes*$AlCl_2$ (**2**) (0.46 g, 1.3 mmol) was added to a toluene solution (5 mL) of 1,4-dilithiobutadiene **3** (0.40 g, 1.3 mmol) at room temperature. The solution was stirred for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in *n*-hexane and filtered. The filtrate was concentrated and stored at −30 °C to afford **1** as colorless crystals (0.28 g, 0.64 mmol, 48 %). m.p. 113–115 °C. ^{1}H NMR (600 MHz, C_6D_6): $\delta = 1.09$ (t, $J = 7.5$ Hz, 6 H, α-CH_2CH_3), 1.12 (t, $J = 7.5$ Hz, 6 H, β-CH_2CH_3), 1.30 (s, 9 H, *p*-C(CH_3)$_3$), 1.55 (s, 18 H, *o*-C(CH_3)$_3$), 2.46 (q, $J = 7.5$ Hz, 4 H, β-CH_2CH_3), 2.48 (q, $J = 7.5$ Hz, 4 H, α-CH_2CH_3), 7.48 ppm (s, 2 H, Ar*H*); ^{13}C NMR (151 MHz, C_6D_6): $\delta = 15.16$ (β-CH_2CH_3), 17.54 (α-CH_2CH_3), 21.99 (β-CH_2CH_3), 24.81 (α-CH_2CH_3), 31.47 (*o*-C(CH_3)$_3$), 31.47 (*p*-C(CH_3)$_3$), 34.83 (*p*-*C*(CH_3)$_3$), 38.22 (*o*-*C*(CH_3)$_3$), 121.12 (*m*-Ar(*C*)), 131.68 (*ipso*-Ar(*C*)), 144.03 (Al−*C*=C), 150.66 (*p*-Ar(*C*)), 156.42 (Al−C=*C*), 158.81 ppm (*o*-Ar(*C*)); No signal was observed in the ^{27}Al NMR spectrum even after a long-time measurement for a few days; HRMS (DART-TOF, positive-mode) *m*/*z* calcd for $C_{30}H_{50}Al$ ([M + H]$^+$): 437.3722, found: 437.3691. Elemental analysis calcd (%) for $C_{30}H_{49}Al$ (**1**): C, 82.51; H, 11.31; found: C, 82.25; H, 11.57.

Synthesis of [Li^+(thf)]$_2$[**1**$^{2-}$]: Lithium (0.015 g, 2.1 mmol) was added to a THF solution (1.5 mL) of alumole **1** (0.16 g, 0.37 mmol) at room temperature, and the mixture was stirred for 12 h. Excess lithium was removed by filtration, and the filtrate was concentrated and stored at −30 °C to afford [Li^+(thf)]$_2$[**1**$^{2-}$] as orange crystals (0.089 g, 0.15 mmol, 41 %). m.p. 149 °C (dec.). ^{1}H NMR (600 MHz, C_6D_6): $\delta = 1.17$–1.20 (m, 8 H, OCH_2CH_2), 1.33 (t, $J = 7.5$ Hz, 6 H, β-CH_2CH_3), 1.41 (t, $J = 7.5$ Hz, 6 H, α-CH_2CH_3), 1.51 (s, 9 H, *p*-C(CH_3)$_3$), 2.11 (s, 18 H, *o*-C(CH_3)$_3$), 2.85 (q, $J = 7.5$ Hz, 4 H, β-CH_2CH_3), 2.89 (q, $J = 7.5$ Hz, 4 H, α-CH_2CH_3), 3.30–3.32 (m, 8 H, OCH_2CH_2), 7.76 ppm (s, 2 H, Ar*H*); ^{13}C NMR (151 MHz, C_6D_6): $\delta =$ 19.84 (β-CH_2CH_3), 21.43 (β-CH_2CH_3), 21.99 (α-CH_2CH_3), 25.26 (OCH_2CH_2), 26.27 (α-CH_2CH_3), 31.88 (*p*-C(CH_3)$_3$), 34.86 (*o*-C(CH_3)$_3$), 35.13 (*p*-*C*(CH_3)$_3$), 38.65 (*o*-*C*(CH_3)$_3$), 68.63 (OCH_2CH_2), 102.62 (Al−*C*=C), 112.56 (Al−C=*C*), 119.23 (*m*-Ar(*C*)), 142.02 (*ipso*-Ar(*C*)), 147.93 (*p*-Ar(*C*)), 159.72 ppm (*o*-Ar(*C*)); ^{7}Li NMR (117 MHz, C_6D_6): $\delta = -5.96$ ppm; ^{7}Li NMR (117 MHz, THF): $\delta = -5.84$ ppm; ^{27}Al NMR (156 MHz, C_6D_6): $\delta = 198$ ppm (s, broad, $\Delta w_{1/2} =$ ca. 7000 Hz); MS (DART-TOF, positive-mode) *m*/*z* 437 ([*M*-[Li(thf)]$_2$]$^+$). Elemental analysis calcd (%) for [Li^+(thf)]$_2$[**1**$^{2-}$]: C, 76.73; H, 11.02; found: C, 75.96; H, 11.20 (Because [Li^+(thf)]$_2$[**1**$^{2-}$] is highly air and moisture sensitive, the elemental analysis was unsatisfactory.)

Computational details: Geometry optimization and frequency calculations were carried out using the B3PW91 functional with 6-31G(d) (**1**, **1**$^{2-}$, and [Li^+(thf)]$_2$[**1**$^{2-}$]) or 6-311 + G(2df) (**4**, **5**, **6**, **4**$^{2-}$, and Li^+_2[**4**$^{2-}$]) basis sets. The optimized geometries of **1** and [Li^+(thf)]$_2$[**1**$^{2-}$] agree well with those found in the crystal structures. Single point energies and NICS values were calculated at the B3PW91/6-311 + G(2df) level using the optimized geometries. The Gaussian 09 program package was used for all the calculations.[19]

Received: May 14, 2013
Revised: May 29, 2013
Published online: August 8, 2013

Keywords: aluminum · density functional calculations · heterocycles · lithium · structure elucidation

[1] H. Braunschweig, T. Kupfer, *Chem. Commun.* **2011**, *47*, 10903.

[2] H. Braunschweig, V. Dyakonov, J. O. C. Jimenez-Halla, K. Kraft, I. Krummenacher, K. Radacki, A. Sperlich, J. Wahler, *Angew. Chem.* **2012**, *124*, 3031; *Angew. Chem. Int. Ed.* **2012**, *51*, 2977.

[3] a) J. J. Eisch, J. E. Galle, S. Kozima, *J. Am. Chem. Soc.* **1986**, *108*, 379; b) C.-W. So, D. Watanabe, A. Wakamiya, S. Yamaguchi, *Organometallics* **2008**, *27*, 3496; c) H. Braunschweig, C.-W. Chiu, J. Wahler, K. Radacki, T. Kupfer, *Chem. Eur. J.* **2010**, *16*, 12229.

[4] Various aromaticity indexes, including nucleus-independent chemical shifts (NICS), harmonic oscillator model of aromaticity (HOMA), and aromatic stabilization energies, have been calculated for parent alumole **4**; these indexes suggest that the antiaromaticity of **4** is much lower compared to that of the parent borole (HBC_4H_4). Similarly, the small positive NICS(0) value of **1** (+2.78 ppm) indicates the quite low antiaromaticity of **1**; a) P. von Ragué Schleyer, P. K. Freeman, H. Jiao, B. Goldfuss, *Angew. Chem.* **1995**, *107*, 332; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 337; b) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; c) M. K. Cyrañsky, T. M. Krygowsky, A. R. Katritzky, P. v. R. Schleyer, *J. Org. Chem.* **2002**, *67*, 1333; d) H. Fallah-Bagher-Shaidaei, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Org. Lett.* **2006**, *8*, 863; e) D. B. Chesnut, L. J. Bartolotti, *Chem. Phys. Lett.* **2000**, *316-331*, 175; f) J. Poater, X. Fradera, M. Duran, M. Solà, *Chem. Eur. J.* **2003**, *9*, 400.

[5] Recently, syntheses and properties of dibenzogallole derivatives have been reported: T. Matsumoto, K. Tanaka, Y. Chujo, *J. Am. Chem. Soc.* **2013**, *135*, 4211.

[6] a) H. Hoberg, R. Krause-Göing, *J. Organomet. Chem.* **1977**, *127*, C29; b) C. Krüger, J. C. Sekutowski, H. Hoberg, R. Krause-Göing, *J. Organomet. Chem.* **1977**, *141*, 141.

[7] Intermediary formation of alumoles: a) E. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai, T. Takahashi, *J. Am. Chem. Soc.* **1996**, *118*, 9577; b) Z. Xi, P. Li, *Angew. Chem.* **2000**, *112*, 3057; *Angew. Chem. Int. Ed.* **2000**, *39*, 2950; c) C. Zhao, P. Li, Z. Xi, *Chem. Eur. J.* **2002**, *8*, 4292; d) J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc.* **1962**, *84*, 1501; e) J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc.* **1966**, *88*, 2976; f) H. Hoberg, W. Richter, *J. Organomet. Chem.* **1980**, *195*, 347.

[8] A. H. Cowley, F. P. Gabbaï, A. Decken, *Angew. Chem.* **1994**, *106*, 1429; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1370.

[9] A. Wakamiya, K. Mishima, K. Ekawa, S. Yamaguchi, *Chem. Commun.* **2008**, 579.

[10] R. J. Wehmschulte, P. P. Power, *Inorg. Chem.* **1996**, *35*, 3262.

[11] L. Liu, W.-X. Zhang, Q. Luo, H. Li, Z. Xi, *Organometallics* **2010**, *29*, 278.

[12] The UV/Vis spectrum of **1** in *n*-hexane has an absorption at $\lambda_{max} = 318$ nm ($\varepsilon = 2.1 \times 10^3$), which is at a much shorter wavelength than those of the previously reported borole derivatives. The hypsochromic shift may be related with the much lower antiaromaticity of **1** compared to those of the borole derivatives. A relationship between the UV/Vis absorption properties and the antiaromaticity of pentaarylborole derivatives has been noted: H. Braunschweig, I. Fernández, G. Frenking, T. Kupfer, *Angew. Chem.* **2008**, *120*, 1977; *Angew. Chem. Int. Ed.* **2008**, *47*, 1951.

[13] Crystallographic data for **1**: triclinic, space group *P*-1, $a = 11.3385(7)$, $b = 14.0940(13)$, $c = 19.1071(14)$ Å, $\alpha = 70.677(4)$, $\beta = 88.960(3)$, $\gamma = 80.284(3)°$, $V = 2837.7(4)$ Å^3, $Z = 4$, R_1 ($I > 2\sigma(I)$) = 0.0538, wR_2 (all data) = 0.1512; Crystallographic data for [Li^+(thf)]$_2$[**1**$^{2-}$]: tetragonal, space group $P4_32_12$, $a = b = 10.4548(3)$, $c = 34.1514(10)$ Å, $V = 3732.9(2)$ Å^3, $Z = 4$, R_1 ($I > 2\sigma(I)$) = 0.0375, wR_2 (all data) = 0.1015. CCDC 915171 (**1**) and 915172 ([Li^+(thf)]$_2$[**1**$^{2-}$]) 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.

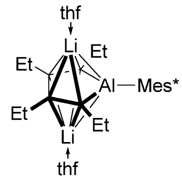
[14] W. Uhl, E. Er, A. Hepp, J. Kösters, J. Grunenberg, *Organometallics* **2008**, *27*, 3346.

[15] Reduction of a pentaphenylalumole/Et_2O complex with lithium and subsequent treatment with $NiBr_2$ afforded a unique triple-decker dinuclear nickel complex that does not contain aluminum: H. Hoberg, R. Krause-Göing, C. Krüger, J. C. Sekutowski, *Angew. Chem.* **1977**, *89*, 179; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 183.

[16] The equilibrium structures of **4**$^{2-}$ and **1**$^{2-}$ are comparable to those of phospholes and heavier group 14 heterole anions. In the

cases of these heteroles, the pyramidal forms and the planar forms correspond to the energy minima and the first-order saddle points on the potential surfaces, respectively: a) W. P. Freeman, T. D. Tilley, F. P. Arnold, A. L. Rheingold, P. K. Gantzel, *Angew. Chem.* **1995**, *107*, 2029; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1887; b) W. P. Freeman, T. D. Tilley, L. M. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **1996**, *118*, 10457; c) L. Nyulászi, *Chem. Rev.* **2001**, *101*, 1229.

[17] A *closo*-7-vetex $AlLi_2C_4$ cluster description as shown below has been proposed for the bonding situation of $[Li^+(thf)]_2[\mathbf{1}^{2-}]$ by a reviewer. The cluster core consists of 16 skeletal electrons (3 electrons from each of the CEt units, 2 electrons from the AlMes* unit, and two negative charges), which agrees with the pentagonal bipyramidal structure as observed in the crystal and optimized structures of $[Li^+(thf)]_2[\mathbf{1}^{2-}]$.



[18] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.

[19] Gaussian 09 (Revision C.01), M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2010**. For full reference, see Supporting Information.