J. Am. Chem. Soc. **2001,** *123,* 9091−9098

Facile Synthesis of Cyclopropene Analogues of Aluminum and an Aluminum Pinacolate, and the Reactivity of LAl[η^2-$C_2(SiMe_3)_2$] toward Unsaturated Molecules (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*-$Pr_2C_6H_3$)

Chunming Cui,[§] Sinje Köpke,[§] Regine Herbst-Irmer,[§] Herbert W. Roesky,*,[§] Mathias Noltemeyer,[§] Hans-Georg Schmidt,[§] and Bernd Wrackmeyer[‡]

Contribution from the Institute of Inorganic Chemistry, University of Goettingen, Tammannstrasse 4, D-37077 Goettingen, Germany, and Department of Chemistry, University of Bayreuth, D-95447 Bayreuth, Germany

Received August 28, 2000

Abstract: Reduction of $LAlI_2$ (**1**) (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*-$Pr_2C_6H_3$) with potassium in the presence of alkynes $C_2(SiMe_3)_2$, C_2Ph_2, and $C_2Ph(SiMe_3)$ yielded the first neutral cyclopropene analogues of aluminum LAl[η^2-$C_2(SiMe_3)_2$] (**3**), LAl(η^2-C_2Ph_2) (**4**), and LAl[η^2-$C_2Ph(SiMe_3)$] (**5**), respectively, whereas reduction of **1** in the presence of Ph_2CO gave an aluminum pinacolate LAl[$O_2(CPh_2)_2$] (**6**), irrespective of the amount of Ph_2CO employed. The unsaturated molecules CO_2, Ph_2CO, and PhCN inserted into one of the Al−C bonds of **3** leading to ring enlargement to give novel aluminum five-membered heterocyclic systems LAl[OC(O)$C_2(SiMe_3)_2$] (**7**), LAl[OC(Ph)$_2C_2(SiMe_3)_2$] (**8**), and LAl[NC(Ph)$C_2(SiMe_3)_2$] (**9**) in high yields. In contrast, **3** reacted with *t*-BuCN, 2,6-$Trip_2C_6H_3N_3$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$), and Ph_3SiN_3 resulting in the displacement of the alkyne moiety to afford LAl[N_2(C*t*-Bu)$_2$] (**10**) with an unprecedented aluminum-containing imidazole ring, and the first monomeric aluminum imides LAlNC$_6H_3$-2,6-$Trip_2$ (**11**) and LAlNSiPh_3 (**12**). All compounds have been characterized spectroscopically. The variable-temperature ^1H NMR studies of **3** and ESR measurements of **3** and **4** suggest that the Al−C−C three-membered-ring systems can be best described as metallacyclopropenes. The ^{27}Al NMR resonances of **2** and **3** are reported and compared. Molecular structures of compounds **3**, **4**, **6**·OEt_2, **8**·OEt_2, and **9** were determined by single-crystal X-ray structural analysis.

Introduction

Heavier main group cyclopropene analogues are of great interest in synthesis due to their high reactivity.[1,2] Previous studies on such species have centered on Group 14 compounds, and the chemistry of such compounds, to a large extent, is related to their carbene analogues R_2M: (M = Si, Ge, Sn). They have been formed either by the reaction of R_2M: with alkynes or the reductive coupling of R_2MX_2 in the presence of alkynes.[3] However, the chemistry of Group 13 cyclopropene analogues has been centered only on that of boron.[2,4] To the best of our knowledge, stable neutral metallacyclopropenes of the heavier congeners (Al, Ga, and In) have not yet been described in the literature.

The recent surge in the number of Group 13 species with a low valent central atom has prompted us to design appropriate ligand systems and synthetic methodologies to access novel Group 13 species. We and others have successfully used the bulky β-diketiminato ligand L (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*-$Pr_2C_6H_3$) for the preparation of the monomeric compound LM (M = Al (**2**) Ga), with the central atom being low valent and two coordinated.[5] Ab initio calculations indicate that the monomeric Al(I) complex **2** possesses a nonbonded electron pair, and is isoelectronic with a singlet carbene.[5a] Initial examination of the two monovalent Al and Ga species showed that they are highly reactive toward organic azides.[6] We now turn our attention to alkynes in the hope of preparing cyclopropene analogues of aluminum since alkynes are well-known labile and effective trapping reagents for main group carbene analogues.[3] Another interesting approach is the reduction of

---

[§] University of Goettingen.

[‡] University of Bayreuth.

(1) Volpin, M. E.; Koreshkov, Yu. D.; Dolova, V. C.; Kursanov, D. N. *Tetrahedron* **1962**, *18*, 107.

(2) (a) Eisch, J. J. In *Advances in Organic Chemistry*; West, R. Y.; Stone, F. G. A., Eds.; Academic Press: New York, 1977; Vol. XVI, p 67. (b) van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kerk-van Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem*. **1983**, *95*, 61; *Angew. Chem., Int. Ed. Engl*. **1983**, *22*, 48. (c) Habben, C.; Meller, A. *Chem. Ber*. **1984**, *117*, 2531. (d) Berndt, A.; Pues, C. *Angew. Chem*. **1984**, *96*, 306; *Angew. Chem., Int. Ed. Engl*. **1984**, *23*, 313 (e) Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc*. **1987**, *109*, 2526. (f) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc*. **1990**, *112*, 1847.

(3) Examples of Group 14 cyclopropene analogues, see: (a) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Yu. T.; Antipin, M. Yu.; Sereda, S. V.; Nefedov, O. M. *J. Organomet. Chem.* **1985**, *290*, C27. (b) Sita, R. L.; Bicherstaff, R. D. *J. Am. Chem. Soc*. **1988**, *110*, 5208. (c) Pea, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc*. **1991**, *113*, 1281. (d) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc*. **1997**, *119*, 2337. (e) Sakamato, K.; Tsutsui, S.; Sakura, H.; Kira, M. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 251.

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

(5) (a) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem*. **2000**, *112*, 4444; *Angew. Chem., Int. Ed*. **2000**. *39*, 4274. (b) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun*. **2000**, 1991.

(6) (a) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem.* **2000**, *112*, 4705; *Angew. Chem., Int. Ed.* **2000**, *39*, 4531. (b) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. *Angew. Chem.* **2001**, *113*, 2230; *Angew. Chem., Int. Ed.* **2001**, *40*, 2172.

10.1021/ja003185i CCC: \$20.00

$LAlI_2$ (**1**)[5a] in the presence of alkynes for trapping reduction transients and generating unusual aluminum compounds. The comparison between two reactions would be useful in understanding the reductive coupling mechanism.

The reactions of aluminum compounds (alkyls, hydrides, and halides) with alkynes have been explored extensively.[7] The resulting aluminum vinyl derivatives undergo interesting thermal and photoinduced rearrangements and have proved to be valuable precursors for organic chain growing reactions.[8] Aluminum cyclopropene analogues have been proposed as reactive intermediates in the formation of the related 1,4-(dialumina)cyclohexadienes via dimerization[9] and in the reaction of unstable Al(I) compounds with alkynes.[10] We reasoned that such strained ring systems would show high chemical reactivities and unique reaction patterns. Herein, we report on the synthesis of cyclopropene analogues of aluminum and an aluminum pinacolate by reductive coupling reaction in the presence of alkynes and benzophenone, and the reaction of a cyclopropene analogue of aluminum $LAl[\eta^2\text{-}C_2(SiMe_3)_2]$ (**3**) with CO_2, Ph_2CO, nitriles PhCN and *t*-BuCN, and bulky azides Ph_3SiN_3 and $2,6\text{-}Trip_2C_6H_3N_3$ (Trip = 2,4,6-i-$Pr_3C_6H_2$).

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques or inside a MBraun MB 150-GI glovebox filled with dry nitrogen where the O_2 and H_2O level were strictly controlled below 1 ppm. All solvents were dried using standard methods prior to use.[11] The samples for analytical measurements were prepared inside the glovebox. Commercially available chemicals were purchased from Fluka or Aldrich and used as received. The other compounds used in this paper were prepared according to published procedures: $H_2C[(CMe)(NAr)]_2$ (Ar = 2,6-i-$Pr_2C_6H_3$),[12] Ph_3SiN_3,[13] and $2,6\text{-}Trip_2C_6H_3N_3$ (Trip = 2,4,6-i-$Pr_3C_6H_2$).[14]

Physical Measurements and Analysis. The melting points of all compounds described in this paper were measured on a Bühler SPA-1 apparatus in sealed capillaries and uncorrected. ^1H, ^{13}C, ^{27}Al, and ^{29}Si NMR spectra were recorded on Avance-500, Avance-200, Bruker MSL-400, AM-250, and AM-200 instruments. The chemical shifts are reported in ppm with reference to external standards, namely $SiMe_4$ for ^1H, ^{13}C, and ^{29}Si nuclei and 1 M aqueous $AlCl_3$ for ^{27}Al NMR. Heteroatomic spectra were recorded ^1H-decoupled. If not otherwise stated, the operation temperature was in the range from 293 to 300 K. ESR measurements were performed on a Varian (9.6 MHz) instrument. UV spectra were recorded on a PERKIN ELMER 320 instrument.

X-ray Structure Determinations and Refinements. Data for crystal structures of **3** and **6**$\cdot OEt_2$ were collected on a STOE-AED2 four-circle diffractometer and data for the structures of **4**, **8**$\cdot OEt_2$, and **9** were collected on a Stoe-Siemens-Huber four circle diffractometer equipped with a CCD area detector using Mo Kα radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods (SHELXS-96)[15] and refined against F^2 using SHELXL-97.[16] All heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atom. The Et_2O molecule in **6**$\cdot OEt_2$ was disordered over two positions. It was refined with distance restraints and restraints for the anisotropic displacement parameters. The structure of **4** was refined as a pseudomerohedral twin. The twin law is [−100 010 001]. The fractional contribution of the second domain refines to 0.4511(8). Additionally the structure shows pseudosymmetry. A great number of the atoms fulfill the symmetry of space group $P2_1/n$. But refinement in this space group was much worse even if disorder was modeled. Crystal data, data collection details, structural solution and refinement procedures for all compounds are summarized in Table 1.

Synthesis of $LAl[\eta^2\text{-}C_2(SiMe_3)_2]$ (3). A solution of $LAlI_2$ (**1**)[5a] (1.40 g, 2 mmol) and bis(trimethylsilyl)alkyne (0.34 g, 2 mmol) in toluene (20 mL) was added to a suspension of finely divided potassium (0.16 g, 4.1 mmol) at room temperature. The mixture was stirred at room temperature for 2 d. The solution developed a red-black color and all the potassium appeared consumed. Subsequently all volatiles were removed under vacuum, and the residue was extracted with *n*-hexane (20 mL). After filtration the red black filtrate was concentrated (ca 6 mL) and stored at −30 °C overnight affording red-black crystals of **3** (0.68 g, 55.4%). Mp: 182−184 °C. ^1H NMR (d_8-toluene, 298 K, 500.13 MHz): δ 6.97−7.09 (m, 6 H, Ar−H), 4.78 (s, 1 H, γ-C*H*), 3.33 (sept, 4 H, $J = 6.8$ Hz, C*H*Me_2), 1.43 (s, 6 H, Me), 1.42 (d, 12 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.11 (d, 12 H, $J = 6.8$ Hz, CH*Me*$_2$), 0.10 (s, 18 H, $SiMe_3$). ^{13}C NMR (C_6D_6, 100.60 MHz): δ 228.5 (Al−C), 174.1(CN), 143.5, 140.4, 124.3 (Ph), 97.2 (γ-C), 28.7 (*C*HMe_2), 25.6, 24.1 (CH*Me*$_2$), 24.0 (Me), 1.8 ($SiMe_3$). ^{27}Al NMR (d_8-toluene, 130.32 MHz): δ 90 ± 5 ($\nu_{1/2} \approx 2500$ Hz). ^{29}Si NMR (C_6D_6, 79.46 MHz): δ −24.7.

Synthesis of $LAl(\eta^2\text{-}C_2Ph_2)$ (4). Compound **4** was prepared in a similar manner as **3**. $LAlI_2$ (**1**) (1.4 g, 2 mmol), diphenylalkyne (0.36 g, 2 mmol), and potassium (0.16 g, 4.1 mmol) were used. After filtration and partial removal of the solvents, the solution was stored at −30 °C overnight affording orange crystals of **4** (0.86 g, 70%). Mp: 260 °C (dec). ^1H NMR (C_6D_6, 200.13 MHz): δ 6.8−7.15 (m, 16 H, Ar−H), 4.89 (s, 1 H, γ-C*H*), 3.39 (sept, 4 H, $J = 6.8$ Hz, C*H*Me_2), 1.53 (s, 6 H, Me), 1.21 (d, 12 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.11 (d, 12 H, $J = 6.8$ Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 177.2 (Al−C), 173.1 (CN), 144.2, 144.0, 139.2, 131.9, 128.6, 128.4, 124.5, 124.0 (Ph), 97.3 (γ-C), 29.1 (*C*HMe_2), 25.0, 24.4 (CH*Me*$_2$), 23.5 (Me).

Synthesis of $LAl[\eta^2\text{-}C_2Ph(SiMe_3)]$ (5). Compound **5** was prepared similarly to **3**: $LAlI_2$ (**1**) (1.4 g, 2 mmol), 1-phenyl-2-(trimethylsilyl)-alkyne (0.35 g, 2 mmol), and potassium (0.16 g, 4.1 mmol) were employed. Crystallization from toluene at −30 °C gave orange crystals of **5** (0.74 g, 60%). Mp: 242 °C. ^1H NMR (d_8-toluene, 200.13 MHz): δ 7.06−7.12 (m, 11 H, Ar−H), 4.87 (s, γ-CH), 3.36, 3.21 (dsept, 2 H, $J = 6.8$ Hz, C*H*Me_2), 1.53 (s, 6 H, Me), 1.45 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.13 (d, 6 H, $J = 6.7$ Hz, CH*Me*$_2$), 1.12 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.08 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), −0.04 (s, 9 H, $SiMe_3$). ^{13}C NMR (d_8-toluene, 125.76 MHz): δ 211.9 (Al−C), 187.2 (Al−C), 173.2 (CN), 148.9, 144.2, 143.6, 139.6, 137.5, 128.8, 128.1, 125.3, 125.1, 124.9, 123.6 (Ph), 97.3 (γ-C), 29.1, 28.9 (*C*HMe_2), 25.4, 24.7, 24.5, 24.1 (CH*Me*$_2$), 23.6 (Me), 2.2 ($SiMe_3$). ^{29}Si NMR (d_8-toluene, 99.36 MHz): δ −20.5.

Synthesis of $LAl[O_2(CPh_2)_2]$ (6). A solution of $LAlI_2$ (**1**) (1.4 g, 2 mmol) and Ph_2CO (0.36 g, 2 mmol) in toluene (15 mL) was added to a suspension of finely divided potassium (0.16 g, 4.1 mmol). Immediately a purple color was observed. The mixture was stirred at room temperature for 24 h and the solution finally developed a red color. After filtration the filtrate was concentrated and stored at −30 °C overnight to afford yellow crystals of **6** (0.56 g, 35%). Mp: 272 °C.

---

[7] For examples: (a) Schäfer, W. *Angew. Chem.* **1966**, *78*, 716; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 669. (b) Eisch, J. J.; Harrell, R. L., Jr. *J. Organomet. Chem.* **1969**, *20*, 257. (c) Clark, G. M.; Zweifel, G. *J. Am. Chem. Soc.* **1971**, *93*, 527. (d) Albright, M. J.; Butler, W. M.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 3995. (e) Hoberg, H.; Gotor, V. *J. Organomet. Chem.* **1977**, *127*, C32. (d) Hoberg, H.; Aznar, F. *J. Organomet. Chem.* 1**980**, *193*, 161.

[8] (a) Eisch, J. J.; Amtmann, R. *J. Org. Chem.* **1972**, *37*, 3410. (b) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1941. (c) Hoberg, H.; Aznar, F. *J. Organomet. Chem.* **1978**, *141*, 1. (d) Hoberg, H.; Aznar, F. *J. Organomet. Chem.* **1980**, *193*, 155.

[9] (a) Hoberg, H.; Gotor, V.; Milchereit, A.; Krüger, C.; Sekutowski, J. C. *Angew. Chem.* **1977**, *89*, 563; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 539. (b) Hoberg, H.; Aznar, F. *J. Organomet. Chem.* **1979**, *164*, C13.

[10] (a) Schnöckel, H.; Leimkühler, M.; Lotz, R.; Mattes, R. *Angew. Chem.* **1986**, *98*, 929; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 921. (b) Üffing, C.; Ecker, A.; Köppe, R.; Merzweiler, K.; Schnöckel, H. *Chem. Eur. J.* **1998**, *4*, 2142.

[11] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: London, 1988.

[12] (a) Qian, B.; Ward, D. L.; Smith, M. R., III *Organometallics* **1998**, *17*, 3070. (b) Budzelaar, D. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485.

[13] Schulz, S.; Voigt, A.; Roesky, H. W.; Häming, L.; Herbst-Irmer, R. *Organometallics* **1996**, *15*, 5252.

[14] Twamley, B.; Hwang, C.-S.; Hardman, N. J.; Power, P. P. *J. Organomet. Chem.* **2000**, *609*, 152.

[15] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[16] Sheldrick, G. M. *SHELXL*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

Table 1. Crystallographic Data for Compounds **3**, **4**, **6**·OEt_2, **8**·OEt_2, and **9**

	3	**4**	**6**·OEt_2	**8**·OEt_2	**9**
formula	$C_{37}H_{59}AlN_2Si_2$	$C_{43}H_{51}AlN_2$	$C_{59}H_{71}AlN_2O_3$	$C_{54}H_{79}AlN_2O_2Si_2$	$C_{44}H_{64}AlN_3Si_2$
formula weight	615.02	622.84	883.16	871.35	718.14
temp (K)	200(2)	133(2)	203(2)	133(2)	133(2)
cryst color	red-black	yellow	yellow	colorless	orange
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a, Å	11.160(4)	18.785(3)	22.027(4)	12.767(3)	11.445(2)
b, Å	11.978(5)	20.832(4)	11.464(2)	17.086(3)	12.591(3)
c, Å	16.460(7)	18.823(3)	20.857(4)	23.583(5)	16.521(3)
α, deg	85.68(3)	90	90	90	106.30(3)
β, deg	80.20(2)	90.08(3)	105.02(2)	90	90.82(3)
γ, deg	64.11(2)	90	90	90	108.90(3)
V, Å^3	1950.6(14)	7366(2)	5086.8(16)	5144.3(19)	2147.3(7)
Z	2	8	4	4	2
d(calcd), mg/m^3	1.047	1.123	1.153	1.125	1.111
abs coeff, mm^{-1}	0.138	0.086	0.086	0.126	0.135
F(000)	672	2688	1904	1896	780
cryst size, mm	1.0 × 0.6 × 0.3	0.7 × 0.4 × 0.15	0.8 × 0.6 × 0.5	0.4 × 0.3 × 0.2	0.5 × 0.3 × 0.3
θ range, deg	3.51 to 25.12	2.23 to 27.50	3.52 to 25.03	2.10 to 28.02	2.17 to 27.76
no. of reflns collected	7806	143864	12230	109910	58404
no. of indep. reflns	6894	32699	8973	12113	9997
R_{int}	0.0708	0.0839	0.0434	0.0710	0.0519
GOF/F^2	1.033	1.028	1.034	1.053	1.065
R indices [$I > 2\sigma(I)$]	$R1 = 0.0698$ $wR2 = 0.1853$	$R1 = 0.0506$ $wR2 = 0.1045$	$R1 = 0.0476$ $wR2 = 0.1015$	$R1 = 0.0395$ $wR2 = 0.0856$	$R1 = 0.0437$ $wR2 = 0.1030$
(all data)	$R1 = 0.0849$ $wR2 = 0.2049$	$R1 = 0.0780$ $wR2 = 0.1177$	$R1 = 0.0710$ $wR2 = 0.1161$	$R1 = 0.0486$ $wR2 = 0.0897$	$R1 = 0.0548$ $wR2 = 0.1084$
extinction coeff		0.00176(12)			
largest diff. peak and hole, eÅ^{-3}	0.491−0.490	0.249−0.270	0.295−0.245	0.241−0.229	0.394−0.308

^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.01−6.58 (m, 26 H, Ar−H), 5.04 (s, 1 H, γ-CH), 3.55 (sept, 4 H, C*H*Me$_2$), 1.39 (s, 6 H, Me), 1.11 (d, 12 H, $J = 6.9$ Hz, CH*Me*$_2$), 1.07 (d, 12 H, $J = 6.8$ Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 174.2 (CN), 149.6, 143.9, 142.5, 130.4, 129.3, 128.5, 126.1, 125.6, 124.9, 124.8 (Ph), 99.3 (γ-C), 92.7 (CO), 28.8 (*C*HMe$_2$), 25.2, 24.6, 24.0 (CH*Me*$_2$), 23.1 (Me).

Synthesis of LAl[OC(O)C_2($SiMe_3$)$_2$] (7). When a solution of **3** (0.31 g, 0.5 mmol) in *n*-hexane (15 mL) was exposed to dry CO_2 at room temperature, the red-black color changed to yellow within 10 min. The solvent was removed under vacuum to give a slightly yellow powder, which was subsequently washed with cold pentane (5 mL) to give analytically pure **7** (0.30 g, 91%). Mp: 258−260 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.03 (m, 6 H, Ar−H), 5.11 (s, 1 H, γ-C*H*), 3.10, 3.35 (sept, 4 H, $J = 6.8$ Hz, C*H*Me$_2$), 1.51 (s, 6 H, Me), 1.23 (dd, 12 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.02 (dd, 12 H, $J = 6.8$ Hz, CH*Me*$_2$), 0.49, −0.09 (s, 9 H, SiMe$_3$). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 178.1 (β-*C*SiMe$_3$), 172.9 (CN), 161.5 (CO), 145.4, 143.1, 142.8, 139.8, 125.8, 125.2, 124.2, 123.6 (Ph), 100.7 (γ-C), 29.0, 28.6, 28.1, 25.6, 24.9, 24.7, 24.5, 24.4, 23.8, 23.4 (CHMe$_2$ and Me), 2.37, 2.29 (SiMe$_3$). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ −7.9, −12.0 (SiMe$_3$).

Synthesis of LAl[OC(Ph)$_2C_2$($SiMe_3$)$_2$] (8). To a mixture of **3** (0.61 g, 1 mmol) and Ph_2CO (0.18 g, 1 mmol) was added diethyl ether (20 mL). The mixture was stirred at room temperature for 30 min. The solution was concentrated and stored at −30 °C overnight to give colorless crystals of **8** (0.59 g, 74%). Mp: 215 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.70 (m, 2 H, Ar−H), 7.07−6.84 (m, 14 H, Ar−H), 4.91 (s, 1 H, γ-C*H*), 3.20 (sept, 4 H, $J = 6.8$ Hz, C*H*Me$_2$), 1.38 (s, 6 H, Me), 1.33 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.20 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.12 (d, 6 H, $J = 6.7$ Hz, CH*Me*$_2$), 1.02 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 0.64 (s, 9 H, SiMe$_3$), 0.01 (s, 9 H, SiMe$_3$). ^{13}C NMR (C_6D_6, 125.8 MHz): δ 195.5 (Al−C), 190.8 (β-C), 171.5 (CN), 148.5, 144.7, 143.5, 141.8, 132.0, 130.2, 130.0, 127.3, 126.6, 125.6, 125.2, 124.3 (Ph), 99.9 (γ-C), 90.1 (CO), 28.7, 28.6 (*C*HMe$_2$), 25.3, 25.2, 25.1, 24.7 (CH*Me*$_2$), 24.4 (Me), 5.7, 4.1 (SiMe$_3$).

Synthesis of LAl [NC(Ph)C_2($SiMe_3$)$_2$] (9). To a solution of **3** (0.31 g, 0.5 mmol) in diethyl ether (20 mL) was added neat PhCN (0.052 g, 0.5 mmol) at room temperature, and the mixture was stirred at room temperature overnight. The solution was concentrated (ca. 5 mL) and stored at −30 °C overnight to give orange crystals of **9** (0.22 g, 61%). Mp: 235−236 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.65 (m, 2 H, Ar−H), 7.15−7.05 (m, 7 H, Ar−H), 5.27 (s, 1 H, γ-C*H*), 3.25 (sept, 4 H, $J = 6.8$ Hz, C*H*Me$_2$), 1.60 (s, 6 H, Me), 1.34 (d, 6 H, $J = 6.7$ Hz, CH*Me*$_2$), 1.31 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 1.13 (d, 6 H, $J = 6.7$ Hz, CH*Me*$_2$), 1.06 (d, 6 H, $J = 6.7$ Hz, CH*Me*$_2$), 0.09 (s, 9 H, SiMe$_3$), 0.03 (s, 9 H, SiMe$_3$). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 183.8 (Al−C), 181.5 (β-C), 177.3 (Ph*C*N), 172.4 (CN), 149.7, 145.2, 143.5, 141.3, 127.4, 127.3, 127.2, 124.8, 124.4 (Ph), 102.0 (γ-C), 28.7, 28.2 (*C*HMe$_2$), 25.9, 25.1, 25.0 (CH*Me*$_2$), 24.0 (Me), 3.4, 3.2 (SiMe$_3$). ^{29}Si NMR (C_6D_6, 99.36 MHz): δ −10.3, −11.8.

Synthesis of LAl[N_2(C*t*-Bu)$_2$] (10). To a solution of **3** (0.31 g, 0.5 mmol) in diethyl ether (20 mL) was added *t*-BuCN (0.042 g, 0.5 mmol) at room temperature. The black-red color disappeared within 2 h. The solution was stirred for an additional 4 h. The solvents were partially removed (ca. 10 mL) and the solution was stored at −5 °C for 2 days to give colorless crystals (0.10 g, 42%). Mp: 249−250 °C. ^{1}H NMR (C_6D_6, 200.13 MHz): δ 7.01 (m, 6 H, Ar−H), 5.08 (s, 1 H, γ-CH), 3.42 (sept, 4 H, $J = 6.8$ Hz, C*H*Me$_2$), 1.58 (s, 6 H, Me), 1.47 (d, 12 H, $J = 6.7$ Hz, CH*Me*$_2$), 1.25 (br s, 18 H, *t*-Bu), 1.06 (12 H, $J = 6.8$ Hz, CH*Me*$_2$). ^{13}C NMR (C_6D_6, 125.76 MHz): δ 193.6 (N*Ct*-Bu), 170.6, 170.5 (CN), 144.9, 143.6, 143.3, 142.1, 141.9, 127.3, 127.2, 124.9, 124.5 (Ph), 97.8 (γ-C), 41.4, 40.8 (*C*Me$_3$), 29.9, 29.5 (*C*HMe$_2$), 29.3, 29.1, 29.0, 28.9, 27.8 (CH*Me*$_2$), 25.5 (Me), 24.9, 24.8, 24.5, 24.0, 23.8 (C*Me*$_3$).

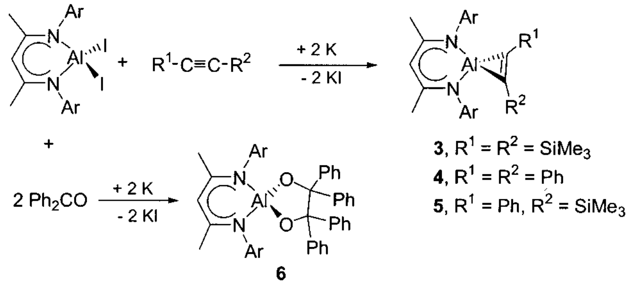
Synthesis of LAlNC_6H_3-2,6-Trip$_2$ (11)^{6b} and LAlNSiPh$_3$ (12). Method A: To a mixture of {HC[(CMe)(NAr)]$_2$}Al (**2**) (0.22 g, 0.5 mmol) and 2,6-Trip$_2C_6H_3N_3$ or Ph_3SiN_3 (0.15 g, 0.5 mmol) was added toluene (15 mL) at −60 °C. The mixture was allowed to warm to room temperature and a slow color change from orange red to yellow was observed during 1 h. After being stirred at room temperature for an additional 3 h, the solution was concentrated (ca. 5 mL) and stored at room temperature for 2 days to afford the pale yellow solid of **11** (0.26 g, 52%) or the white solid of **12** (0.28 g, 80%), respectively.

Method B: To a mixture of **3** (0.31 g, 0.5 mmol) and equal amounts of the azides used in method A was added toluene (15 mL) at 0 °C. The mixture was allowed to warm to room temperature within 1 h. During this period, the solution developed a slightly yellow color. After the solution was stirred for additional 1 h, all volatiles were removed. The residue was crystallized from toluene to give pure **11** and **12** in ca. 80% yield, respectively. Data for **12**: Mp: 203 °C. ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.32−6.88 (m, 21 H, Ar−H), 4.18 (s, 1 H, γ-C*H*), 3.40 (sept, 2 H, C*H*Me$_2$), 2.35 (sept, 2 H, C*H*Me$_2$), 1.47 (s, 6 H, Me), 0.85 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 0.68 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 0.56 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$), 0.49 (d, 6 H, $J = 6.8$ Hz, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$, 125.76 MHz): δ 172.0 (CN), 145.3, 143.6, 140, 4, 137.1, 136.5, 128.4, 127.3, 125.4, 124.8 (Ph), 102.3 (γ-*C*), 28.4, 28.1 (*C*HMe$_2$), 25.4 (*Me*), 24.8, 24.7, 24.6, 24.5 (CH*Me*$_2$).

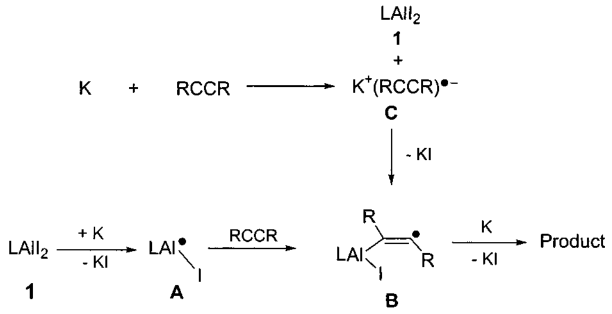
Results and Discussion

Reduction of LAlI$_2$ (1) in the Presence of Alkynes and Ph$_2$CO. The diiodide LAlI$_2$ (**1**) (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) is easily accessible in high yield through the reaction of LAlMe$_2$[12a] with 2 equiv of I$_2$ in toluene. **1** can be reduced at room temperature to afford the first two coordinated aluminum compound LAl (**2**),[5a] which is not paramagnetic as disclosed by an ESR study. Ab initio calculations show that the electronic structure of **2** is carbene-like. Unlike reactive carbenes, **2** does not undergo a [1 + 2] cycloaddition with bis(trimethysilyl)alkyne at room temperature. However, as **1** can be easily reduced, we reasoned that the reductive coupling reactions of **1** in the presence of selected alkynes may be an alternative route to access unique species which otherwise are not easily available. As expected, reduction of **1** with potassium in the presence of bis(trimethylsilyl)alkyne, diphenylalkyne, and 1-phenyl-2-trimethylsilylalkyne at room temperature afforded LAl[η^2-C$_2$(SiMe$_3$)$_2$] (**3**), LAl(η^2-C$_2$Ph$_2$) (**4**), and LAl[η^2-C$_2$Ph(SiMe$_3$)] (**5**) in modest yields, respectively (Scheme 1). Compound **3** was isolated as red-black crystals, soluble in hydrocarbon solvents, and extremely air- and moisture-sensitive as indicated by the immediate color change from red-black to yellow when exposed to air. Yellow crystals of **4** and orange-red crystals of **5** were obtained from toluene and are sparingly soluble in *n*-hexane.

Scheme 1



Scheme 2



The inertness of **2** to alkynes at room temperature suggests that the reductive coupling reactions should not proceed through a [1 + 2] cycloaddition. Two possible mechanisms may be assumed for the reductive coupling reaction (Scheme 2) because both (LAlI)$^\bullet$ (**A**) and K$^+$(RCCR)$^{\bullet-}$ (**C**) could be generated under the reducing conditions considering the long period of the reductive coupling reaction (2−3 d). One of the species may be involved in the partial reduction of **1** to give the transient radical **A**, which couples with alkynes. Another possible mechanism is that the radical anion **C**, formed by electron transfer from K to the alkyne, substitutes the iodide in **1**. Both mechanisms would generate the same intermediate LAlI(RCCR)$^{\bullet-}$ (**B**), which undergoes a further electron-transfer reaction to give the desired products. However, we were unable to monitor the reaction under vigorous stirring due to its heterogeneous nature.

To make a comparison, we performed the reduction of **1** in the presence of Ph$_2$CO since Ph$_2$CO can be rapidly reduced by Na and K at room temperature to give the ketyl M$^+$(OCPh$_2$)$^{\bullet-}$(M = Na, K) with a typical deep blue color. When a solution of benzophenone was added to a suspension of **1** and potassium in toluene, immediately a deep blue color was formed, indicating the formation of the ketyl K$^+$(OCPh$_2$)$^{\bullet-}$.[17] The deep blue color gradually changed to purple, then red over a period of 6 h. This reaction in the presence of 1 or 2 equiv of benzophenone yielded the aluminum pinacolate {HC[(CMe)(NAr)]$_2$}Al[O$_2$(CPh$_2$)$_2$] (**6**) (Scheme 1). Therefore it is assumed that this reaction mainly proceeds through the initial replacement of the iodide by the ketyl to form the radical LAl(OCPh$_2$)$^\bullet$, which could easily couple with another ketyl, followed by elimination of KI, to yield **6**. The facile formation of **6** instead of an aluminum η^2-ketone complex LAl(η^2-OCPh$_2$) also supports this mechanism. Moreover the reaction implies that in the former reaction RCCR should not be as easily and rapidly reduced as Ph$_2$CO in toluene, otherwise alkyne coupling would be observed. Therefore it seems reasonable to assume that the former reaction mainly proceeds through transient **A**. This mechanism was further supported by the following experiment: in a NMR tube, compounds **1**, **2**, and alkyne PhCCPh were dissolved in d_8-toluene at room temperature; the ^{1}H NMR spectra indicate the formation of compound **4** in this system within 2 h. We reasoned that the radical **A** could be easily generated in this system by the reaction of **1** and **2**. It was trapped by the alkyne to generate **B**, which could be further oxidized by low-valent species existing in the system.

Compounds **3**−**6** have been characterized by EI-mass,^{1}H, ^{13}C NMR, and IR spectra. The EI-MS spectrum of **3** shows the (M$^+$ − SiMe$_3$) ion as the fragment with the highest mass, while those of **4**, **5**, and **6** give the parent ions. The ^{13}C NMR spectrum of **3** shows a weak resonance at δ 228.5 ppm, corresponding to the coordinated C=C group. In the ^{13}C NMR spectrum of **4** the corresponding resonance appears at δ 177.2 ppm, and in that of **5** two resonances (δ 211.9, 187.2 ppm) for the carbon atoms of the coordinated C=C group were observed. The IR spectra for the three compounds all show a characteristic absorption band centering at 1590 cm^{-1}, which could be assigned to the stretching frequencies of the coordinated C=C groups.

The variable-temperature ^{1}H NMR investigations of **3** (193−373 K, see Supporting Information) show that **3** does not dissociate up to 373 K, indicating that the C=C moiety is strongly bonded to the aluminum atom of **3** and the Al−C−C ring is intact in toluene solution even at high temperature. This result suggests that the compound can be described as rather a metallocyclopropene (Al(III)) than an aluminum alkyne complex (π complexation). The assumption is also supported by ESR studies of compounds **3** and **4**, in whose spectra no resonances were observed for both compounds. Furthermore, the ^{27}Al NMR spectrum of **3** shows a resonance (90 ppm) in the range of those

---

[17] Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*; Plenum Press: New York and London, 1991; p 668.

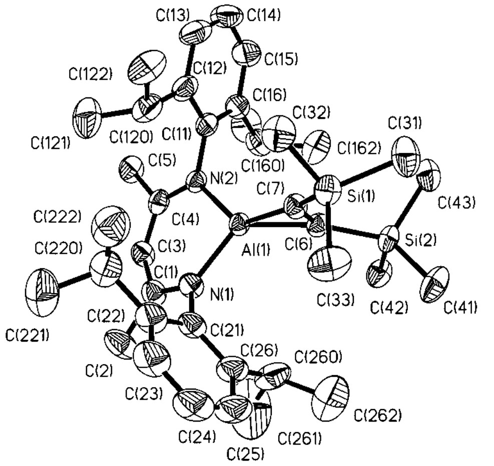


Figure 1. ORTEP drawing of **3** (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

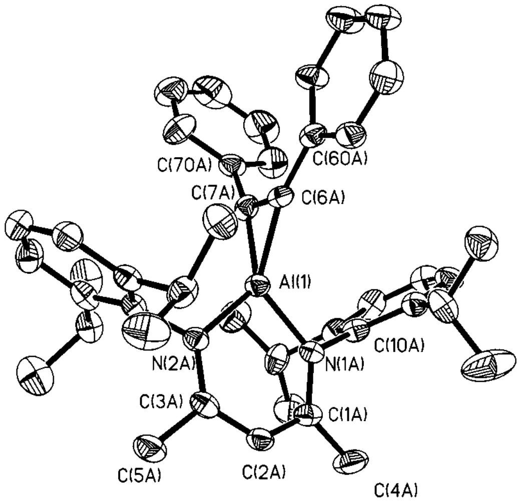


Figure 2. ORTEP drawing of one molecule of **4** (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **3**, **4**, and **6**·OEt$_2$

	3		
Al(1)−N(1)	1.889(2)	Al(1)−C(6)	1.899(3)
C(6)−C(7)	1.382(4)	Al(1)−N(2)	1.892(2)
Al(1)−C(7)	1.908(3)		
C(6)−Al(1)−C(7)	42.57(11)	Al(1)−C(6)−C(7)	69.04(15)
Al(1)−C(7)−C(6)	68.39(15)	N(1)−Al(1)−N(2)	97.33(10)
N(1)−Al(1)−C(6)	126.85(11)	N(1)−Al(1)−C(7)	124.63(11)
N(2)−Al(1)−C(6)	128.25(11)	N(2)−Al(1)−C(7)	132.17(11)
C(7)−C(6)−Si(2)	134.0(2)	C(6)−C(7)−Si(1)	133.7(2)
Si(1)−C(7)−Al(1)	156.35(16)	Si(2)−C(6)−Al(1)	156.73(16)
	4		
Al(1)−N(1A)	1.885(3)	Al(1)−N(2A)	1.875(4)
Al(1)−C(6A)	1.889(4)	Al(1)−C(7A)	1.894(3)
C(6A)−C(7A)	1.356(5)		
C(6A)−Al(1)−C(7A)	42.02(14)	C(7A)−C(6A)−Al(1)	69.2(2)
C(6A)−C(7A)−Al(1)	68.80(19)	N(1A)−Al(1)−C(6A)	126.98(15)
N(1A)−Al(1)−C(7A)	124.09(15)	N(2A)−Al(1)−N(1A)	97.03(13)
N(2A)−Al(1)−C(6A)	130.52(15)	Al(1)−C(7A)−C(70A)	160.9(3)
N(2A)−Al(1)−C(7A)	131.08(15)	C(7A)−C(6A)−C(60A)	130.4(3)
Al(1)−C(6A)−C(60A)	160.0(2)	C(6A)−C(7A)−C(70A)	129.8(3)
	6·OEt$_2$		
Al(1)−O(1)	1.7324(14)	Al(1)−O(2)	1.7355(14)
Al(1)−N(1)	1.8978(17)	Al(1)−N(2)	1.9038(16)
O(1)−C(6)	1.430(2)	O(2)−C(7)	1.427(2)
C(6)−C(7)	1.670(3)		
N(1)−Al(1)−N(2)	96.91(7)	O(1)−Al(1)−O(2)	92.70(6)
O(1)−Al(1)−N(1)	124.68(7)	O(1)−Al(1)−N(2)	110.56(7)
O(1)−C(6)−C(7)	106.75(15)	O(2)−Al(1)−N(1)	111.39(7)
O(2)−Al(1)−N(2)	123.09(7)	O(2)−C(7)−C(6)	106.03(14)
C(6)−O(1)−Al(1)	115.73	C(7)−O(2)−Al(1)	116.08(11)

for four-coordinated aluminum compounds. In contrast, the Al(I) compound **2** gives the most highly shielded resonance (590 ± 40 ppm, $\nu_{1/2} \approx 30\,000$ Hz) experimentally observed so far. The detailed explanation for these data is currently unavailable although the ^{27}Al NMR resonances for monovalent aluminum compounds have been computed ranging from −170 to 850 ppm.[18]

The UV spectra of the colored solution of compounds **3** and **4** in *n*-hexane show several maxima in the range of 240 to 400 nm. A maximum at 320 nm ($\epsilon \approx 4000$ M^{-1} cm^{-1}) for **3** as well as a maximum at 340 ($\epsilon \approx 3000$ M^{-1} cm^{-1}) for **4** disappears when the solutions are exposed to air. The absorptions might be due to electronic transitions within the Al−C−C three-membered-ring system.

X-ray Structures of Compounds 3, 4, and 6·OEt$_2$. The red-black crystals of **3** and yellow crystals of **4** suitable for X-ray structure analysis were obtained from *n*-hexane and toluene at −30 °C, respectively. The structures of **3** and **4** are shown in Figures 1 and 2 and important bond lengths and angles are listed in Table 2. The Al−C−C ring system of **3** forms an isosceles triangle with the Al−C bond lengths of 1.899(3) and 1.908(3) Å, which are shorter than the Al−C bond lengths of the corresponding dimethyl derivative {HC[(CMe)(NAr)]$_2$}AlMe$_2$ (av 1.96 Å).[12a] The C(6)−C(7) bond length (1.382(4) Å) in **3** is consistent with double bond character. The C(6)−Al−C(7) angle (42.57(11)°) is very acute. The Al(1) and C(3) atoms lie out of the N(1)−C(1)−C(4)−N(2) plane (mean deviation of the plane = 0.006 Å) by 0.37 and 0.11 Å, respectively. The two fused planes N(1)−Al(1)−N(2) and C(6)−Al(1)−C(7) (angle 94.3°) are arranged nearly perpendicular to each other. Compound **4** crystallizes in the monoclinic space group $P2_1$. The asymmetric unit contains four molecules only marginally different in bond lengths and angles. Figure 2 shows one of the four independent molecules. The structure of **4** is comparable to that of **3**.

The molecular structure of compound **6**·OEt$_2$ also has been determined by single-crystal X-ray structural analysis. The structure is shown in Figure 3, and selected bond distances and angles are tabulated in Table 2. The aluminum atom is four coordinated and acts as the center atom for the two fused rings. The Al−N distances (av 1.90 Å) are similar to those of LAl(SeH)$_2$ (av 1.90 Å)[19] and LAl[(NSiMe$_3$)$_2$N$_2$] (av 1.89 Å).[6a] It is noteworthy that the C(6)−C(7) bond length (1.670(3) Å) is longer by 0.13 Å compared to normal C−C single bond lengths (ca. 1.54 Å)[20] due to the electronic and steric effects afforded by two phenyl groups on each carbon atom. The O(1)−Al(1)−O(2) angle (92.70(7)°) is the smallest among the internal angles of the five-membered AlOCCO cycle.

Reaction of LAl[η^2-C$_2$(SiMe$_3$)$_2$] (3) with CO$_2$, Ph$_2$CO, and PhCN. Reduction of the carbonyl groups by activated metals or metal complexes constitutes a powerful strategy for C−C bond formation reactions.[21] The success in the synthesis of compounds **3**−**5** with the highly strained three-membered

---

[18] Gauss, J.; Schneider, U.; Ahlrichs, R.; Dohmeier, C.; Schnöckel, H. *J. Am. Chem. Soc.* **1993**, *115*, 2402.

[19] Cui, C.; Roesky, H. W.; Hao, H.; Schmidt, H.-G.; Noltemeyer, M. *Angew Chem.* **2000**, *112*, 1885; *Angew. Chem., Int. Ed.* **2000**, *39*, 1815.

[20] See ref 17; p 11.

[21] Kahn, B. E.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733.

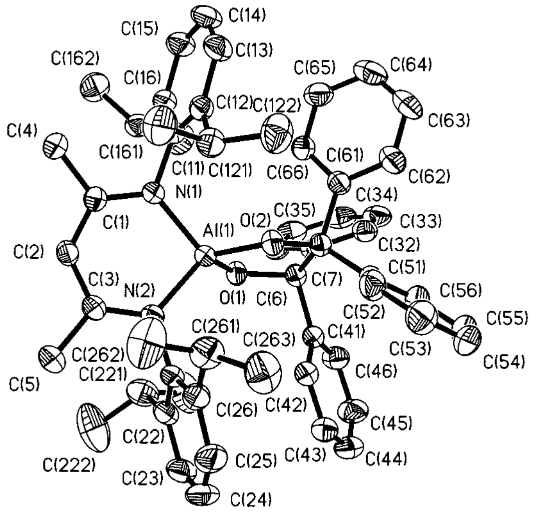
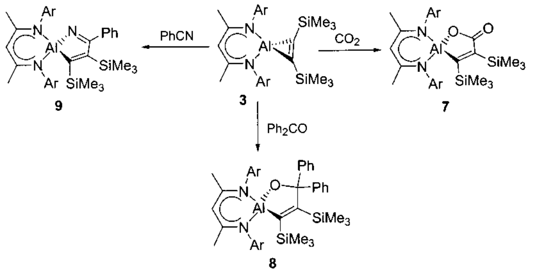


Figure 3. ORTEP drawing of **6** (50% thermal ellipsoids). Hydrogen atoms and solvent Et$_2$O have been omitted for clarity.

Scheme 3



C−C−Al ring systems prompted us to examine the reactivities of this unique species toward unsaturated molecules. It is well-known that reactivities of base-stabilized neutral aluminum complexes are dramatically retarded compared to those of base-free aluminum compounds. However, ring strain within the Al−C−C cycles would increase the reactivities of the Al−C bonds toward unsaturated molecules, leading to organic chain growing reactions, although the Al atom in these systems is four coordinated. In addition, this type of reaction should be an effective route for the synthesis of novel aluminum-containing ring systems.

Reaction of **3** with CO$_2$ proceeds smoothly at room temperature leading to C−C coupling with the formation of a new class of aluminum heterocycles, LAl[OC(O)C$_2$(SiMe$_3$)$_2$] (**7**), in high yield (Scheme 3). The EI-MS spectrum shows the molecular ion with high intensity consistent with the formulation as a monomer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra all gave two distinct resonances for the Me$_3$Si nuclei, indicating that CO$_2$ only inserts into one of the Al−C bonds. The IR spectrum shows a very strong band at 1666 cm^{-1}, suggesting the formation of an α,β-unsaturated ketone unit.

Reaction of **3** with benzophenone (Ph$_2$CO) in diethyl ether at room temperature also leads to C−C coupling with the formation of an aluminadihydrofuran LAl[OC(Ph)$_2$C$_2$(SiMe$_3$)$_2$] (**8**) despite the bulkiness of the ketone (Scheme 3). It has been observed previously that trialkyl aluminum compounds can reduce carbonyl groups with competitive alkyl insertion and β-hydrogen insertion to form aluminum oxides.[22] The neat insertion of carbonyls into an Al−C (vinyl) bond was observed in this case. Compound **8** is the first example of an aluminum compound with a metalladihydrofuran ring structure. The two low-field resonances (δ 195.5 and 190.8 ppm) and a resonance at δ 90.1 ppm for the carbon atoms in the Al−C−C−C−O ring in the ^{13}C NMR spectrum are consistent with the aluminum dihydrofuran structure.

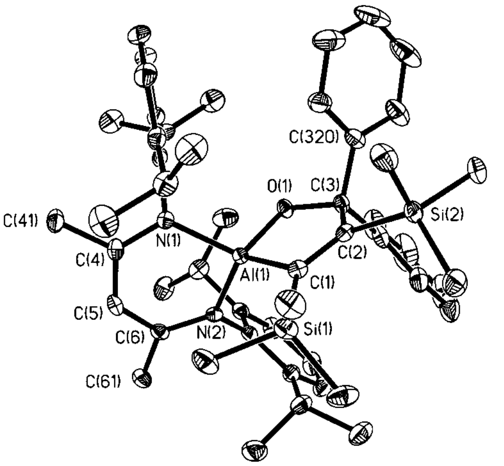


Figure 4. ORTEP drawing of **8** (50% thermal ellipsoids). Hydrogen atoms and solvent Et$_2$O have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compounds **8**·OEt$_2$ and **9**

	8·OEt$_2$		
Al(1)−O(1)	1.7273(12)	Al(1)−N(1)	1.9124(15)
Al(1)−N(2)	1.9108(14)	Al(1)−C(1)	1.9852(16)
O(1)−C(3)	1.4268(18)	C(1)−C(2)	1.359(2)
C(2)−C(3)	1.574(2)		
N(1)−Al(1)−N(2)	97.90(6)	N(1)−Al(1)−C(1)	118.54(7)
O(1)−Al(1)−C(1)	93.56(6)	O(1)−Al(1)−N(1)	111.13(6)
O(1)−Al(1)−N(2)	112.03(6)	N(2)−Al(1)−C(1)	124.08(7)
	9		
Al(1)−N(1)	1.9109(13)	Al(1)−N(2)	1.8887(13)
Al(1)−N(3)	1.8678(15)	Al(1)−C(8)	1.9917
N(3)−C(6)	1.2741(19)	C(6)−C(7)	1.552(2)
C(7)−C(8)	1.366(2)		
N(1)−Al(1)−N(2)	96.39(6)	N(1)−Al(1)−C(8)	125.92(6)
N(1)−Al(1)−N(3)	108.35(6)	N(2)−Al(1)−C(8)	124.56(6)
N(2)−Al(1)−N(3)	106.48(6)	N(3)−Al(1)−C(8)	93.33(7)

Compound **3** also reacts with benzonitrile PhCN at room temperature to give a new aluminum-containing unsaturated ring system LAl[NC(Ph)C$_2$(SiMe$_3$)$_2$] (**9**) in a moderate yield (Scheme 3). Compound **9** crystallized from diethyl ether as orange crystals, very soluble in aromatic solvents but only sparingly soluble in *n*-hexane. The EI-MS spectrum shows a peak of highest mass at (M$^+$ + H). The ^{1}H and ^{29}Si NMR spectra give two distinct resonances for the Me$_3$Si nuclei, respectively, indicating that PhCN inserts only into one of the Al−C bonds in **3**. The ^{13}C NMR spectrum of **9** shows three resonances (δ 183.8, 181.5, and 173.3 ppm) corresponding to the carbon atoms of the Al−C−C−C−N five-membered ring.

Molecular Structures of 8·OEt$_2$ and 9. Single crystals of **8**·OEt$_2$ were obtained from diethyl ether at 0 °C. The structure is shown in Figure 4, and some important bond distances and angles are summarized in Table 3. The aluminum atom is four coordinate and has a distorted tetrahedral geometry. The angles N(1)−Al(1)−N(2) (97.90(6)°) and O(1)−Al(1)−C(1) (93.56(6)°) are smaller than 109.28° for an ideal tetrahedral array. The Al(1)−O(1) distance (1.7273(12) Å) is comparable to those of **6** (av 1.73 Å) and shorter than the sum of covalent radii of Al and O, indicating increased ionic interaction between the two atoms. The bond length C(1)−C(2) (1.359(2) Å) is consistent

---

[22] Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Elsevier: Oxford, UK, 1982; p 644.

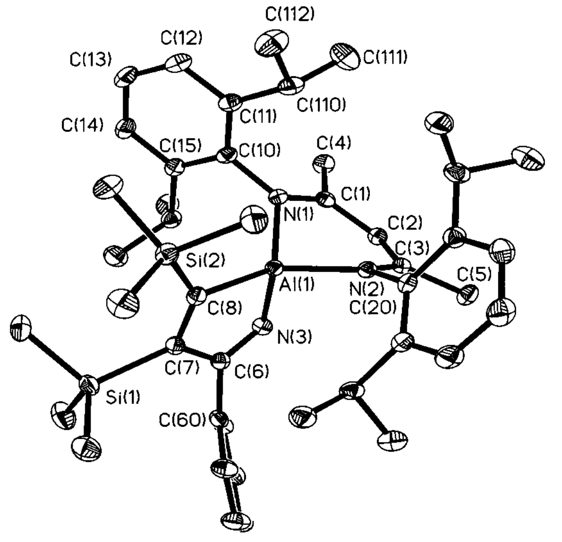
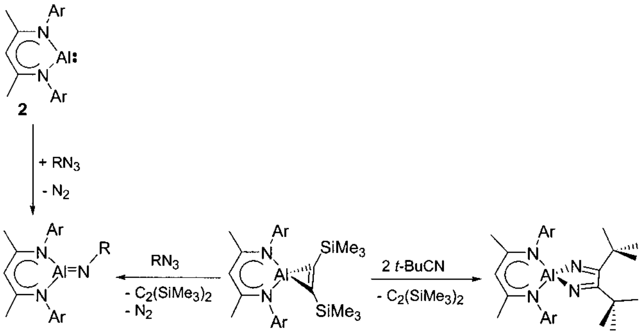


Figure 5. ORTEP drawing of **9** (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

Scheme 4



2

11, R = 2, 6-Trip$_2$C$_3$H$_6$
12, R = Ph$_3$Si

3

10

with a C═C double bond character though shorter than that of **3** (C(6)−C(7) (1.382(2) Å) due to the strained three-membered Al(1)−C(6)−C(7) ring in **3**. The Al(1)−C(1) bond length (1.9852(16) Å) is longer by ca. 0.09 Å than those of the parent compound **3** (av 1.90 Å).

Orange crystals of **9** were obtained from toluene at −5 °C. The structure is shown in Figure 5, and selected bond distances and angles are listed in Table 3. The aluminum atom is coordinated to a terminal iminato group and a vinyl group forming a nearly planar five-membered Al−N−C−C−C ring (mean deviation of the plane corresponds to 0.044 Å). The Al−N(3) distance (1.8678(15) Å) is significantly shorter than those reported for the aluminum iminato complexes $\{(i\text{-Bu})_2\text{Al}[\mu_2\text{−N═C(H)(C}_6\text{H}_3\text{-2,6-Me}_2)]\}_2$ (1.946 Å),[23] in which the iminato groups are bridging two aluminum atoms, due to the low coordination number (2) of the iminato moiety in **9**. The N(3)−C(6) (1.2741(19) Å) and C(7)−C(8) (1.366(2) Å) bond lengths are consistent with N═C and C═C double bonds. The Al−C(8) (1.9917 Å) bond length is comparable to that found in **8**, but longer by ca. 0.1 Å than those in **3**.

Reaction of LAl[η^2-C$_2$(SiMe$_3$)$_2$] (3) with *t*-BuCN and Bulky Azides. Unexpectedly, the reaction of **3** with an equivalent amount of *t*-BuCN at room temperature leads to the displacement of the alkyne moiety with the formation of the first aluminum bis(iminato) complex LAl[N$_2$(C*t*-Bu)$_2$] (**10**) (Scheme 4), which features an unprecedented aluminum-containing imidazole ring. The detailed mechanism for the reaction of **3** with PhCN and *t*-BuCN is currently not clear. It is possible that initial coordination of a nitrile molecule to **3** takes place. As a consequence of steric bulk and electron donation capacity of the *t*-Bu group, the carbon of the CN group is not easily attacked by the alkyne carbon like in the case of PhCN, instead, *t*-BuCN replaces Me$_3$SiCCSiMe$_3$ to give a metal η^2 nitrile intermediate,[24] which is highly reactive and immediately couples with another molecule of *t*-BuCN to give **10**. The isolation of this interesting intermediate is under investigation.

Aluminum iminato complexes prepared by reduction of nitriles with trialkylalane or alkylaluminum hydrides have been employed as intermediates in the preparation of aldehydes, primary amines, Schiff bases, and azacyclic compounds.[25] However, the utilization of unsaturated aluminum ring systems for the reduction of nitriles has not been reported to date. Here formal coupling of an unsaturated molecule with a nitrile induced by an aluminum complex was observed for the first time. Obviously, this is a new approach to synthesize novel cyclic aluminum iminato complexes.

The ^{1}H NMR spectrum of **10** does not show low-field resonances for Me$_3$Si protons, but a broad single resonance (δ 1.25 ppm) can be assigned to the *t*-Bu protons. The integration of all signals is consistent with the formulation of **10**. The compound shows a typical C═N stretch (1704 cm^{-1}) in the IR spectrum, which is comparable to that found in **9** (1697 cm^{-1}) but at higher wavenumbers (ca. 60 cm^{-1}) than those of bridged iminato groups of aluminum compounds.[23,26] A low-field resonance (δ 193.6 ppm) in the ^{13}C NMR spectrum can be assigned to the carbon atoms in the Al−N−C−C−N five-membered ring. The EI-mass spectrum gives a peak of highest mass at [M$^+$ − *t*-Bu]. The molecular structure of this unique compound was determined by single-crystal X-ray structural analysis. Single crystals of **10** were obtained from diethyl ether. Unfortunately the quality of the crystal measured was not satisfactory to enable determination of precise bond parameters; however, the molecular array of **10** has been elucidated as proposed. The structure is consistent with the spectroscopic data of **10**.

The reaction of **3** with bulky azides 2,6-Trip$_2$C$_6$H$_3$N$_3$ and Ph$_3$SiN$_3$ also proceeds through replacement of the alkyne moiety with the formation of the first monomeric aluminum imides LAlNC$_6$H$_2$-2,6-Trip$_2$ (**11**) and LAlNSiPh$_3$ (**12**) in high yield (Scheme 4). The two compounds have also been generated by the direct reaction of the Al(I) species LAl (**2**) with the corresponding azides (Scheme 4). The EI-mass spectra of both compounds show a peak of highest mass corresponding to the monomeric formula of **11** and **12**, respectively. The two compounds have also been characterized by NMR spectra and elemental analysis, which are consistent with the proposed structure and composition. The corresponding compound LGaNC$_6$H$_3$-2,6-Trip$_2$ has been characterized by X-ray structural analysis, which shows a monomeric structure with a short Ga−N distance.[6b] Unfortunately, attempts to grow X-ray quality crystals

---

[23] Jensen, J. A. *J. Organomet. Chem.* **1993**, *456*, 161.

[24] For a few well-characterized η^2-nitrile metal complexes see: (a) Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans*. **1986**, 2017. (b) Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650.

[25] (a) Cainelli, G.; Panunzio, M.; Andreoli, P.; Martelli, G.; Spunta, G.; Giacomini, D.; Bandini, E. *Pure Appl. Chem.* **1990**, *62*, 605. (b) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (c) Goering, H. L.; Tseng, C. C. *J. Org. Chem.* **1981**, *46*, 5252. (d) Andreoli, P.; Billi, L.; Cainelli, G.; Panunzio, M.; Martelli, G.; Spunta, G. *J. Org. Chem.* **1990**, *55*, 4199. (e) Bogdanovic, B.; Konstantinovic, S. *Liebigs Ann. Chem.* 1**970**, *738*, 202. (f) Overman, L. E.; Burk, R. M. *Tetrahedron Lett.* **1984**, *25*, 5737.

[26] Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, *37*, 6906.

of **11** and **12** in various solvents and using different temperatures were unsuccessful to date.

Summary

We have prepared the first neutral cyclopropene analogues of aluminum incorporating a bulky β-diketiminato ligand L (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) by facile alkali metal reduction LAlI$_2$ (**1**) in the presence of alkynes. The route also might be applicable to other Group 13 metals. The utilization of the very bulky ligand may be crucial to preventing association, thus highly strained Al−C−C three-membered rings were obtained. The bulky chelating ligand might render the monomeric Al(I) species LAl (**2**) unreactive to alkynes. However, two types of reactions were observed for LAl[η^2-C$_2$(SiMe$_3$)$_2$] (**3**). One involves the insertion of small unsaturated molecules into one of the Al−C bonds, and another the substitution of the alkyne moiety by bulky nitrile (*t*-BuCN) and azides to generate the same products as those of the reaction of LAl (**2**) with the corresponding azides, indicating that in some specific cases **3** could be used as the LAl (**2**) source. Further investigations of the reactions of **2** and **3** are currently in progress.

Acknowledgment. Dedicated to Professor Robert W. Parry. This work was supported by the Deutsche Forschungsgemeinschaft and the Göttinger Akademie der Wissenschaften.

Supporting Information Available: VT NMR data for **3**, MS, IR, and elemental analysis data for compounds **3**−**12**, and details of the X-ray structure determinations of compounds **3**, **4**, **6**·OEt$_2$, **8**·OEt$_2$, and **9** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003185I