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Main Group “Constrained Geometry” Complexes

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The bridged amidocyclopentadienide ligand [$Me_2Si(\eta\text{-}C_5Me_4)$-(N-*t*-Bu)]$^{2-}$ (**1**), which was developed originally in the context of single-component scandium catalysts,[1] has also resulted in some exciting developments in group 4 transition metal chemistry.[2] As evidenced by the patent literature,[3] these so-called “constrained geometry complexes” have proved to be inter alia highly effective olefin polymerization catalysts. It is interesting therefore that, apart from a (presumably nonchelated) bis(Grignard) reagent,[4] ligand **1** has not been employed in main group chemistry. Herein we describe the first aluminum and gallium complexes that feature ligand **1**. Our desire to prepare such compounds stemmed from the analogy between the half-sandwich constrained geometry complexes and the corresponding metallocenes,[5] the current interest in the structures and bonding in cyclopentadienyl/main group compounds,[6] and the fact that aluminocenium cations function as olefin polymerization catalysts.[7] From the standpoint of the trends observed for transition metal derivatives, it was anticipated that the amidocyclopentadienide group 13 cations might exhibit higher reactivities than those of the corresponding metallocenium cations.

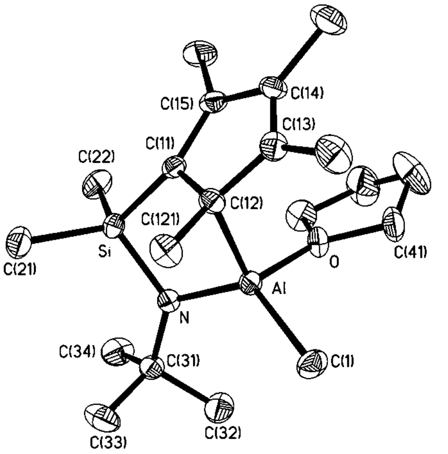

Figure 1. Molecular structure of **2**. Important structural parameters: bond lengths (Å), angles (deg) (corresponding values for **3** shown in parentheses): Al−C(1) 1.988(3) (1.968(3)), Al−N 1.838(2) (1.886(2)), Al−O 1.891(2) (2.070(2)), Al−C(12) 2.071(3) (2.055(2)), N−Si 1.734(2) (1.723(2)), Si−C(11) 1.876(3) (1.871(2)), C(11)−C(12) 1.484(3) (1.495(3)), C(12)−C(13) 1.451(3) (1.471(3)), C(13)−C(14) 1.370(4) (1.353(4)), C(14)−C(15) 1.439(4) (1.449(4)), C(11)−C(15) 1.397(3) (1.377(3)), Al−N−Si 106.36(11) (109.01(10)), Al−N−C(31) 126.4(2) (121.3(2)), Si−N−C(31) 126.74(15) (128.43(15)), C(1)−Al−O 101.98(12) (98.01(11)), N−Al−C(12) 102.46(10) (98.78(9)), C(12)−Al−O 110.46(10) (105.73(9)), C(14)−Al−C(12) 110.09(12) (120.00(11)), N−Al−C(1) = 124.07(11) (128.18(11)), N−Al−C(41) 107.60(9) (103.23(8)).

The complexes [$Me_2Si(\eta^1\text{-}C_5Me_4)$(N-*t*-Bu)]MMe·THF (**2**, M = Al; **3**, M = Ga) were prepared by treatment of the di-Grignard reagent, [$Me_2Si(C_5Me_4)$(N-*t*-Bu)]$(MgCl)_2$·THF,[4] with $MMeCl_2$ in THF solution.[8] Both compounds, which were isolated as THF adducts, were characterized by X-ray crystallography.[9] Although **2** and **3** crystallize in different space groups, the molecular structures are very similar (Figure 1). In contrast to d- and f-block amidocyclopentadienide complexes,[1,2] **2** and **3** feature σ- rather than π-bonding interactions with the C_5Me_4 ring due to the lack of appropriate acceptor orbitals on aluminum or gallium and the presence of a coordinated Lewis base. The Me_4C_5 ring possesses a localized diene structure, and the σ-attachment of the group 13 element occurs at an α position with respect to the μ-$SiMe_2$ group since this affords a five-membered M−C−C−Si−N ring. As reflected by the sums of angles, the nitrogen geometries are very close to trigonal planar in both compounds. Although the group 13 element geometries are nominally tetrahedral, there is a wide departure of bond angles from the ideal values, particularly in the case of **3**. The M-Me substituent is arranged in an *exo* fashion with respect to the tethered ligand, and the THF molecule is located between the underside of the cyclopentadienyl moiety and the N-*t*-Bu group. The ambient temperature ^{13}C and ^{1}H NMR spectra[10,11] for **2** and **3** indicate that on a time-averaged basis the molecular symmetry is C_s rather than the C_1 structure determined by X-ray diffraction. Thus, only two types of ring Me resonances are detected rather than four, and the methyl groups on the $SiMe_2$ fragment are equivalent. However, at 213 K, the $SiMe_2$ and C_4-Me_4 ring methyl resonances of **2** become nonequivalent.[11] A plausible fluxional process involves rapid dissociation/reassociation of the THF molecule in concert with the reversible migration of the group 13 element between C(12) and C(15) (Figure 1) in the base-free complexes, [$Me_2Si(\eta^3\text{-}C_5Me_4)$(*N*-*t*-Bu)MMe] (M =

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(1) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867; Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623.

(2) See, for example, Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451; Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649; Woo, T. K.; Margl, P. M.; Lohrenz, J. C. W.; Blochl, P. E.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 13021.

(3) Canich, J. M.; Hlatky, G. G.; Turner, H. W. PCT Appl. WO 92-00333, 1992; *Chem. Abs.* **1992**, *116*, 174967z. Canich, J. M. Eur. Pat. Appl. EP 420 436-Al 1991; *Chem. Abstr.* **1991**, *115*, 184145y. Stevens, J. C. Timmers, F. J.; Wilson, D. R. Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Pat. Appl. EP 416 815-A2, 1991; *Chem. Abstr.* **1991**, *115*, 93163m.

(4) Strickler; J. R.; Power; J. M.; U.S. Patent 5,359,105, 1994; *Chem. Abstr.* **1995**, *122*, 133408y.

(5) Okuda, J.; Eberle, T. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: New York, 1997; Chapter 7.

(6) For reviews, see Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, 99, 969; Shapiro, P. J. *Coord. Chem. Rev.* **1999**, *189*, 1.

(7) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226; Burns, C. T.; Shapiro, P. J.; Budzelaar, P. H. M.; Vij, A. *Organometallics* **2000**, *19*, 3361.

(8) **2**: A colorless hexane solution of $MeAlCl_2$ (2.3 mL of a 1.0 M solution, 2.3 mmol) was syringed slowly into a stirred pale yellow solution of [$Me_2Si(C_5Me_4)$(N-*t*-Bu)]$(MgCl)_2$·THF[4] (1.0 g, 2.3 mmol) in 75 mL of THF at −78 °C. The reaction mixture was allowed to warm to room temperature then stirred for 12 h. The solvent and volatiles were removed under reduced pressure, and the resulting pale yellow solid was extracted with 50 mL of toluene and filtered through Celite to give a yellow solution. Storage of the concentrated solution at ambient temperature afforded a crop of colorless cube-shaped crystals (0.54 g, 65% yield) of **2** (mp 102−5 °C). HRMS (CI$^+$, CH_4) calcd for M$^+$, $C_{20}H_{38}AlNOSi$, 363.253810; found, 363.252559; calcd for (M − THF)$^+$, $C_{16}H_{30}AlNSi$, 291.196295; found, 291.195746. Colorless, crystalline **3** (mp 70−72 °C) was prepared analogously in 55% yield except that the order of addition of $MeGaCl_2$ and [$Me_2Si(C_5Me_4)$(N-*t*-Bu)]$(MgCl)_2$·THF was reversed and the extractant solvent was hexanes. HRMS (CI, CH_4) calcd for (M − H)$^+$, $C_{20}H_{37}GaNOSi$, 404.190024; found, 404.190972; calcd for (M + H − THF)$^+$ $C_{16}H_{31}GaNSi$, 334.148160; found, 334.146901. **4**: A dark yellow solution of 1,3,5,6,-tetramethylimidazol-2-ylidene[13] (0.35 g, 2.8 mmol) in 25 mL of toluene was added dropwise to a stirred pale yellow solution of **2** (1.0 g, 2.8 mmol) in 50 mL of toluene at −78 °C. The reaction mixture was allowed to warm to room temperature and then stirred overnight. Storage of the concentrated pale yellow solution at ambient temperature afforded a crop of colorless cube-shaped crystals (1.1 g, 95% yield) of **4** (mp 100 °C dec). HRMS (CI, CH_4) calcd for M$^+$, $C_{23}H_{42}AlN_3Si$, 415.2963; found, 415.2965. Colorless, crystalline **5** (mp 90 °C dec) was prepared analogously in 75% yield. However, in this case the pure product was obtained by removal of the solvent and volatiles from the crude reaction mixture followed by recrystallization from toluene. HRMS (CI, CH_4) calcd for M$^+$, $C_{23}H_{42}GaN_3Si$, 457.240383; found, 457.240669.

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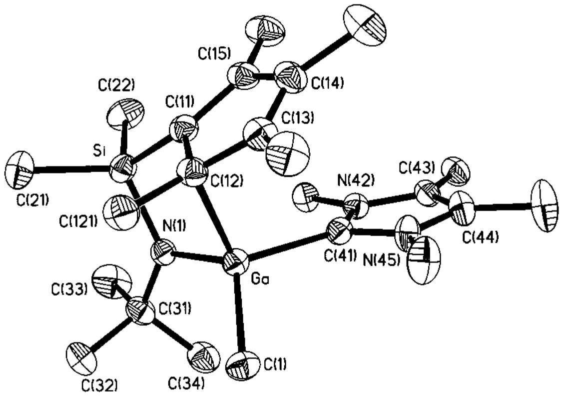
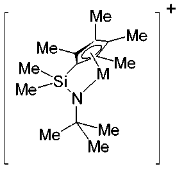


Figure 2. Molecular structure of **5**. Important structural parameters: bond lengths (Å), angles (deg) (corresponding values for **4** shown in parentheses) Ga−C(1) 2.009(3) (2.041(3)), Ga−C(41) 2.074(3) (2.041(3)), Ga−N(1) 1.933(3) (1.853(3)), Ga−C(12) 2.172(3) (2.166(3)), N−Si 1.725(3) (1.737(3)), Si−C(11) 1.872(3) (1.862(3), C(11)−C(12) 1.466(5) (1.478(4)), C(12)−C(13) 1.456(5) (1.439(4)), C(13)−C(14) 1.366(5) (1.381(5)), C(14)−C(15) 1.427(5) (1.422(4)), C(11)−C(15) 1.402(5) (1.410(5)), Al−N(1)−Si 105.69(13) (103.34(12)), Al−N(1)−C(31) 124.5(2) (128.5(2)), Si−N(1)−C(31) 128.3(2) (126.4(2)), C(1)−Al-C(41) 108.89(14) (107.19(13)), C(1)−Al−N(1) 118.43(13) (115.92(12)), C(1)−Al−C(12) 108.38(13) (105.60(11)), C(12)−Al−(C41) 108.82(12) (111.43(13)), N(1)−Al−C(12) 103.34(12) (99.50(12)), N(1)−Al−(41) 113.11(13) (111.02(11)).

Al, Ga).[12] Such a suggestion receives support from the observation that the treatment of **2** and **3** with tetramethylimadazol-2-ylidene[13] results in elimination of THF and quantitative formation of the adducts [$Me_2Si(\eta^5$-$C_5Me_4)$(*N*-*t*-Bu)]MMe•carbene (**4**, M = Al; **5**, M = Ga).[8] In turn, the ^{1}H and ^{13}C NMR spectra[10] for **4** and **5** are indicative of static C_1 structures as a consequence of the superior donor strength of carbene versus THF. As determined by X-ray analysis,[9] the overall structural features of **4** and **5** (Figure 2) are similar to those of the THF adducts **2** and **3**. Thus, the carbene ligand is located between the underside of the cyclopentadienyl ring and the N-*t*-Bu group, and the M-Me substituent occupies an *exo* position with respect to the chelate ligand. The Al−$C_{carbene}$ (2.041(3) Å) and Ga−$C_{carbene}$ (2.074(3) Å) bond distances are similar to those reported for (carbene)AlR_3 (2.124-(6) Å) and (carbene)GaR_3 (2.13(2) Å) adducts (R = H,[14a] Me;[14b] carbene = 1,3-diisopropyl-2,4-dimethylimidazol-2-ylidene).

The mass spectrum of **2** (CI,$^+$ CH_4) exhibits a peak at *m*/*e* 276 along with other fragments that correspond to cation **6**. Accordingly, the model cation **7** was investigated by means of BP86 DFT calculations.[15] Geometry optimization, together with frequency calculations, indicate that the ground-state geometry of **7** possesses C_1 symmetry, but is very close to C_s symmetry. The Cp group is attached to aluminum in a pentahapto fashion, and the computed Al-ring centroid and Al−N distances are 1.762 and 1.795 Å, respectively. Of particular import is the morphology of the LUMO, which in each case is a primarily metal-based orbital having a symmetry suitable for coordination by olefins. For **7** the energy of the LUMO (−0.30412 au) is 55.8 kcal/mol lower than the LUMO energy calculated for $[Cp_2Al]^+$ (−0.21255 au) which has been shown to be an effective α-olefin polymerization catalyst.[7] The presence of a lower-energy LUMO suggests that, as observed for group 4 transition metals,[2] aluminum cation **7** is likely to be a more active olefin polymerization catalyst than is its metallocene analogue.



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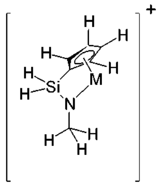

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Methanide abstraction from **1** by $B(C_6F_5)_3$ has been attempted in toluene solution. Judging from the detection of the $[MeB(C_6F_5)_3]^-$ anion by ^{1}H, ^{19}F, and ^{11}B NMR spectroscopy, this process evidently occurs. However, thus far it has not proved possible to isolate crystalline material suitable for X-ray diffraction.

In conclusion, we have synthesized the first examples of main group constrained geometry complexes, which were isolated as either THF or carbene adducts. Preliminary experiments indicate that [$Me_2Si(\eta^1$-$C_5Me_4)$(*N*-*t*-Bu)]AlMe•THF undergoes methanide abstraction when treated with $B(C_6F_5)_3$. DFT calculations on a model aluminum cation suggest that these cations will be more active than the corresponding aluminocenium cations.

Acknowledgment. Funding of this work by the National Science Foundation and the Robert A. Welch Foundation is gratefully acknowledged.

Supporting Information Available: X-ray experimental details with positional parameters and full bond distances and angles for **2**−**5** and a summary of DFT calculated structures and energies; ^{13}C NMR data for **2**−**5**, and low-temperature ^{1}H NMR data for **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data. Single crystals were covered with mineral oil and mounted on either a Siemens P4 diffractometer at 213(2) K (**2** and **3**) or a Nonius KAPPA-CCD at 153(2) K (**4** and **5**). All data sets were collected using Mo Kα (λ = 0.71073 Å), and each structure was solved by direct methods. **2**: $C_{20}H_{38}AlNOSi$, orthorhombic, *Fdd*2, a = 33.429(10) Å, b = 34.035(9) Å, c = 7.939(2) Å, V = 9033.0(43) Å^3, Z = 16, D_{calcd} = 1.069 g cm^{-3}, μ(Mo Kα) = 0.150 mm^{-1}, 3879 unique reflections measured in the range 3.42 $\leq 2\theta <$ 55.02°; wR_2 = 0.0740, R_1 = 0.0367. **3**: $C_{20}H_{38}GaNOSi$, triclinic, $P\bar{1}$, a = 8.234(5) Å, b = 8.537(5) Å, c = 16.350(5) Å, α = 99.503(5)°, β = 90.309(5)°, γ = 99.151(5)°, V = 1118.5(10) Å^3, Z = 2, D_{calcd} = 1.206 g cm^{-3}, μ(Mo Kα) = 1.290 mm^{-1}, 5177 unique reflections measured in the range 2.52 $< 2\theta <$ 56.56°; wR_2 = 0.0909, R_1 = 0.0381. **4**: $C_{23}H_{42}AlN_3Si$, orthorhombic, $Pc2_1b$, a = 8.886(5) Å, b = 14.301(5) Å, c = 19.386(5) Å, V = 2463.5(18) Å^3, Z = 4, D_{calcd} = 1.121 g cm^{-3}, μ(Mo Kα) = 0.144 mm^{-1}, 6378 unique reflections measured in the range 6.22 $< 2\theta <$ 60.92°; wR_2 = 0.1222, R_1 = 0.0833. **5**: $C_{23}H_{42}GaN_3Si$, orthorhombic, $Pc2_1b$, a = 8.991(5) Å, b = 14.370(5) Å, c = 19.607(5) Å, V = 2533.2(18) Å^3, Z = 4, D_{calcd} = 1.202 g cm^{-3}, μ(Mo Kα) = 0.146 mm^{-1}, 5364 unique reflections measured in the range 6.14 $< 2\theta <$ 54.80°; wR_2 = 0.0780, R_1 = 0.0360. All structures were solved and refined using the Siemens SHELXL PLUS 5.0 (PC) software package.[16] All hydrogens were included as calculated positions and refined using a riding model and a general isotropic thermal parameter.

(10) NMR data. **2**: ^{1}H NMR (300 MHz, 295 K, C_6D_6): δ −0.48 (s, 3H, AlMe), 0.65 (s, 6H, $SiMe_2$), 0.98 (m, 4H, THF), 1.36 (s, 9H, $NCMe_3$), 2.06 (broad s, 6H, C_5Me_2), 2.19 (s, 6H, C_5Me_2), 3.27 (m, 4H, THF). ^{27}Al NMR (78.21 MHz, 295 K, C_6D_6): δ 130.03 (br s, $w_{1/2}$ 2, 890 Hz). **3**: ^{1}H NMR (300 MHz, 295 K, toluene-d_8): δ −0.01 (s, 3H, GaMe), 0.58 (s, 6H, $SiMe_2$), 1.21 (m, 4H, THF), 1.34 (s, 9H, $NCMe_3$), 1.93 (s, 6H, C_5Me_2), 1.95 (s, 6H, C_5Me_2), 3.30 (m, 4H, THF). **4**: ^{1}H NMR (300 MHz, 295 K, toluene-d_8): δ −0.28 (s, 3H, AlMe), 0.62 (s, 3H, SiMe), 0.67 (s, 3H, SiMe), 1.25 (s, 6H, carbene C-Me), 1.49 (s, 9H, $NCMe_3$), 1.65 (s, 3H, C_5Me), 1.88 (s, 3H, C_5-Me), 2.24 (s, 3H, C_5Me), 2.54 (s, 3H, C_5Me), 3.09 (br s, 6H, carbene N-Me). ^{27}Al NMR (78.21 MHz, 295 K, CD_2Cl_2): δ 125.02 (br s, $w_{1/2}$ 2, 410 Hz). **5**: ^{1}H NMR (300 MHz, 295 K, toluene-d_8): δ 0.13 (s, 3H, GaMe), 0.61 (s, 3H, SiMe), 0.67 (s, 3H, $SiMe_2$), 1.25 (s, 6H, carbene C-Me), 1.49 (s, 9H, $NCMe_3$), 1.69 (s, 3H, C_5Me), 1.80 (s, 3H, C_5Me), 2.17 (s, 3H, C_5Me), 2.38 (s, 3H, C_5Me), 3.12 (br s, 6H, carbene N-Me).

(11) See Supporting Information for ^{13}C NMR data for **2**−**5** and low-temperature ^{1}H NMR data for **2**.

(12) DFT calculations indicate that the geometry-optimized structures of the base-free complexes involve η^3-attachment of the cyclopentadienyl ring.

(13) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.

(14) (a) Francis, M. D.; Hibbs, D. E.; Hursthouse, M. B.; Jones, C.; Smithies, N. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3249. (b) Li, X.-W.; Su, J.; Robinson, G. H. *Chem. Commun.* **1996**, 2683.

(15) (a) Becke, A. D. *Phys. Rev.* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev.* **1986**, *33*, 8822. All DFT calculations were performed using the Gaussian 94 (revision B2) suite of programs. All electron basis sets were used for C,H (6−31 G(d)) and the group 13 elements (6-31+G(d)).

(16) Sheldrick, G. M., SHELXTL PC Version 5.0, Siemens Analytical X-ray Instruments, Inc., 1994.