Synthesis of an Aluminatacyclopropene Derivative with an AlC_2 Heterocycle and an Exocyclic AlR_2 Substituent: Evidence for a Nonclassical Bonding Situation

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An aluminatacyclopropene derivative (**2**) was synthesized by the reaction of tetrakis[bis(trimethylsilyl)methyl]dialane(4) **1** with lithium phenylethynide, of which the anionic carbon atom was inserted into the Al−Al single bond. By the interaction of the second ethynide carbon atom with one of the aluminum atoms a three-membered heterocycle resulted containing an Al atom and a C═C double bond. As shown by a crystal structure determination, hyperconjugation makes an important contribution to the bonding in the anionic heterocyclic part of the molecule. The exocyclic Al−C bond to the unsaturated Al atom is very short (188.6 pm), while one of the endocyclic Al−C bonds is lengthened to 205.2 pm. Quantum chemical calculations verified a 3c2e AlCAl bond and a bonding situation, that is similar to that observed before in some boron compounds.

Introduction

For a long time, boron seemed to be a singular element in the third main-group, and an essential part of its chemistry was determined by the formation of inorganic and organic compounds, which required a delocalized bonding description for a complete understanding. In the past decade, however, more and more compounds of aluminum and its heavier homologues were synthesized, which impressively showed a strong similarity to the chemistry of boron. Among these were cluster compounds such as the icosahedral anion $[Al_{12}iBu_{12}]^{2-}$,[1] the tetrahedral E_4R_4 derivatives,[2] and carbaalanes, which possess large clusters of exclusively aluminum and carbon atoms and obey Wade's rules for *closo* or *arachno* configurations [$Al_8Me_8(CCH_2C_6H_5)_5H$, for instance].[3] Tetrakis[bis(trimethylsilyl)methyldielement(4) derivatives with Al−Al,[4] Ga−Ga,[5] and In−In single bonds[6] and the elements aluminum, gallium, and indium in an unusual low oxidation state of +II[7] seemed to be appropriate starting materials for the syntheses of further compounds with a delocalized bonding situation. But although we observed six different types of reaction[8] and isolated many compounds with a broad variety of structures, all these products could be described completely by simply using the classic valence-dash formula. One of the most important reactions was the insertion of atoms, molecules, or molecular fragments into the E−E single bonds. Isonitriles inserted with their terminal carbon atoms, and by the interaction of the nitrogen lone pair with an aluminum[9] or gallium atom,[10] heterocycles were formed. Only the diindium derivative did not give the insertion products, but yielded adducts, in which two isonitrile molecules were weakly bonded to the coordinatively unsaturated indium atoms.[11] Alkynide anions are isoelectronic to isonitriles, and we wish to report here on the reaction of the dialuminum compound with lithium phenylethynide, which gave a product with a delocalized bonding situation similar to organoboron compounds reported before in the literature.[12]

Results and Discussion

The dialuminum compound **1** and lithium phenylethynide did not react at room temperature in *n*-pentane as a solvent, but upon addition of a small quantity of the chelating Lewis base *N*,*N*,*N*′,*N*′-tetramethylethyl-

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[1] Hiller, W.; Klinkhammer, K.-W.; Uhl, W.; Wagner, J. *Angew. Chem.* **1991**, *103*, 182; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 179.

[2] (a) Uhl, W. *Rev. Inorg. Chem.* **1998**, *18*, 240. (b) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem.* **1996**, *108*, 141; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 129.

[3] (a) Uhl, W.; Breher, F. *Angew. Chem.* **1999**, *111*, 1578; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1477. Aluminium atoms in borane or carbaborane clusters: (b) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046. (c) Morrison, C. A.; Smart, B. A.; Brain, P. T.; Rankin, D. W. H.; Downs, A. J. *J. Chem. Soc., Dalton Trans.* **1998**, 2155.

[4] Uhl, W. *Z. Naturforsch., B. Chem. Sci.* **1988**, *43*, 1113.

[5] Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289.

[6] Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 139.

[7] Further compounds of this type were published later on: (a) Wiberg, N.; Amelunxen, K.; Nöth, H.; Schmidt, M.; Schwenk, H. *Angew. Chem.* **1996**, *108*, 110; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 65. (b) Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J. *Organometallics* **1998**, *17*, 5431. (c) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983. (d) He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem.* **1993**, *105*, 761; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 717. (e) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070. (f) Saxena, A. K.; Zhang, H.; Maguire, J. A.; Hosmane, N. S.; Cowley, A. H. *Angew. Chem.* **1995**, *107*, 378; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 332.

[8] Uhl, W. *Coord. Chem. Rev.* **1997**, *163*, 1.

[9] (a) Uhl, W.; Schütz, U.; Hiller, W.; Heckel, M. *Chem. Ber.* **1994**, *127*, 1587. (b) Uhl, W.; Schütz, U.; Pohl, S.; Saak, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 373.

[10] Uhl, W.; Hahn, I.; Schütz, U.; Pohl, S.; Saak, W.; Martens, J.; Manikowski, J. *Chem. Ber.* **1996**, *129*, 897.

[11] Uhl, W.; Hannemann, F.; Wartchow, R. *Organometallics* **1998**, *17*, 3822.

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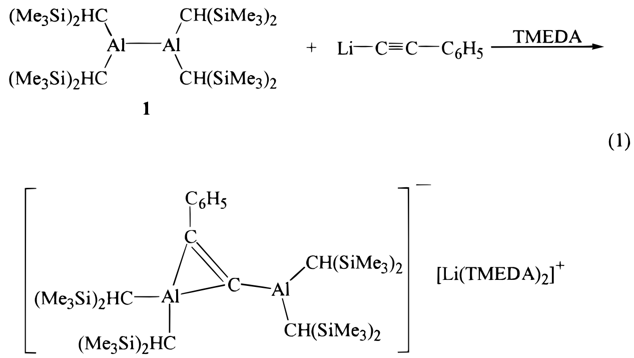
enediamine (TMEDA), the mixture rapidly became red and a dark red solid of the product precipitated (eq 1). It was filtered off and recrystallized from diethyl ether to give compound **2** with the counterion $[Li(TMEDA)_2]^+$ in a yield of about 50%. The product is quite stable in THF solution at room temperature, while in diethyl ether small amounts of unknown secondary products are formed slowly. The NMR spectroscopic characterization clearly showed that a product was obtained that was similar to the insertion product of one isonitrile molecule into the Al−Al bond[9] and had an aluminatacyclopropene structure with an exocyclic dialkylaluminum substituent. Three singlets were observed for the $SiMe_3$ groups with an intensity ratio of 1:2:1. The most intensive resonance was attributed to the $CH(SiMe_3)_2$ groups of the tricoordinated, exocyclic aluminum atom, while the $SiMe_3$ substituents at the tetracoordinated aluminum atom of the heterocycle became diastereotopic, as often observed before in tetracoordinated bis(trimethylsilyl)methyl aluminum compounds.[13] Two signals were detected for the methine protons with a large difference of their chemical shifts ($\delta = -0.39$ and -1.16 ppm). The first one is in the characteristic range of compounds with tricoordinated aluminum atoms, while the high-field shift is indicative for tetracoordinated, coordinatively saturated Al atoms.[8,9,13] A similar pattern was observed in the ^{13}C NMR spectrum. The carbon atoms attached to the tetracoordinated aluminum atoms showed a broad resonance at $\delta = 1.9$, while those of the unsaturated aluminum atom were observed at $\delta = 8.1$. The first resonance is in a characteristic range, but the second one is shifted to higher field compared with further bis(trimethylsilyl)methyl compounds containing tricoordinated aluminum atoms (e.g., **1**: $\delta = 17.7$;[4] $AlR_xR'_{3-x}$ [$R' = CH(SiMe_3)_2$, $x = 0$ or 1] in a narrow range between $\delta = 11$ and 13[13g−j]). This unusual shift may be caused by the particular bonding situation in the anion of **2** with a hyperconjugative electron transfer to that aluminum atom, as discussed below. Two weak resonances at 220.4 and 210.8 ppm were assigned to the atoms of the C═C double bond. The last one is broad and deviates only slightly from background noise. It should be discussed with some reservation, although the occurrence of both resonances with a difference of 10 ppm was predicted by theory (see below). The carbon atom attached to both aluminum atoms should be observed at a higher field, which is in accordance with the broad resonance at 210.8 ppm. Its broadness may be caused by the contact to two chemically different aluminum atoms possessing a high quadrupole moment ($I = 5/2$).



1

(1)

2

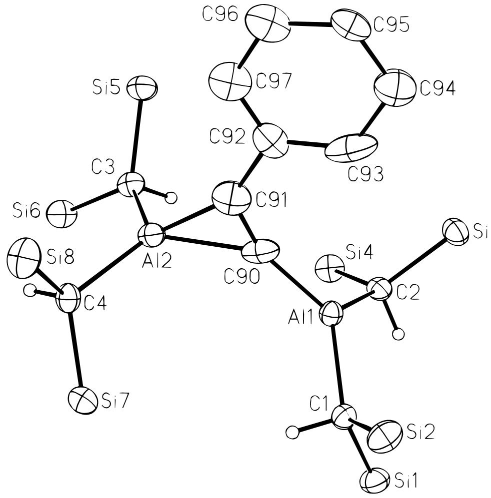


Figure 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å) and angles (deg): Al1−C90 1.886(3); Al1−C1 1.995(2), Al1−C2 1.987(3), Al2−C90 2.052(3), Al2−C91 1.951(3); Al2−C3 2.018(3), Al2−C4 2.007(3), C90−C91 129.4(4), C91−C92 154.5(4), C90−Al1−C1 120.6(1), C90−Al1−C2 122.3(1), C1−Al1−C2 116.4(1), Al1−C90−Al2 134.2(2), Al1−C90−C91 158.8(3), C90−Al2−C91 37.6(1), C90−Al2−C3 117.8(1), C90−Al2−C4 122.7(1), C91−Al2−C3 119.4(1), C91−Al2−C4 120.5(1), Al2−C91−C90 75.5(2), Al2−C90−C91 66.9(2), Al2−C91−C92 154.8(3), C90−C91−C92 129.6(3).

The aluminatacyclopropene structure with a C═C double bond and an exocyclic dialkylaluminum substituent was verified by a crystal structure determination (Figure 1). Similar compounds with AlC_2 saturated or unsaturated three-membered heterocycles have, to the best of our knowledge, not been characterized before by crystal structure determinations, but few were postulated as reactive intermediates.[14] Bora[15] and bo-

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(12) (a) Wieczorek, C.; Allwohn, J.; Schmidt-Lukasch, G.; Hunold, R.; Massa, W.; Berndt, A. *Angew. Chem.* **1990**, *102*, 435; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 398. (b) Steiner, D.; Balzereit, C.; Winkler, H.-J.; Stamatis, N.; Hofmann, M.; Schleyer, P. v. R.; Massa, W.; Berndt, A. *Angew. Chem.* **1994**, *106*, 2391; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2303. (c) Balzereit, C.; Kybart, C.; Winkler, H.-J.; Massa, W.; Berndt, A. *Angew. Chem.* **1994**, *106*, 1579; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1487. (d) Höfner, A.; Ziegler, B.; Massa, W.; Berndt, A. *Angew. Chem.* **1989**, *101*, 188; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 186. (e) Willershausen, P.; Schmidt-Lukasch, G.; Kybart, C.; Allwohn, J.; Massa, W.; McKee, M. L.; Schleyer, P. v. R.; Berndt, A. *Angew. Chem.* **1992**, *104*, 1417; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1384. Review: (f) Berndt, A.; *Angew. Chem.* **1993**, *105*, 1034; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 985.

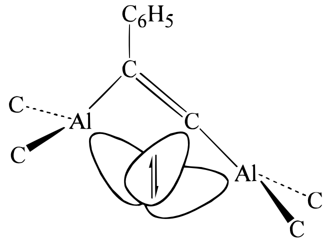
(13) (a) Uhl, W.; Layh, M. *Z. Anorg. Allg. Chem.* **1994**, *620*, 856. (b) Uhl, W.; Koch, M.; Heckel, M.; Hiller, W.; Karsch, H. H. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1427. (c) Uhl, W.; Koch, M.; Vester, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 359. (d) Uhl, W.; Koch, M.; Wagner, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 249. (e) Uhl, W.; Schnepf, E.; Wagner, J. *Z. Anorg. Allg. Chem.* **1992**, *613*, 67. (f) Uhl, W.; Vester, A. *Chem. Ber.* **1993**, *126*, 941. (g) Layh, M.; Uhl, W. *Polyhedron* **1990**, *9*, 277. (h) Uhl, W. *Z. Anorg. Allg. Chem.* **1989**, *579*, 75. (i) Uhl, W.; Schnepf, J. E. O. *Z. Anorg. Allg. Chem.* **1991**, *595*, 225. (j) Uhl, W.; Vester, A.; Fenske, D.; Baum, G. *J. Organomet. Chem.* **1994**, *464*, 23.

(14) (a) Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 6257. (b) Tse, J. S.; Morris, H. *J. Chem Soc., Chem. Commun.* **1989**, 78. (c) Mitchell, S. A.; Simard, B.; Rayner, D. M.; Hackett, D. A. *J. Phys. Chem.* **1988**, *92*, 1655. Cited literature.

(15) (a) Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 2526. (b) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847.

rata cyclopropenes[16] containing heterocycles formed by one boron atom and two carbon atoms were, however, reported in the literature. But some important structural parameters of **2** showed that this simple picture of a three-membered heterocycle is an oversimplification. The endocyclic C−C double bond of **2** [C90−C91 = 129.4(4) pm] is a little shorter than the standard value of C═C double bonds,[17] but similar to those observed for many cyclopropene derivatives.[18] The Al−C distances Al2−C90 and Al2−C91 in the ring differ by 10 pm. A short one is observed to the carbon atom C91 bearing the phenyl group [195.1(3) pm], while the second bond including C90, which is attached to the exocyclic atom Al1, is lengthened to 205.2(3) pm. The inner ring angle at Al2 is very acute (37.6°), while those at C90 and C91 are 66.9° and 75.5°. The angle Al1−C90−C91 is almost linear (158.8°); the second exocyclic angle including the C═C double bond is 129.6° (C90−C91−C92). The bond Al1−C90 to the coordinatively unsaturated exocyclic Al atom is very short [188.6(3) pm]. Similar short distances below 190 pm were observed in a few organoaluminum compounds containing electron-withdrawing substituents and small alkyl groups; in some cases they seemed to be caused by a disorder.[19] The normal of the plane Al1C1C2 is almost exactly perpendicular to that of the heterocycle (89.3°), and the empty p-orbital at Al1 is parallel to the bond Al2−C90 of the ring. Al1 is almost planar coordinated by the atoms C90, C1, and C2 (sum of the angles 359.8°). Thus, in accordance with the results of the quantum chemical calculations discussed below, the bonding situation in compound **2** is best described by a 3c2e bond including the atoms Al1, C90, and Al2, as schematically shown in Scheme 1. This multicenter bonding strengthens the exocyclic bond Al1−C90 by some π contribution and weakens the endocyclic σ bond between Al2 and C90. Similar delocalized bonds were observed in heterocyclic boron compounds with exocyclic, coordinatively unsaturated boron atoms.[12] The bonding situation in these derivatives corresponds to a hyperconjugative interaction between an endocyclic B−C or Al−C σ bond and the empty p-orbitals at the exocyclic boron or aluminum atoms.

Scheme 1



Both conventional Hartree−Fock and density functional theory (in particular the hybrid functional approach Becke3LYP) methods were employed to optimize several models of the anion in compound **2**. To assess the reliability of these approaches, a series of calculations was performed with two different basis sets (6-31G* and 6-31+G(2d,p)) and varying substituents of the model compounds (**2a**−**2d**). Selected bond lengths and angles of these calculated molecules are summarized in Table 1. All methods show a quite good agreement with the experimental data (Figure 1), and it is interesting to note that the larger basis set does not influence the deviation from the experimentally determined structure. Generally, the Al−C bond lengths are calculated slightly too short, while the central C−C double bond is too long. It is furthermore surprising to find that the application of the HF methods gives an almost equally good description of the system compared to the B3LYP approach. An important feature of the X-ray structure is the bond angle φ including both carbon atoms of the C═C double bond and the exo Al atom Al1 (Scheme 2), which is schematically defined in Table 1. If the angle φ is larger than 180°, both Al atoms approach, while an angle smaller than 180° such as experimentally determined (158.8°) causes a larger distance between the endo and exo Al atoms. Most calculations (both at the HF and B3LYP level of theory) fail to reproduce this structural motif; they predict the endo group to be directed toward the second aluminum atom. However, an increasing steric demand of both aluminum-containing groups leads to smaller angles and a better approach to the real structure (see Table 1). But only the calculations with the Hartree−Fock method of the largest model compounds (**2c**, **2d**) give the correct orientation. Clearly, the situation with φ smaller than 180° and longer Al−Al distances as observed in **2** is caused mainly by a steric interaction between the very bulky substituents. However, as shown in Table 1, both quantum chemical approaches are suitable for the analysis of the bonding situation in compound **2**. While it can be expected to give good results with the DFT methods, it is surprising to find an almost equally well-suited description when utilizing Hartree−Fock theory.

To completely characterize and understand the bonding situation of this unusual molecule, NBO population analyses were performed for our largest models **2d** at HF/6-31G* and **2c** at the Becke3LYP/6-31G* level. The bonding situation can best be described by the occurrence of a two-electron three-center Al−C−Al bond (Scheme 1). The corresponding molecular orbital possesses a high p-orbital character and is formed mainly by the C p_z-orbital and to a somewhat lesser extent by both aluminum p_x-orbitals. The composition of the DFT-

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(16) Kropp, M. A.; Schuster, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 2316.

(17) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985.

(18) Recent examples: (a) Klimova, E. I.; Ramirez, L. R.; Klimova-Berestneva, T.; Garcia, M. M.; Moreno-Esparza, R.; Toledano, S. A.; Toscano, R. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1998**, 499. (b) Schulte, N.; Möller, M. H.; Rodewald, U.; Wurthwein, E.-U. *Chem. Ber.* **1994**, *127*, 1287. (c) Ting, P.-C.; Lin, Y.-C.; Lee, G.-H.; Cheng, M.-C.; Wang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6433. (d) Ting, P.-C.; Lin, Y.-C.; Cheng, M.-C.; Wang, Y. *Organometallics* **1994**, *13*, 2150. (e) Golobish, T. D.; Dailey, W. P. *J. Org. Chem.* **1995**, *60*, 7865.

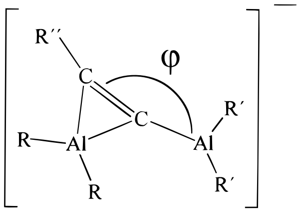
(19) (a) Smith, J. M.; Bott, S. G. *J. Chem. Soc., Chem. Commun.* **1996**, 377. (b) Herzog, A.; Roesky, H. W.; Jäger, F.; Steiner, A.; Noltemeyer, M. *Organometallics* **1996**, *15*, 909. (c) Corey, E. J.; Sarshar, S.; Bordner, J. *J. Am. Chem. Soc.* **1992**, *114*, 7938. (d) Atwood, J. L.; Gardiner, M. G.; Jones, C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1996**, 2487. (e) Atwood, D.; Jegier, J. *Inorg. Chem.* **1996**, *35*, 4277. (f) Harlan, C. J.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1997**, 637. (g) Harlan, C. H.; Gillan, E. G.; Bott, S. G.; Barron, A. R. *Organometallics* **1996**, *15*, 5479. (h) Atwood, J. L.; Crissinger, K. D.; Rogers, R. D. *J. Organomet. Chem.* **1978**, *155*, 1. (i) Scollary, G. R. *Aust. J. Chem.* **1978**, *31*, 411. (j) Harlan, C. J.; Mason, M. R.; Barron, A. R.; *Organometallics* **1994**, *13*, 2957. (k) Hitchcock, P. B.; Smith, J. D.; Thomas, K. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1433. (l) Kim, N. E.; Nelson, N. J.; Shriver, D. F. *Inorg. Chim. Acta* **1973**, *7*, 393. (m) Bott, S. G.; Elgamal, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 1796.

Table 1. Comparison of Important Structural Data of Aluminatacyclopropene Anions Analogous to 2 Obtained Experimentally and by Quantum Chemical Calculations (numbering of the atoms according to Figure 1, distances in pm, angles in deg)

method	R	R′	R″	Al1−C90	C90═C91	Al2−C91	Al2−C90	φ[a]	C90═C91−R″	C90−Al2−C91
X-ray (**2**)	$CH(SiMe_3)_2$	$CH(SiMe_3)_2$	Ph	188.6	129.4	195.1	205.2	158.8	129.6	37.6
HF/6-31G* (**2a**)	Me	H	Me	183.7	131.6	194.5	210.7	190.4	127.2	37.6
HF/6-31G* (**2b**)	Me	Me	Me	184.0	132.1	193.6	208.9	187.5	126.8	38.1
B3LYP/6-31G* (**2b**)	Me	Me	Me	185.8	132.7	195.8	212.5	195.2	127.8	37.6
HF/6-31+G(2d,p) (**2b**)	Me	Me	Me	184.1	132.2	193.1	209.1	188.6	126.5	38.1
B3LYP/6-31+G(2d,p) (**2b**)	Me	Me	Me	185.2	132.8	194.6	211.4	193.8	127.6	37.9
HF/6-31G* (**2c**)	Me	$CH(SiH_3)_2$	Me	185.1	132.8	191.4	204.1	176.8	127.0	39.1
B3LYP/6-31G* (**2c**)	Me	$CH(SiH_3)_2$	Me	186.2	133.1	193.7	207.9	190.9	128.1	38.5
HF/6-31G* (**2d**)	$CH(SiH_3)_2$	$CH(SiH_3)_2$	Me	184.9	133.4	191.3	203.7	165.4	126.9	39.3

[a] φ is defined as shown in Scheme 2; an angle > 180° means that both Al atoms are at the same site of the C═C double bond.

Scheme 2



calculated orbital of **2c** is 66% C90 ($2p_z$-orbital coefficient 0.841), 15% Al1 (exocyclic, $3p_x$ coefficient −0.822), and 19% Al2 ($3p_x$ coefficient 0.897). The HF data obtained for **2d** are similar [76% C90 (0.807), 9% Al1 (−0.716), and 15% Al2 (0.890)].

In accordance with the results of the crystal structure determination, the endocyclic interaction between Al2 and C90 is thus weaker than expected for a classic localized bonding description, while the bond Al1−C90 to the exocyclic, coordinatively unsaturated Al atom is strengthened and has some π character. The calculated bond order between Al1 and C90 (0.753) in **2d** is considerably higher than that of any other Al−C bond in the molecule (C90−Al2 0.499, C91−Al2 0.546, Al1−C(1,2) 0.423, Al2−C(3,4) 0.409), indicating the strengthening of the bonding interaction between these two atoms (only the ratio between bond orders may be discussed; the absolute values are not really significant). The bond order between both aluminum atoms is also significant (0.111).

The energetic significance and contribution of this three-center molecular orbital to the total energy of the anion was proved at the HF/6-31G* level of theory by comparison between the minimum structure **2b** and a conformation (**2e**) in which the exo Al1C1C2 group was in plane with the triangular heterocycle. The structure of **2e** was calculated by constraining the angle Al1−C90−C91 to that value found in **2b** and fixing the dihedral angle C1−Al1−C90−Al2 to 180°. An additional molecular geometry, **2f**, was optimized by releasing the fixed bond angle. Both new structures possess one imaginary frequency. Analyses of these negative eigenvalues indicate that the obtained geometries are transition states for the rotation of the Al1C1C2 group around the Al1−C90 bond. The energetic difference between the minimum structure and **2e** (with an almost linear Al1−C90−C91 angle) is 57 kJ/mol. Even after relaxation of the bond angle, **2f** (bond angle 137°) is still 35 kJ/mol less stable than **2b**. It seems to be clear from these results that the anion of **2** is significantly stabilized by the formation of the two-electron three-center bond.

The calculation of the ^{13}C NMR data for the model compound **2d** (HF/6-31G* geometry) at the B3LYP/6-31+G** level gave almost correct relative chemical shifts, but the absolute values were underestimated by about 25 ppm, which is caused by systematic errors in the calculations and the different substitution pattern in comparison with compound **2**. Two low-field signals at 182.2 (C90) and 191.8 ppm (C91) were calculated. The difference of 10 ppm was also observed in the experimental spectrum (210.8 and 220.4 ppm). Thus, the assignment of the experimental resonances seems to be reasonable. Two sets of two signals were obtained for the four bis(silyl)methyl carbon atoms at −18.3/−21.3 ppm and −18.8/−21.5 ppm. The former signals correspond to the two carbon atoms at Al1, the latter ones to those at Al2. As expected, only one resonance was detected for each set of chemically equivalent carbon atoms in solution. The occurrence of two signals in the theoretical spectrum originates from the calculated structure, in which these atoms are no longer equivalent due to the different orientation of their substituents.

Experimental Section

All procedures were carried out under purified argon. *n*-Pentane was dried over $LiAlH_4$; diethyl ether, over Na/benzophenone. Commercially available phenylethyne and *n*-butyllithium (Aldrich) were used without further purification. TMEDA was distilled over sodium and stored over molecular sieves. Compound **1** was synthesized as described in ref 1.

[Bis(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)lithium(1+)][1,1-bis{bis(trimethylsilyl)methyl}-2-{bis[bis(trimethylsilyl)methyl]aluminum}-3-phenyl-1-aluminata-2-cyclopropene(1−)], 2·Et_2O. Phenylethyne (0.016 mL, 0.149 mmol) was dissolved in 20 mL of *n*-pentane and treated at 0 °C with 0.093 mL (0.149 mmol) of a 1.6 M solution of *n*-butyllithium in *n*-hexane. The suspension was stirred at room temperature for 1 h and cooled to 0 °C. A solution of compound **1** (0.103 g, 0.149 mmol) in 20 mL of *n*-pentane was added. After 10 min of stirring the mixture was treated with 0.2 mL of TMEDA. A suspension with a dark red precipitate was formed, which was filtered after 16 h. The solid was dissolved in 10 mL of diethyl ether. The solution was filtered, concentrated, and cooled to −30 °C to obtain dark red crystals of the product **2**·Et_2O. Yield: 0.084 g (51%), dec (argon, sealed capillary) 142 °C. Anal. Calcd for $C_{52}H_{123}LiN_4OAl_2Si_8$ (1106.2): Al, 4.9; Li 0.63. Anal. Found: Al, 5.1; Li, 0.8. ^1H NMR (THF-d_8, 300 MHz): $\delta = 7.33$ (2 H, pseudo-d, *o*-H of phenyl), 7.01 (2 H, pseudo-t, *m*-H of phenyl), 6.75 (1 H, pseudo-d, *p*-H of phenyl), 2.31 (8 H, s, CH_2 of TMEDA), 2.15 (24 H, s, CH_3 of TMEDA), 0.12 (18 H, s, $SiMe_3$ of Al2), 0.10 (36 H, s, $SiMe_3$ of Al1), 0.04 (18 H, s, $SiMe_3$ of Al2), −0.39 (2 H, s, AlCH of Al1), −1.16 (2 H, s, AlCH of Al2). ^{13}C NMR (Et_2O-d_{10}, 75.5 MHz): δ 220.4 [C(91)═C], 210.8 [br, C(90)═C], 149.6 (ipso C of phenyl), 127.0 and 126.9 (ortho and meta C of phenyl), 123.1 (meta C of phenyl), 58.9 (CH_2 of TMEDA), 46.2 (CH_3 of TMEDA), 8.1 (C1 and C2, tricoordinated Al atom Al1), 6.2 and 5.6 ($SiMe_3$ of Al2), 5.5 ($SiMe_3$ of Al1), 1.9 (br, C3 and C4, tetracoordinated Al atom Al2). IR (CsBr plates, paraffin, cm^{-1}): 1647 w νC═C; 1582 w phenyl; 1460 vs, 1377 vs paraffin; 1289 m, 1244 s δCH_3; 1182 w, 1158 m, 1127 m, 1098 vw, 1067 w, 1030 m νCC, νCN; 1015 s δCH; 947 m, 920 m, 910 m, 891 m, 843 vs, 775 s, 762 s, 746 s, 723 s ρCH_3(Si); 698 m, 669 m ν_{as}SiC; 640 w, 615 vw, 604 w, 586 vw ν_sSiC, νAlC(?); 546 w, 529 w, 511 w, 488 w, 480 w, 459 w νAlC; 378 vw, 345 vw, 324 vw δSiC.

Crystal Structure Determination. Single crystals of **2**·Et_2O were obtained by cooling of a saturated solution in diethyl ether to −30 °C. The crystals were not dried in vacuo after isolation. The crystallographic data were collected with a STOE imaging plate diffractometer. Relevant crystal data, data collection parameters, and results of the structure refinement are summarized in Table 2. The structures were solved by direct methods and refined with the program SHELXL-93[21] by a full-matrix least-squares method based on F^2. Compound **2** crystallizes with one molecule of diethyl ether each formula unit.

Table 2. Crystal Data, Data Collection Parameters, and Structure Refinement for Compound 2

formula	$C_{52}H_{123}Al_2LiN_4OSi_8$
cryst syst	monoclinic
space group	$P2_1/n$; no. 14[20]
Z	4
temp, K	193(2)
$D_{calcd.}$, g/cm^3	1.008
a, Å	16.019(1)
b, Å	19.803(1)
c, Å	24.330(2)
β, deg	109.171(1)
V, 10^{-30} m^3	7289.9(8)
μ, mm^{-1}	0.169
cryst dimens, mm	0.44 × 0.38 × 0.34
radiation	Mo Kα; graphite monochromator
2Θ range, deg	$4 \le 2\theta \le 52$
index ranges	$-19 \le h \le 18$ $0 \le k \le 23$ $0 \le l \le 30$
scan mode	183 exposures; $\Delta\varphi = 1.2°$
no. of unique rflns	14079
no. of params	645
R1 (6033 reflns $I > 2\sigma(I)$)	0.0402
wR2 (all data)	0.0846
max./min. residual electron density, 10^{30} e/m^3	0.914/−0.281

Quantum Chemical Calculations. Several approaches with the Hartree−Fock[22] and Becke3LYP[23] methods and the 6-31G* and 6-31+G(2d,p) basis sets were used to optimize the ground-state structure and characterize the bonding situation in model compounds of the anion of compound **2**. The located structures were identified as minima or transition states by the calculation and analysis of the vibrational frequencies. All calculations were carried out with the GAUSSIAN 94 system of programs.[24] Population analysis was performed employing the NBO program,[25] and the chemical shifts were calculated with TMS as a reference by the GIAO method;[26] both are included in the GAUSSIAN program system.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository number CCDC-121668.

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(20) Hahn, T., Ed. *International Tables for Crystallography, Space Group Symmetry*, Vol. A; Kluwer Academic Publishers: Dordrecht−Boston−London, 1989.

(21) *SHELXTL PLUS REL. 4.1*; Siemens Analytical X-RAY Instruments Inc.: Madison, 1990. Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Structures*; Universität Göttingen, 1993.

(22) Hehre, W. J.; Radom, L.; Schleyer P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(23) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez C.; Pople, J. A. *Gaussian 94*; Gaussian Inc.: Pittsburgh, PA, 1995.

(25) (a) Forster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066. (c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (e) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(26) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.