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Aluminacyclopropene: Syntheses, Characterization, and Reactivity toward Terminal Alkynes

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Abstract: Reactions of LAl with ethyne, mono- and disubstituted alkynes, and diyne to aluminacyclopropene LAl[η^2-$C_2(R^1)(R^2)$] ((L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$); $R^1 = R^2 = H$, (**1**); $R^1 = H$, $R^2 = Ph$, (**2**); $R^1 = R^2 = Me$, (**3**); $R^1 = SiMe_3$, $R^2 = C{\equiv}CSiMe_3$, (**4**)) are reported. Compounds **1** and **2** were obtained in equimolar quantities of the starting materials at low temperature. The amount of C_2H_2 was controlled by removing an excess of C_2H_2 in the range from −78 to −50 °C. Compound **4** can be alternatively prepared by the substitution reaction of LAl[η^2-$C_2(SiMe_3)_2$] with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ or by the reductive coupling reaction of LAlI$_2$ with potassium in the presence of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$. The reaction of LAl with excess C_2H_2 and PhC≡CH (<1:2) afforded the respective alkenylalkynylaluminum compounds LAl(CH=CH$_2$)(C≡CH) (**5**) and LAl(CH=CHPh)(C≡CPh) (**6**). The reaction of LAl(η^2-C_2Ph_2) with C_2H_2 and PhC≡CH yielded LAl(CPh=CHPh)(C≡CH) (**7**) and LAl(CPh=CHPh)(C≡CPh) (**8**), respectively. Rationally, the formation of **5** (or **6**) may proceed through the corresponding precursor **1** (or **2**). The theoretical studies based on DFT calculations show that an interaction between the Al(I) center and the C≡C unit needs almost no activation energy. Within the AlC_2 ring the computational Al—C bond order of ca. 1 suggests an Al—C σ bond and therefore less π electron delocalization over the AlC_2 ring. The computed Al—η^2-C_2 bond dissociation energies (155−82.6 kJ/mol) indicate a remarkable reactivity of aluminacyclopropene species. Finally, the ^{1}H NMR spectroscopy monitored reaction of LAl(η^2-C_2Ph_2) and PhC≡CH in toluene-d_8 may reveal an acetylenic hydrogen migration process.

Introduction

Aluminacyclopropene, a new entry to the organoaluminum family, is exhibiting a remarkable reactivity and versatile reaction patterns.[1−3] By the reductive coupling reaction, several aluminacyclopropenes LAl[(η^2-$C_2(R^1)(R^2)$] ((L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$); R^1, R^2: SiMe$_3$, Ph) were successfully isolated and characterized.[1] This indicates an experimental access to the olefinic bond-containing AlC_2 ring compounds. For a long time such species were thought to be unstable due to their highly strained structure[4] and only assumed as reactive intermediates in the formation of 1,4-dialuminacyclohexadienes or related dimers.[5,6] In view of these reports on the proposed AlC_2 ring intermediates, the bulky chelating β-diketiminato ligand L utilized here undoubtedly protects the formed AlC_2 ring system from its ring-opening dimerization induced by the Lewis acidic Al center.[5,6]

Already in 1990 Schaefer III and co-workers demonstrated through theoretical studies that an AlC_2 ring model HAl(η^2-C_2H_2) was an energetically lower lying system than the separated AlH and C_2H_2 ($D_{HAl-C_2H_2}$ = ca. 126 kJ/mol) and therefore could be preparatively accessible.[7] However, the question is arising whether the bulkiness of the ligand (L) is responsible for the reactivity of an aluminum(I) monomer LAl[8] directly toward

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(1) Cui, C.; Köpke, S.; Herbst-Irmer, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Wrackmeyer, B. *J. Am. Chem. Soc.* **2001**, *129*, 9091−9098.
(2) Zhu, H.; Chai, J.; Ma, Q.; Jancik, V.; Roesky, H. W.; Fan, H.; Herbst-Irmer, R. *J. Am. Chem. Soc.* **2004**, *126*, 9472−9473.
(3) Zhu, H.; Chai, J.; Fan, H.; Roesky, H. W.; He, C.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M.; Merrill, W. A.; Power, P. P. *Angew. Chem.* **2005**, *117*, 5090−5093; *Angew. Chem., Int. Ed.* **2005**, *44*, 5220−5223.
(4) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Elsevier: Oxford, UK; 1982, pp 555−682.
(5) (a) Hoberg, H.; Gotor, V.; Milchereit, A.; Krüger, C.; Sekutowski, J. C. *Angew. Chem.* **1977**, *89*, 563−564; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 539−540. (b) Hoberg, H.; Aznar, F. *J. Organomet. Chem.* **1979**, *164*, C13−C15.
(6) (a) Schnöckel, H.; Leimkühler, M.; Lotz, R.; Mattes, R. *Angew. Chem.* **1986**, *98*, 929−930; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 921−922. (b) Üffing, C.; Ecker, A.; Köppe, R.; Merzweiler, K.; Schnöckel, H. *Chem.—Eur. J.* **1998**, *4*, 2142−2147.
(7) Xie, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 5393−5400.

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alkynes.[1] In fact, a more recent result reported from our group[3] has shown that LAl can react with acetylene at low temperature (even ca. −100 °C) to form an aluminacyclopropene LAl(η^2-C_2H_2) with the simplest Al(η^2-C_2H_2) moiety. Subsequently, the LAl(η^2-C_2H_2) reacts further with another molecule of C_2H_2 leading to an alkenylalkynylaluminum compound LAl(CH═CH_2)(C≡CH) when an excess of C_2H_2 is used. The structural and multinuclear NMR (^{1}H, ^{13}C) data of the LAl(η^2-C_2H_2) provide unambiguous evidence for such an olefinic bond in metallacyclopropene and are of importance in disclosing the ring property.[9] These reactions can be considered prebiotic as Al(I) species and acetylene are found in the interstellar space.[10,11] All these facts led us to investigate the reaction of LAl with other alkynes (mono- and disubstituted ones and diyne) systematically, as well as further studies of their reactivity. Furthermore, theoretical studies (DFT calculations) were performed in order to understand the AlC_2 ring bond character and the interaction mode between the Al(I) center and the C≡C carbon atoms. The estimation of the Al—η^2-C_2 bond dissociation energy in a series of aluminacyclopropenes by calculation may essentially reveal their reactivities as well as the reaction patterns. The ^{1}H NMR spectra monitored reaction of LAl(η^2-C_2Ph_2) and PhC≡CH in toluene-d_8 is hereby reported.

Experimental Section

General Procedures. All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB glovebox filled with dry nitrogen where the calibrated values of O_2 and H_2O were strictly controlled below 1 ppm. All solvents were dried according to standard methods prior to use. Commercially available chemicals were purchased from Aldrich or Fluka and used as received except for phenyl acetylene and acetylene. Phenyl acetylene was distilled under N_2 prior to use, and acetylene was dried over a P_4O_{10} filled column. The other compounds mentioned in this paper were prepared according to published procedures: LAl(η^2-C_2Ph_2), LAl-[η^2-$C_2(SiMe_3)_2$],[1] $LAlI_2$, LAl,[8] (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*$Pr_2C_6H_3$). Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ^{1}H (200.13, 300.13, and 500.13 MHz), ^{13}C (125.77 MHz), ^{27}Al (78.02 MHz), and ^{29}Si (99.36 MHz) NMR spectra were recorded on a Bruker AM 200, 300, or 500 spectrometer, and IR spectra, on a Bio-Rad Digilab FTS-7 spectrometer. EI mass spectra were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of LAl[η^2-C_2(H)(Ph)] (2). To a toluene solution (25 mL) of LAl (0.41 g, 0.92 mmol) at −78 °C a toluene solution (5 mL) of distilled PhC≡CH (0.101 mL, 0.92 mmol) was added, and an immediate color change of the solution was observed from red to orange. The mixture was allowed to warm to room temperature and stirred for 12 h. The volatiles were removed in vacuum, and the residue was washed with *n*-hexane (2 mL). An orange crystalline solid of **2** was obtained. Yield: 0.44 g (88%). Mp: 148 °C. ^{1}H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 4 × 3 H, CH(CH_3)$_2$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 2 × 3 H, CH(CH_3)$_2$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, 2 × 3 H, CH(CH_3)$_2$), 1.53 (s, 2 × 3 H, β-CH_3), 3.39 (m, 4 × 1 H, CH(CH$_3$)$_2$), 4.92 (s, 1 H, γ-CH), 6.94−7.26 (m, 11 H, Ph-*H*, Ar-*H*), 8.66 (s, 1 H, Al−η^2-C_2H). ^{13}C {^{1}H} NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ 23.5, 24.4, 24.8, 29.0 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 97.1 (γ-*C*), 124.4, 125.3, 127.0, 128.4, 139.0, 143.2, 143.8 (Ph-*C*, Ar-*C*), 165.4, 170.2 (broad, Al−η^2-*C*$_2$), 172.8 (*C*N). ^{27}Al NMR (78.02 MHz, C_6D_6, 298 K, ppm): no resonances were observed. EI-MS: *m*/*z* (%) 445 (100, [M$^+$ − PhC≡CH + 1]), 545 (5, [M$^+$ − 1]). Anal. Calcd (%) for $C_{37}H_{47}AlN_2$ (M_r = 546.78): C, 81.28; H, 8.67; N, 5.12. Found: C, 80.83; H, 8.48; N, 5.23.

Synthesis of LAl(η^2-C_2Me_2) (3). To a toluene solution (25 mL) of LAl (0.22 g, 0.5 mmol) at −78 °C an excess of distilled MeC≡CMe was added, and an immediate color change of the solution was observed from red to orange. The mixture was allowed to warm to room temperature and stirred for 12 h. All volatiles were removed in vacuum, and the residue was immediately washed with *n*-hexane (1 mL). An orange crystalline solid of **3** was afforded in almost quantitative yield (>95%). Mp: 182 °C. ^{1}H NMR (500.13 MHz, toluene-d_8, 298 K, ppm): δ 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 4 × 3 H, CH(CH_3)$_2$), 1.47 (d, $^3J_{HH}$ = 6.8 Hz, 4 × 3 H, CH(CH_3)$_2$), 1.57 (s, 2 × 3 H, β-CH_3), 1.89 (s, 2 × 3 H, ═C*Me*), 3.37 (sept, 4 × 1 H, CH(CH$_3$)$_2$), 4.92 (s, 1 H, γ-CH), 7.02−7.14 (m, 6 H, Ar-*H*). ^{13}C {^{1}H} NMR (125.77 MHz, toluene-d_8, 298 K, ppm): δ 16.1, 23.0, 23.4, 24.2, 24.7, 28.9, 32.0 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$, ═C*Me*), 96.5 (γ-*C*), 124.2, 137.4, 137.5, 139.6, 143.8 (Ar-*C*), 169.4 (broad, Al−η^2-*C*$_2$), 172.3 (*C*N). EI-MS: *m*/*z* (%) 468 (100, [M$^+$ − 2 Me]), 483 (7, [M$^+$ − Me]), 498 (3, [M$^+$]). Anal. Calcd (%) for $C_{33}H_{47}AlN_2$ (M_r = 498.74): C, 79.47; H, 9.50; N, 5.62. Found: C, 79.01; H, 9.38; N, 5.73.

Synthesis of LAl[η^2-C_2(SiMe$_3$)(C≡CSiMe$_3$)] (4). Method A: A toluene solution (10 mL) of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (0.38 g, 2 mmol) was added to a toluene solution (30 mL) of LAl[η^2-$C_2(SiMe_3)_2$] (1.23 g, 2 mmol) at room temperature. By stirring, the solution slowly changed from dark brown into an orange color within 10 min. After additional stirring for 12 h, all volatiles were removed in vacuum. The residue was washed with *n*-hexane (2 × 2 mL) to afford an orange crystalline solid of **4**. Yield: 1.19 g, 93%. Mp: 198 °C. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K, ppm): δ 0.03 (s, 3 × 3 H, Si*Me*$_3$), 0.34 (s, 3 × 3 H, Si*Me*$_3$), 0.98 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.10 (d, 4 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.45 (s, 2 × 3 H, β-CH_3), 1.47 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.53 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 3.18 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 3.31 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 4.87 (s, 1 H, γ-CH), 7.00−7.05 (m, 6 H, Ar-*H*). ^{13}C {^{1}H} NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ 0.29, 0.65 (Si*Me*$_3$), 23.4, 24.0, 24.7, 25.1, 25.2, 28.8, 29.0, 30.2 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 97.2 (γ-*C*), 107.6, 108.8 (*C*≡*C*), 123.9, 125.0, 127.9, 128.0, 138.7, 142.6, 145.0 (Ar-*C*), 173.5 (*C*N), 190.0, 193.2 (broad, Al−η^2-*C*$_2$). ^{29}Si {^{1}H} NMR (99.36 MHz, C_6D_6, 298 K, ppm): δ −20.9, −16.4. ^{27}Al NMR (77.13 MHz, C_6D_6, 298 K, ppm): no resonances were observed. IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 2065 (C≡C). EI-MS: *m*/*z* (%) 429 (100, [M$^+$ − $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ − Me]), 638 (15, [M$^+$]). Anal. Calcd (%) for $C_{39}H_{59}AlN_2Si_2$ (M_r = 639.069): C, 73.30; H, 9.31; N, 4.38. Found: C, 72.49; H, 9.24; N, 4.26. X-ray quality crystals were obtained by recrystallization from a mixture of toluene and *n*-hexane (1:3).

Method B: To a mixture of LAl (0.22 g, 0.5 mmol) and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (0.095 g, 0.5 mmol) was added toluene (20 mL). The solution was stirred for ca. 1 h without changing its red color. Afterwards the solution was allowed to heat to reflux, and a color change of the solution to orange was observed. Finally the solution was refluxed for 4 h and then cooled to room temperature. All solvents were removed in vacuum. The residue was washed with a little *n*-hexane to afford an orange crystalline solid (almost in a quantitative yield, >95%). Melting point measurement and spectral analysis confirmed compound **4**.

Method C: A suspension of $LAlI_2$ (1.40 g, 2 mmol), K (0.17 g, 4.2 mmol), and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (0.38 g, 2 mmol) in toluene (50 mL) was vigorously stirred for 3 d. After filtration the orange solution was concentrated (8 mL), and to it *n*-hexane (5 mL) was added. The solution was kept at 4 °C for 1 week to afford orange crystals (in a

(8) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem.* **2000**, *112*, 4444−4446; *Angew. Chem., Int. Ed.* **2000**, *39*, 4274−4276.
(9) Roskamp, E.; Roskamp C. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 305−332.
(10) Gail, H.-P.; Sedlmayr, E. *Faraday Discuss.* **1998**, *109*, 303−319.
(11) Smith, I. W. M. *Chem. Soc. Rev.* **2002**, *31*, 137−146.

relatively low yield, 20%). Melting point measurement and spectral analysis proved compound **4**.

Synthesis of LAl(CH═CHPh)(C≡CPh) (6). To a toluene solution (30 mL) of LAl (0.57 g, 1.28 mmol) at −78 °C a toluene solution (5 mL) with a little excess of distilled PhC≡CH (0.40 mL, 3.64 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 3 d; a color change of the solution from red to orange, to yellow, and finally to almost colorless was observed. All volatiles were removed in vacuum. The residue was washed with *n*-hexane (2 × 2 mL) to afford an off-white solid of **6**. Yield: 0.62 g (75%). Mp: 346 °C. ^{1}H NMR (500.13 MHz, C_6D_6, 298 K, ppm): δ 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 2 × 3 H, CH(CH_3)$_2$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 4 × 3 H, CH(CH_3)$_2$), 1.56 (d, $^3J_{HH}$ = 6.8 Hz, 2 × 3 H, CH(CH_3)$_2$), 1.60 (s, 2 × 3 H, β-CH_3), 3.35 (sept, $^3J_{HH}$ = 6.8 Hz, 2 × 1 H, CH(CH$_3$)$_2$), 3.94 (sept, $^3J_{HH}$ = 6.8 Hz, 2 × 1 H, CH(CH$_3$)$_2$), 4.98 (s, 1 H, γ-CH), 6.67−6.72, 6.94−7.26 (m, 16 H, Ph-*H*, Ar-*H*), 7.41, 7.42 (d, 2 × 1 H, CH═CH). ^{13}C {^{1}H} NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ 23.4, 23.7, 24.7, 24.9, 25.0, 26.4, 28.8, 28.9 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 98.2 (γ-*C*), 107.8 (≡*C*Ph), 124.4, 124.8, 126.1, 126.3, 127.1, 127.2, 127.5, 132.0, 132.2, 140.3, 140.6, 144.2, 145.3, 148.7 (═*C*HPh, Ph-*C*, Ar-*C*), 131.0, 134.0 (Al−*C*═, Al−*C*≡), 170.8 (*C*N). EI-MS: *m*/*z* (%) 545 (100, [M$^+$ − HC═CHPh]), 648 (10, [M$^+$]). IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 2128 (C≡C). Anal. Calcd (%) for $C_{45}H_{53}AlN_2$ (M_r = 648.92): C, 83.29; H, 8.23; N, 4.31. Found: C, 82.93; H, 8.36; N, 4.25. Single crystals of X-ray quality of **6** were obtained by recrystallization from a mixture of *n*-hexane and toluene.

Synthesis of LAl(CPh═CHPh)(C≡CH) (7). A toluene solution (30 mL) of LAl(η^2-C_2Ph_2) (0.62 g, 1 mmol) was exposed to dried HC≡CH under reduced pressure and stirred for 12 h. After workup, all volatiles were removed in vacuum, and the residue was extracted with a 1:5 mixture of toluene and *n*-hexane (15 mL). The extract was kept at 4 °C for a week to afford colorless X-ray quality crystals of **7**. Yield: 0.27 g, 42%. Mp: 200 °C. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K, ppm): δ 1.08 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.26 (d, 4 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.30 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.59 (s, 2 × 3 H, β-CH_3), 1.82 (s, 1 H, C≡CH), 3.38 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 3.86 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 5.07 (s, 1 H, γ-CH), 6.66 (broad, 1 H, C═CH), 6.40−6.52, 6.80−7.00 (m, 10 H, C(*Ph*)═CH(*Ph*)), 7.04−7.12 (m, 6 H, Ar-*H*). ^{13}C {^{1}H} NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ 23.5, 24.5, 24.6, 24.8, 26.5, 28.3, 29.1 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 93.9 (broad, ≡*C*H), 99.6 (γ-*C*), 124.4, 124.3, 125.4, 126.4, 127.1, 127.4, 129.6, 139.0, 141.3, 141.5, 143. 4, 145.9, 146.2 (*Ph*, Ar-*C*, ═*C*), 153.0, 156.0 (broad, Al−*C*═, Al−*C*≡), 171.2 (*C*N). IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 1996 (C≡C), 3270 ((≡)C−H). EI-MS: *m*/*z* (%) 469 (100, [M$^+$ − C(Ph)═CH(Ph)]), 648 (2, [M$^+$]). Anal. Calcd (%) for $C_{45}H_{53}AlN_2$ (M_r = 648.92): C, 83.29; H, 8.23; N, 4.31. Found: C, 83.16; H, 8.18; N, 4.34.

Synthesis of LAl(CPh═CHPh)(C≡CPh) (8). To a toluene solution (30 mL) of LAl(η^2-C_2Ph_2) (1.24 g, 2 mmol) a toluene solution (10 mL) of an excess of PhC≡CH (0.33 mL, 3 mmol) was added. After stirring for 12 h, the solution was dried in vacuum, and the residue was extracted with *n*-hexane (20 mL). The extract was kept at 4 °C for a week to afford colorless X-ray quality crystals of **8**·0.5 *n*-hexane. Yield: 1.12 g, 73%. Mp: 187 °C. ^{1}H NMR (300.13 MHz, C_6D_6, 298 K, ppm): δ 0.86∼0.90 (m, 7 H, *n*-hexane), 1.11 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.24 (d, 4 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.35 (d, 2 × 3 H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.61 (s, 2 × 3 H, β-CH_3), 3.44 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 4.01 (sept, 2 × 1 H, $^3J_{HH}$ = 6.8 Hz, CH(CH$_3$)$_2$), 5.08 (s, 1 H, γ-CH), 6.72 (broad, 1 H, C═CH), 6.40∼6.52, 6.80−7.00 (m, 10 H, C(*Ph*)═CH(*Ph*)), 7.08∼7.24, 7.42∼7.54 (m, 6 H, Ar-*H*). ^{13}C {^{1}H} NMR (125.77 MHz, C_6D_6, 298 K, ppm): δ 14.3 (*n*-hexane), 23.0, 24.5, 24.8, 24.9, 26.1, 28.7, 29.2, 31.9 (*C*H(*C*H$_3$)$_2$, β-*C*H$_3$), 99.5 (γ-*C*), 106.6 (broad, ≡*C*Ph), 124.1, 124.2, 125.4, 126.4, 127.1, 127.4, 128.0, 129.6, 131.4, 132.0, 139.1, 141.3, 143.2, 145.9, 146.7 (*Ph*, Ar-*C*, ═*C*), 144.5, 153.8 (broad, Al−*C*═, Al−*C*≡), 171.1 (*C*N). IR (KBr plate, Nujol mull, cm^{-1}): $\tilde{\nu}$ 2124 (C≡C). EI-MS: *m*/*z* (%) 545 (100, [M$^+$ − C(Ph)═CH(Ph)]), 724 (4, [M$^+$ − 1]). Anal. Calcd (%) for $C_{54}H_{64}AlN_2$ (**8**·0.5 *n*-hexane, M_r = 768.102): C, 84.44; H, 8.40; N, 3.65. Found: C, 84.81; H, 8.42; N, 3.61.

X-ray Structure Determination and Refinement. The crystallographic data for compounds 2·**4**, **6**, and **8**·0.5 *n*-hexane were collected on a Stoe IPDS II-array detector system using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and for compound **7** on a Bruker three-circle detector system using Cu Kα radiation (λ = 1.541 78 Å). All structures were solved by direct methods (SHELXS-96)[12] and refined against F^2 using SHELXL-97.[13] The non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically. In **6** the C≡CPh and CH═CHPh groups both are disordered and located into two positions with the same occupation ratio of 0.671(13)/0.329-(13). The hydrogen atoms were included in geometrically idealized positions with the U_{iso} tied to that of the parent atoms and were refined with the riding model except for the acetylenic hydrogen in **7**, which was located by difference Fourier synthesis and refined isotropically. A summary of cell parameters, data collection, and structure solution and refinement is given in Table 1.

Computational Details. The calculations for the bond situation of a series of aluminacyclopropenes as well as the corresponding Al−η^2-C_2 bond dissociation energies made use of the established DFT variant B3LYP method.[14,15] The computations were carried out with the Gaussian G03 program suite.[16] All the molecule geometries were fully optimized to the equilibrium structures according to their respective real or related ones. To get a suitable description of the binding situation of the AlN_2C_3 ring, a modified 6-31-G basis set extended with additional diffuse functions was employed.[17] To get a clear picture of the binding situation of the AlC_2 ring, a method established by Mayer[18] was used, and then a complete NBO analysis[19] was performed. The Al−η^2-C_2 bond dissociation energy was calculated by analyzing the energy difference between LAl[η^2-C_2(R^1)(R^2)] and the separated LAl and R^1C≡CR^2 species.

The calculations of the reaction system energy changes of LAl and C_2H_2 based on Al···C_{C2H2} distances were carried out on DFT level (RI-BP86) with the SV(P) basis sets (double-ζ quality with one polarized function). The program used is TURBOMOLE 5.5.[20]

Results and Discussion

Synthesis and Characterization of Aluminacyclopropene LAl[η^2-C_2(R^1)(R^2)]. As shown in Scheme 1, LAl (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) reacts readily with the respective ethyne, mono- and disubstituted alkynes, and diyne, leading to aluminacyclopropene LAl[η^2-C_2(R^1)(R^2)] (R^1 = R^2 = H, **1**; R^1 = H, R^2 = Ph, **2**; R^1 = R^2 = Me, **3**; R^1 = SiMe$_3$, R^2 = C≡CSiMe$_3$, **4**) in excellent yield. Compounds **1** and **2** were obtained when the precursor reagents were used in exactly equimolar quantities at low temperature. Without this equimolar ratio, the products obtained were different (vide infra). On the other hand, when LAl was reacted further with an excess

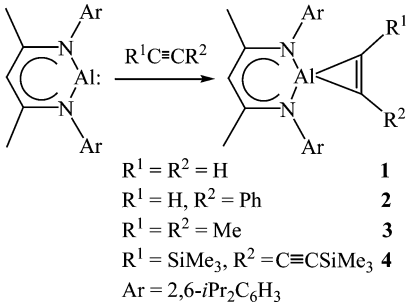
(12) Sheldrick, G. M. SHELXS-90, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−475.
(13) Sheldrick, G. M. SHELXL-97, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−790.
(15) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200−206.
(16) Frisch, M. J. et al. *Gaussian 03*, revision C.02. Gaussian, Inc.: Wallingford, CT, 2004.
(17) (a) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081−6090. (b) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193−2218.
(18) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270−274.
(19) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736−1740.
(20) Ahlrichs, R. et al. *TURBOMOLE 5.5*; University of Karlsruhe, Germany, 2002.

Table 1. Crystallographic Data for Compounds **4**, **6**, **7**, and **8**·0.5 *n*-Hexane

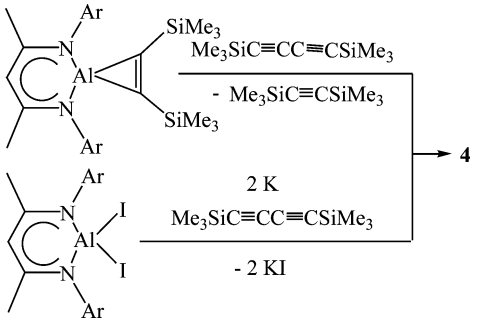
	2·**4**	**6**	**7**	**8**·0.5 *n*-hexane
formula	$C_{78}H_{118}Al_2N_4Si_4$	$C_{45}H_{53}AlN_2$	$C_{45}H_{53}AlN_2$	$C_{54}H_{64}AlN_2$
fw	1278.08	648.87	648.87	768.05
temp (K)	133(2)	100(2)	100(2)	133(2)
crystal syst	orthorombic	triclinic	monoclinic	monoclinic
space group	*Pca*2(1)	$P\bar{1}$	*P*2(1)/*n*	*P*2(1)/*n*
a (Å)	40.070(8)	11.118(2)	15.768(3)	14.641(3)
b (Å)	18.332(4)	12.440(3)	12.973(3)	19.674(4)
c (Å)	10.556(2)	15.279(3)	18.678(4)	16.162(3)
α (deg)	90.00	73.57(3)	90.00	90.00
β (deg)	90.00	75.60(3)	98.39(3)	99.78(3)
γ (deg)	90.00	72.74(3)	90.00	90.00
V (Å^3)	7754(3)	1904.2(7)	3779.8(14)	4587.7(16)
Z	4	2	4	4
ρ_c (Mg/m^3)	1.095	1.132	1.140	1.112
μ (mm^{-1})	0.142	0.086	0.703	0.081
F(000)	2784	700	1400	1660
θ range (deg)	1.22−24.81	1.76−26.39	3.43−60.33	1.65−24.89
index ranges	$-47 \le h \le 45$ $-21 \le k \le 21$ $-12 \le l \le 12$	$-13 \le h \le 13$ $-15 \le k \le 15$ $-19 \le l \le 19$	$-17 \le h \le 17$ $-14 \le k \le 14$ $-21 \le l \le 21$	$-17 \le h \le 17$ $-23 \le k \le 23$ $-19 \le l \le 19$
no. of reflns collected	43 701	36 703	17 868	49 895
no. of indep reflns (R_{int})	13 073 (0.1187)	7784 (0.0381)	5560 (0.0288)	7919 (0.0648)
no. of data/restraints/params	13073/1/825	7784/0/443	5560/1/447	7919/0/524
GOF/F^2	0.721	1.221	1.016	0.986
$R1^a$, $wR2^b$($I > 2\sigma(I)$)	0.0494, 0.0628	0.0789, 0.1670	0.0328, 0.0766	0.0430, 0.1020
$R1^a$, $wR2^b$(all data)	0.1310, 0.0782	0.0871, 0.1714	0.0415, 0.0814	0.0671, 0.1100
largest diff peak/hole (e·Å^{-3})	0.187/−0.242	0.612/−0.467	0.236/−0.242	0.170/−0.204

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

Scheme 1



Scheme 2



quantity of MeC≡CMe and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, there were no more surprises; the expected compounds **3** and **4** were isolated. This indicates an inertness of **3** and **4** toward further reaction with the respective disubstituted alkyne precursor. Compounds **1**−**3** can be formed at low temperature (even at ca. −100 °C), while compound **4** is generated under refluxing conditions. Alternatively, **4** can be obtained by the substitution reaction using LAl[η^2-$C_2(SiMe_3)_2$] and $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ or by the reductive coupling reaction of $LAlI_2$ with potassium in the presence of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ both at room temperature (Scheme 2). Reductive couplings are not successful in the presence of C_2H_2 and PhC≡CH for the preparation of aluminacyclopropene derivatives due to the metalation of the acetylenic hydrogen.

Compounds **1**−**4** are easily separated as orange crystalline solids by removing all volatiles and then by washing the residue with *n*-hexane. They are air-sensitive and highly soluble in aromatic solvents, but slightly soluble in aliphatic hydrocarbons. Compounds **1**−**4** have been fully characterized by mass spectrometry and IR and multinuclear NMR (^{1}H, ^{13}C, or/and ^{29}Si) spectroscopy as well as by X-ray crystallography in the cases of **1** and **4**. X-ray quality crystals were grown from a solvent mixture of *n*-hexane and toluene. Attempts to grow single crystals of **2** were not successful.

In the ^{1}H NMR spectra the proton(s) at the AlC_2 carbon atom(s) resonate(s) at 8.82 ppm for **1** and at 8.66 ppm for **2**. In the ^{13}C NMR spectra the AlC_2 carbon atoms resonate in the range of 165.4 to 193.2 ppm (177.2, **1**; 165.4, 170.2, **2**; 169.4, **3**; 190.0, 193.2 ppm, **4**). These chemical shifts both appear significantly downfield when compared to those of the respective protons and carbons in normal organic alkenyl systems.[21] The ^{13}C resonances are comparable to that found in such a SnC_2 ring compound (163.9 ppm).[22] These suggest a speciality of the olefinic bond in metallacyclopropene. The observation of two kinds of carbon resonances in **2** and **4**, respectively, indicates an asymmetric AlC_2 ring induced by the different groups (H and Ph, **2**; $SiMe_3$ and $C{\equiv}CSiMe_3$, **4**) at the AlC_2 carbon atoms. Furthermore, the environmentally different $SiMe_3$ groups in **4** are evident from its ^{29}Si NMR spectrum, in which two silicon resonances were observed (−20.9 and −16.4 ppm). Moreover, the C≡C functionality in **4** is confirmed from its

(21) Vollhardt, K. P. C.; Schore, N. E. *Organic Chemistry: Structure and Function*, 3rd ed.; W.H. Freeman: New York, 1999; pp 438−483.
(22) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5208−5209.

Table 2. Geometric Parameters within the AlC_2 Ring of Aluminacyclopropenes

compound	Al—C (Å)	C—C (Å)	C—Al—C (deg)	Al—C—C (deg)	ref
HAl(η^2-C_2H_2)[a]	1.844−1.852	1.362−1.384			7
LAl(η^2-C_2H_2)[b]	1.878(2), 1.885(2)	1.358(2)	42.30(7)	68.57(10), 69.13(10)	3
LAl(η^2-C_2Ph_2)	1.899(3), 1.908(3)	1.382(4)	42.57(11)	68.39(15), 69.04(15)	1
LAl[η^2-$C_2(SiMe_3)_2$]	1.889(4), 1.894(3)	1.356(5)	42.02(14)	68.80(19), 69.20(20)	1
LAl[η^2-$C_2(SiMe_3)$(C≡C$SiMe_3$)][c]	1.862(8), 1.909(9)	1.369(11) 1.395(11)	42.0(3)	66.5(5), 70.1(5)	this work
	1.904(8), 1.918(9)		43.4(3)	68.5(5), 69.6(5)	

[a] This species is based on a theoretical model, and the corresponding data are obtained by calculation. [b] L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$. [c] By X-ray structural analysis the two independent molecules are revealed, corresponding to two sets of structural data.

Table 3. Geometric Parameters of the Al—C=C and Al—C≡C Functionalities in Compounds **5**−**8**

compound	Al—$C_{C=C}$ (Å)	Al—$C_{C\equiv C}$ (Å)	C=C (Å)	C≡C (Å)	Al—C=C (deg)	Al—C≡C (deg)	ref
LAl(CH=CH_2)(C≡CH)[a,b]	1.944(11)	1.962(11)	1.323(18)	1.170(14)	124.6(14)	175.4(19)	3
LAl(CH=CHPh)(C≡CPh)[b]	1.952(3)	1.941(3)	1.334(11)	1.189(11)	121.8(9)	169.3(6)	this work
LAl(CPh=CHPh)(C≡CH)	1.961(2)	1.952(2)	1.349(2)	1.196(2)	119.53(11)	173.11(14)	this work
LAl(CPh=CHPh)(C≡CPh)	1.972(2)	1.941(2)	1.343(3)	1.217(2)	119.69(13)	169.07(17)	this work

[a] L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$. [b] Both CH=CH_2 (or CH=CHPh) and C≡CH (or C≡CPh) groups are disordered in two positions, and therefore the averaged C—C bond lengths and Al—C—C angles are given.

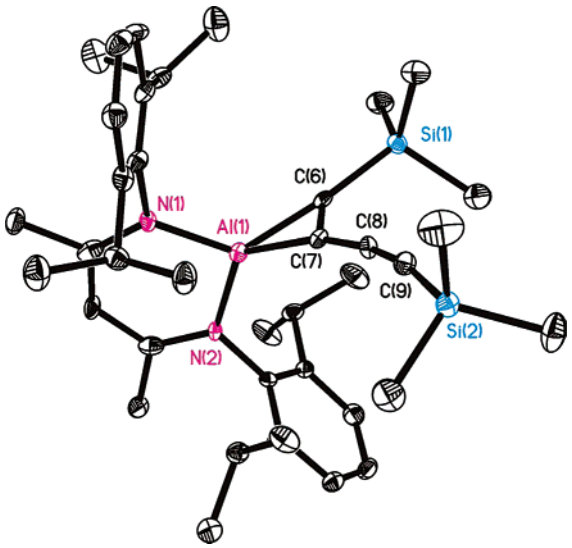
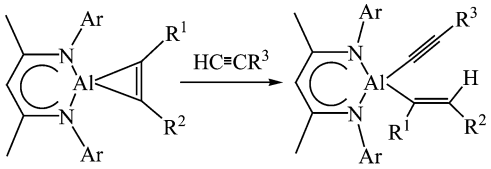


Figure 1. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% level, and the hydrogen atoms are omitted for clarity.

characteristic carbon resonances (107.6 and 108.8 ppm) and IR absorption band (2065 cm^{-1}).

The structural analysis, with two independent molecules of **4** that crystallize in space group *Pca*2(1), unambiguously exhibits this structural feature. The structure of one molecule is shown in Figure 1. The geometric parameters of the AlC_2 ring in **4** and the other aluminacyclopropenes including the computationally derived one are shown in Table 2. These data exhibit that the Al−C bond lengths within the AlC_2 ring range from 1.844 to 1.918(9) Å and the C−C bond distances from 1.356(5) to 1.395(11) Å. These Al−C bond lengths are shorter than the experimental ones (1.95 to 2.05 Å, the value of 2.07 Å is based on the covalent radii).[23] However, the C−C bond distances appear longer than those observed for terminal aluminum vinyl system (1.325(17) to 1.349(2) Å, Table 3), and are ranging between C−C double and single bonds. A comparison of the bond lengths in four-,[3] five-,[1] and six-membered[5,6] aluminum-atom-contained ring compounds (Al−C, 1.932(3) to 1.992(2) Å; C−C, 1.342(4) to 1.366(2) Å) shows that the Al−C bond lengths are still shorter, while the C−C bond distances

Scheme 3



$R^1 = R^2 = R^3 = H$ **5**
$R^1 = H, R^2 = R^3 = Ph$ **6**
$R^1 = R^2 = Ph, R^3 = H$ **7**
$R^1 = R^2 = R^3 = Ph$ **8**
Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

are comparable. In a group 14 metal-containing MC_2 ring, the C−C bond lengths are observed in the range from 1.331(9) to 1.39(1) Å.[22,24] Finally, it is important to note that the AlC_2 ring is nearly perpendicular to its fused AlN_2C_3 ring formed by the chelating L groups at the Al center (the dihedral angle 88.6°, **1**; 88.3°, 88.8°, **4**).

Synthesis and Characterization of Alkenylalkynylaluminum Compound LAl(CR^1=CHR^2)(C≡CR^3). The reaction of LAl with excess C_2H_2 and PhC≡CH (<1:2) affords LAl(CH=CH_2)(C≡CH) (**5**) and LAl(CH=CHPh)(C≡CPh) (**6**), respectively. Compounds **1** and **2** have been isolated from the corresponding reactions in an exact molar ratio of 1:1 at low temperature. Therefore we rationalized that **5** and **6** are formed proceeding through **1** and **2** as the respective intermediates. Nonetheless, we have still investigated the reaction of LAl[η^2-C_2Ph_2] with C_2H_2 and PhC≡CH, and as expected compounds LAl(CPh=CHPh)(C≡CH) (**7**) and LAl(CPh=CHPh)(C≡CPh) (**8**) were isolated, respectively (Scheme 3).

Compounds **5**−**8** were obtained as colorless crystalline solids. The molecular structures of **5**−**8** are shown in Figures 2−4. The chelating character of the L ligand by the two N atoms at the Al center is known,[1−3,26] and the geometric data for the functionalities Al(CR^1=CHR^2)(C≡CR^3) are listed in Table 3.

(23) Brothers, P. J.; Power, P. P. *Adv. Organomet. Chem.* **1996**, *39*, 1−69.
(24) (a) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Yu. T.; Antipin, Y. M.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27−C30. (b) Ando, W.; Ohgaki, H.; Kabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 659−661.
(25) Lide, D. R. In *Handbook of Chemistry and Physics* **2003**−**2004**, *84*, (9-)16−17.
(26) Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070−3076.

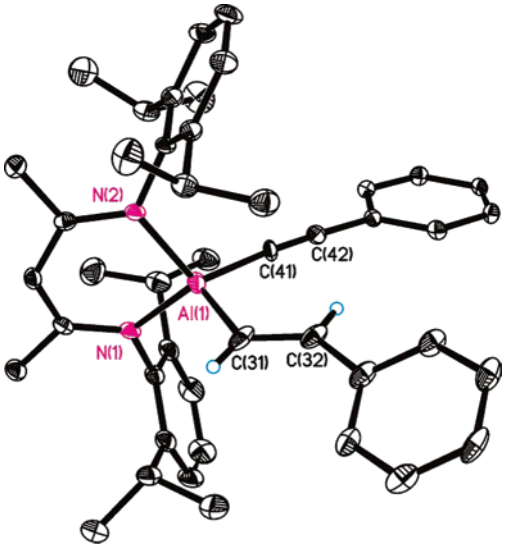


Figure 2. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% level. The olefinic hydrogen atoms are presented, and the other ones are omitted for clarity. The CH═CHPh and C≡CPh groups both are in the occupancies of 0.671(13).

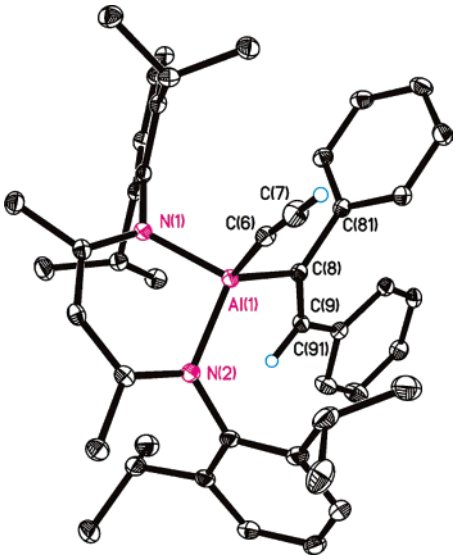


Figure 3. Molecular structure of **7**. Thermal ellipsoids are drawn at the 50% level. The acetylenic and olefinic hydrogen atoms are presented, and the other ones are omitted for clarity.

Precluding the phenyl groups in these functionalities, the C—C bond lengths are ranging from 1.171(4) to 1.217(2) Å and from 1.325(17) to 1.349(2) Å, respectively. They essentially fall in the range of the respective sp hybridized organic acetylenic (1.174−1.183 Å) and sp^2 hybridized olefinic linkage (1.299−1.331 Å),[25] indicating the respective C≡C triple and C═C double bond system. Correspondingly, the Al—C≡C (169.07(17)−173.9(2)°) and Al—C═C bond angles (119.53(11)−124.6(12)°) are close to the ideal 180° and 120°, respectively. The Al—C bond lengths (Al—$C_{C\equiv C}$, 1.941(2)−1.962(11); Al—$C_{C=C}$, 1.944(11)−1.972(2) Å) are comparable to those found in the literature (1.95−2.05 Å)[23] and are also close to those in β-diketiminato aluminum alkyls $LAlMe_2$ (1.955(4), 1.961(3) Å) and $L'AlMe_2$ (L′ = HC[C(Me)N-*p*-toluene]$_2$, 1.958(3), 1.970(3) Å).[26] This may imply here much lesser interaction of π electrons in C—C multiple bonds extending to its adjacent Lewis acidic Al atom.

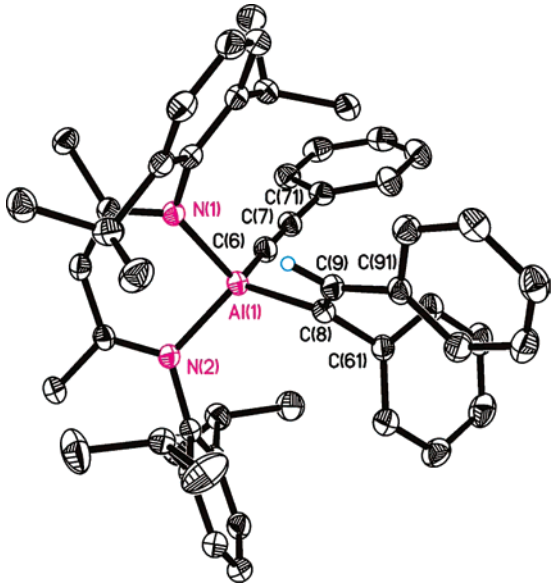


Figure 4. Molecular structure of **8**. Thermal ellipsoids are drawn at the 50% level. The olefinic hydrogen atom is presented, and the other ones are omitted for clarity.

The selected spectral data (IR, ^{1}H and ^{13}C NMR) of the Al(CR^1═CHR^2)(C≡CR^3) functionalities in compounds **5**−**8** are shown in Table 4. The olefinic proton resonances range from 5.79 to 7.42 ppm with a variety of signals due to the adjacent H—H coupling. A similar pattern was observed for α-methylstyrene (9%) (5.20 ppm) and *trans*-β-methylstyrene (7%) (6.15 ppm), the hydrolysis products of the reaction of $AlMe_3$ with monophenyl acetylene.[27] The acetylenic protons resonate at around 1.80 ppm as a singlet (1.73, **5**; 1.82 ppm, **7**) and the corresponding carbons (≡*C*R^3) in the characteristic range 93.9 to 107.8 ppm as one broad resonance. In the IR spectra, the C≡C and (≡)C—H vibrations are clearly observed in the respective modes both as weak absorption bands ($\nu_{C\equiv C}$: 1992 **5**, 2128 **6**, 1996 **7**, 2124 cm^{-1} **8**; $\nu_{(\equiv)C-H}$: 3277 **5**, 3270 cm^{-1} **7**).

Bonding Character of Al—N and the AlC_2 Ring in Aluminacyclopropenes. We have previously discussed, using variable-temperature ^{1}H NMR investigation and ESR studies as well as ^{27}Al NMR spectral analysis, that the AlC_2 ring compound like $LAl[\eta^2\text{-}C_2R_2]$ (R = Ph, $SiMe_3$) can be better described as a metallacyclopropene (Al(III)) more than as an alkyne π-complex.[1] Furthermore, the AlC_2 ring structural data in a series of aluminacyclopropenes clearly indicate a shortening of the Al—C bond length and an elongation of the C—C bond distance when compared with the covalent Al—C single and C═C double bonds. These structural findings can be compared with those in the corresponding borirenes, in which π-electron delocalization over the BC_2 ring is invoked whether by experimental data[28] or by calculations.[29] Therefore it is interesting for us to investigate the bonding properties of this AlC_2 ring system by DFT calculations. Comparable features are also observed in group 14 metal MC_2 ring compounds.[22,24] The

(27) Mole, T.; Surtees, J. R. *Aust. J. Chem.* **1964**, *17*, 1229−1235.
(28) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847−1853.
(29) (a) Pittman, C. U., Jr.; Kress, A.; Patterson, T. B.; Walton, P.; Kispert, L. D. *J. Org. Chem.* **1974**, *39*, 373−378. (b) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589−2594. (c) Jug, K. *J. Org. Chem.* **1984**, *49*, 4475−4478.

Table 4. Selected Spectral Data (IR, ^{1}H and ^{13}C NMR) of the Al−CR^1═CHR^2 and Al−C≡CR^3 Functionalities in Compounds **5**−**8**[a]

	IR ($\tilde{\nu}$, cm^{-1})	^{1}H NMR (δ, ppm)			^{13}C NMR (δ, ppm)	
compound	C≡C	(≡)C−H	≡C*H*	═C*H*	≡C*R*^{3}	ref
LAl(CH═CH$_2$)(C≡CH)	1992	3277	1.73 (s)	5.79 (dd), 6.04 (dd), 6.12 (dd)	94.6	3
LAl(CH═CHPh)(C≡CPh)	2128			7.41 (d), 7.42 (d)	107.8	this work
LAl(CPh═CHPh)(C≡CH)	1996	3270	1.82 (s)	6.66 (s)	93.9	this work
LAl(CPh═CHPh)(C≡CPh)	2124			6.72 (s)	106.6	this work

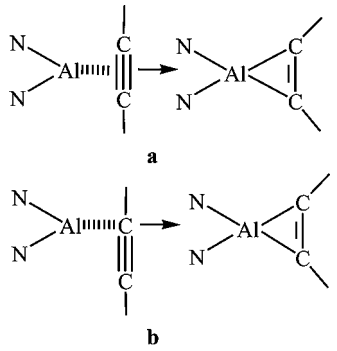
[a] L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

Table 5. Selected Computational Bond Orders and Dissociation Energies ($D_{Al-\eta^2-C_2}$, ΔE, kJ/mol) of Aluminacyclopropenes

	bond order			
compound	Al−N	Al−C	C−C[a]	ΔE[b]
LAl(η^2-C$_2$H$_2$)[c]	0.610, 0.610	1.103, 1.103	1.667	142.2, 155[d]
LAl[η^2-C$_2$(H)(Ph)]	0.612, 0.612	1.076, 1.083	1.573	134.3
LAl(η^2-C$_2$Ph$_2$)	0.614, 0.615	1.037, 1.058	1.518	107.9
LAl[η^2-C$_2$(SiMe$_3$)$_2$]	0.612, 0.613	1.030, 1.032	1.483	82.6
LAl[η^2-C$_2$(SiMe$_3$)-(C≡CSiMe$_3$)]	0.623, 0.624	1.005, 1.063	1.436	92.1

[a] C−C in the AlC$_2$ ring. [b] $\Delta E = E$(LAl + alkyne) − E(aluminacyclopropene); the calculations made use of the established DFT variant B3LYP method. [c] L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$. [d] This value is calculated on DFT level (RI-BP86) with the SV(P) basis sets.

Scheme 4



calculations have been carried out using the established DFT variant B3LYP method,[15] and the computational bond order data (the sum of σ and π contributions) for all bonds in a series of aluminacyclopropene molecules are obtained. The bond order values of the Al−N as well as those of the Al−C and C−C bonds within the AlC$_2$ ring are listed in Table 5.

The two Al−N bond orders of these aluminacyclopropenes are calculated in the range of 0.610 to 0.623 and of 0.610 to 0.624, respectively. Due to the bonding character of monovalent β-diketiminato L with Al by the two adjacent N atoms, the general σ-bond order of two Al−N bonds should be around 1. The total calculated Al−N bond order is ca. 1.23. This value is a little high and yet normal when compared with calculated data for those of ethane (1.25) and ethylene (2.16).[30] These two sets of data are prone to be equal, suggesting the equivalence and therefore give not a clear distinction of the two Al−N bonds. In fact, the bidentate β-diketiminato skeleton is a conjugated system, and in the majority of β-diketiminato metal complexes the two Al−N bond lengths are almost equal based on the structural data.[31]

In the AlC$_2$ ring, the Al−C bond orders range from 1.01 to 1.10, and those of the C−C bond from 1.67 to 1.44 with the variation of substituents at the C atoms. The former is close to 1 and could be related to indicate the Al−C σ-bond. This suggests less π electron delocalization over the AlC$_2$ ring. However it is in contrast to the lower C−C bond orders, since the results differ when compared with those of the calculated congeneric BC$_2$ ring model, HB(CH)$_2$ (B−C vs C−C bond order: 1.623 vs 1.737, by INDO; 1.614 vs 1.899, by SINDO1 calculations).[29] Thus, the corresponding structural and multinuclear NMR (^{1}H, ^{13}C) data, which are most important for the ring description, may hide some complexity of the MC$_2$ ring in comparison with the organic ones. Insight into the ring properties of aluminacyclopropene must await further investigation on such a compound with a planar three-coordinate Al atom.[32]

Interaction of the Al(I) Center with the C≡C Carbon Atoms. LAl reacts with 1 equiv of alkyne leading to aluminacyclopropene. A formation of Al−C σ bonds proposed above and the conversion of the C≡C triple bond to the C═C double bond, in which an elongation of the C═C bond length is evident, indicate that this reaction is better described as an oxidative cycloaddition. Some related calculations demonstrate that there is a complexation energy responsible for such a reaction.[2,7] This implies that an interaction that occurs between the Al(I) center and the C≡C carbon atoms may correlate with the energy changes of the reaction system. Thus an approach of an alkyne molecule to the Al(I) center to form the final AlC$_2$ ring and the energy changes for this system based on DFT calculations have been investigated. The unlimited Al···C separation between LAl and C$_2$H$_2$ is set as zero potential energy surface, and the settled one is proposed to indicate one state that will correspond to a relative potential energy surface. In the meantime, two possible approaching modes are considered: a C≡C center is set close to the Al atom (channel a), and one terminal C≡C atom to the Al atom (channel b) (Scheme 4).

By calculations, a series of potential energy surface points versus Al···C distances (4.00−1.80 Å) were obtained. With a line drawn according to these points, the potential energy curve is given in Figure 5 (the black curve corresponds to channel a, and the red one, to b). In Figure 5 we find that the reaction system energy varies with the separation between LAl and C$_2$H$_2$. Of which there is an energy barrier (the most height is at ca. 145 kJ/mol, which was found by calculating the cross section of the potential energy surfaces of the two adjacent states) in a, while almost no barrier is formed in b. Channel b is energetically

(30) Jug, K. *J. Org. Chem.* **1983**, *48*, 1344−1348.
(31) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031−3065.

(32) In a series of aluminacyclopropenes presented in this work, the Al center is involved in two fused ring systems, in which C−C or C−N multiple bonds are contained, in a tetrahedral coordinative geometry. This may give rise to the complexity of the AlC$_2$ ring properties in calculations. Volpin, M. E.; Koreshkov, Y. D.; Dulova, V. G.; Kursanov, D. N. *Tetrahedron* **1962**, *18*, 107−122.

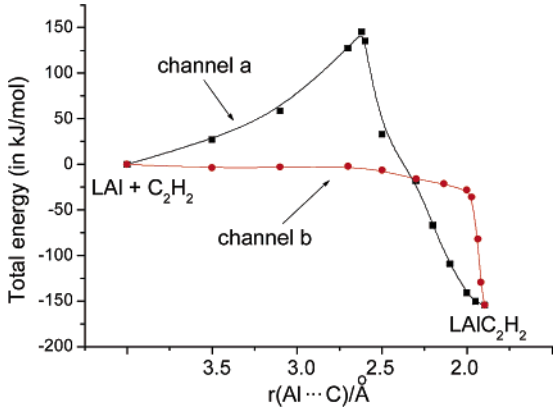


Figure 5. The potential energy curve of the reaction system of LAl and C_2H_2 versus Al···$C_{C_2H_2}$ distances.

favored, which means that almost no activation energy is needed for the reaction of LAl with C_2H_2 to form LAl(η^2-C_2H_2). This is in good agreement with our experimental observation that LAl can react with C_2H_2 at low temperature (ca. −100 °C). Channel a may be depicted as a π-complexation process. Ab initio MO calculations have suggested that a lone pair of electrons is accommodated at the Al atom of LAl,[8] and therefore an electronic interaction between Al(I) center and C≡C bond could be involved. This would conversely favor the occurrence of channel b.

The relative potential energy corresponding to the final LAl(η^2-C_2H_2) state is about 155 kJ/mol, which is suggestive of the reaction complexation energy of LAl and C_2H_2 (that is the Al−η^2-C_2 bond dissociation energy, $D_{Al-\eta^2-C_2}$). This value can be compared with that of HAl(η^2-C_2H_2) (av 126 kJ/mol).[7] Moreover we computed such $D_{Al-\eta^2-C_2}$ values of other aluminacyclopropenes for comparison. The results are shown in Table 4. On one hand, the $D_{Al-\eta^2-C_2}$ values range from 155 to 82.62 kJ/mol and are much smaller than that of Al−C_{methyl} in $AlMe_3$ (281.4 kJ/mol).[4] This implies a weak Al−η^2-C_2 bonding and essentially indicates a remarkable reactivity of the AlC_2 ring compound. Indeed, the insertion of small molecules or substitution of the AlC_2 ring has been experimentally observed.[1−3] On the other hand, the $D_{Al-\eta^2-C_2}$ varies with the substituents at the AlC_2 carbon atoms. This shows an influence of such substituents (for example, steric bulk and electronic factors) on the Al−η^2-C_2 bond dissociation energy and hence an effect on the complexation of LAl with alkynes where such a bulkiness of L actually exists. While aluminacyclopropenes **1**−**3** are formed at low temperature (−100 °C), the LAl[(η^2-C_2(R^1)(R^2)] (R^1, R^2: $SiMe_3$, Ph) could be made at room temperature.[33] Thus, **4** is obtained under refluxing conditions.

An Acetylenic Hydrogen Migration to One of the AlC_2 Carbon Atoms. Among the reactions of aluminum(III) alkyls or hydrides with alkynes, a preliminary π-complexation is generally suggested due to an interaction of the π electrons of the C≡C bond with a Lewis acidic aluminum(III) center.[4,34]

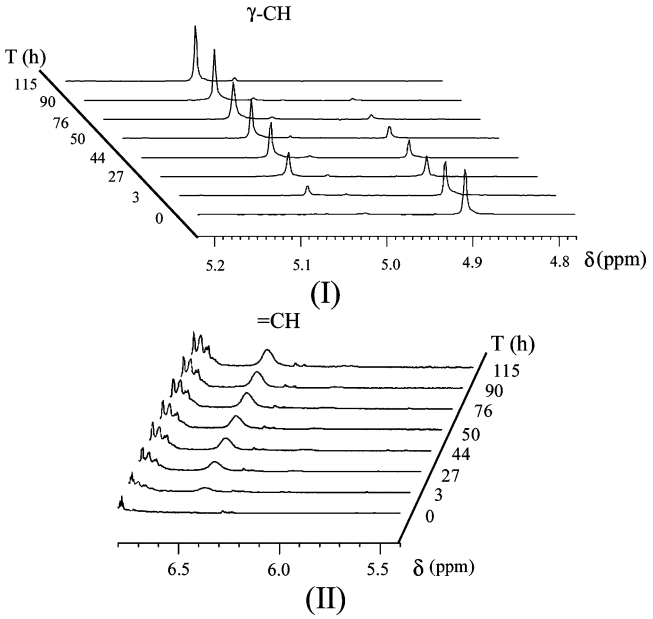
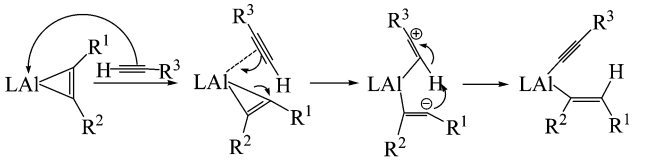


Figure 6. The ^{1}H NMR spectroscopy studies of a reaction of LAl(η^2-C_2-Ph_2) with a small excess of PhC≡CH in toluene-d_8. This reaction was kept at 40 °C (behaved like a sample under stirring). (I) and (II) record the resonance changes of the respective γ-CH proton of L and olefinic proton of CPh=CHPh (ppm) with reaction time (h).

Scheme 5



Some experimental data support this assumption.[6,35] Further Al−H or Al−C addition to the C≡C triple bond can result in aluminum vinyl derivatives,[4,34] while the corresponding metalation can occur with acetylenic hydrogen leading to aluminum acetylides.[4,36] The reaction of aluminacyclopropene with terminal alkynes generating alkenylalkynylaluminum compounds may proceed through such a preliminary π-complexation, followed by an acetylenic hydrogen migration to one of the olefinic carbons under AlC_2 ring opening. The proposed mechanism is shown in Scheme 5.

To gain further insight into such a reaction process, the ^{1}H NMR studies on the reaction of LAl(η^2-C_2Ph_2) and PhC≡CH in toluene-d_8 was accomplished. Figure 6 shows the resonance changes of the γ-CH proton in L, which is a good indicator for the reactant and product, and the olefinic one in the AlCPh=CHPh group with reaction time. In (I), the gradual consumption of LAl(η^2-C_2Ph_2) and the corresponding generation of **8** are clearly observed. In the meantime, the integral intensity ratios of resonances of PhC≡CH and referenced toluene-d_8 methyl protons varied from 0.37:1, 0.34:1, 0.33:1, · · ·, and finally to 0.27:1, indicating the reduction of PhC≡CH. Instead, in (II),

(33) The respective NMR tube reaction of LAl with a little excess of Me_3SiC≡$CSiMe_3$ and PhC≡CPh in toluene-d_8 at room temperature has been accomplished. The solution color changes and ^{1}H NMR spectral analysis indicates the occurrence of both reactions and the formation of the corresponding aluminacyclopropenes LAl[(η^2-C_2($SiMe_3$)$_2$] and LAl(η^2-C_2-Ph_2).

(34) Ziegler, K. In *Organometallic Chemistry*; Zeiss, H. H., Ed.; Reinhold Publishing Corp.: New York, 1960; pp 195−269.

(35) (a) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Eisch, J. J.; Considine, L. *J. Am. Chem. Soc.* **1974**, *96*, 1941−1942. (b) Dolzine, T. W.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 1737−1740. (c) Hausen, H.-D.; Tödtmann, J.; Weidlein, J. *Z. Naturforsch.* **1994**, *49B*, 430−433.

(36) (a) Mole, T.; Surtees, J. R. *Chem. Ind.* (London) **1963**, 1727−1728. (b) Zheng, W.; Mösch-Zanetti, N. C.; Roesky, H. W.; Hewitt, M.; Cimpoesu, F.; Schneider, T. R.; Stasch, A.; Prust, J. *Angew. Chem.* **2000**, *112*, 3229−3231; *Angew. Chem., Int. Ed.* **2000**, *39*, 3099−3101.

the concomitant increasing of the olefinic proton resonance corresponds to the formation of the terminal AlCPh=CHPh group of **8**. This undoubtedly draws a picture of the PhC≡CH hydrogen migration process. However, in the ^{1}H NMR monitored reaction, no resonances were observed, which could be assigned to be those of the proposed π-complex of PhC≡CH. This could explain that the π-complexation of alkyne to LAl is only a transition state, which is extremely unstable, in the formation of the product.

Conclusions

In summary, the Al(I) center stabilized by the bulky β-diketiminato ligand L can readily react with the C≡C of various alkynes, resulting in the formation of aluminacyclopropenes. DFT calculations suggest that the C≡C unit approaching mode to the Al(I) center needs almost no activation energy. The temperature variation in the formation of the AlC_2 ring by the reaction of LAl with various alkynes reflects an influence of the substituents at the C≡C linkage in the presence of the bulky L. Similar reaction behavior has been widely observed in organic cycloaddition of transient carbene to the C—C multiple bonds.[37] Based on the energy calculations, much lower Al—η^2-C_2 bond dissociation energies reveal a remarkable reactivity of such AlC_2 species, which have been viewed from its highly strained structure.[1,3,4] This is well demonstrated by its reaction chemistry reported in recent years[1−3,5,6] and in this work. The existing Lewis acidity of the Al(III) center (although four coordinate) of the AlC_2 ring indicates a large possibility that the Al center can allow an attack from other Lewis basic reagents. Therefore, the reaction of aluminacyclopropene with terminal alkyne forming alkenylalkynylaluminum compounds may proceed through an initial π-complexation, following with an acetylenic hydrogen migration under opening of the AlC_2 ring.

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Supporting Information Available: CIF files for compounds 2·**4**, **6**, **7**, and **8**·0.5*n*-hexane, selected results of DFT calculations, and a detailed author name list of refs 16 and 20. This material is available free of charge via the Internet at http://pubs.acs.org.

JA057731P

(37) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.