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Substituted Aluminacyclopent-3-enes: [*meso*-$\{RC(Me_3Si)HC\}_2Al(Cl)NMe_2CH_2]_2$ (R = H, Me)

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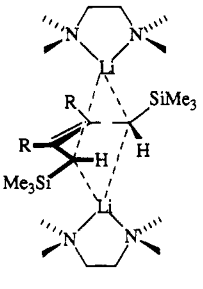
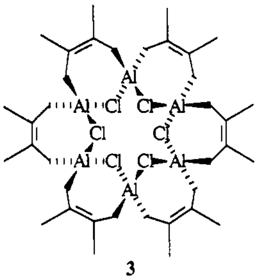
Treatment of (*Z*)-1,4-dilithio-1,4-bis(trimethylsilyl)but-2-ene and (*Z*)-1,4-dilithio-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene adducts of TMEDA (≡*N,N,N′,N′*-tetramethylethylenediamine), $[\{Li(TMEDA)\}_2\{(Me_3SiCHCR)_2\}]$, R = H (**1a**) and Me (**1b**) with $AlCl_3$ in diethyl ether results in stereospecific formation of the corresponding metallacyclopent-3-enes, isolated as [*meso*-$\{RC(Me_3Si)HC\}_2Al(Cl)NMe_2CH_2]_2$, R = H (**2a**) and Me (**2b**); reaction of **1a** with MCl_3, M = Ga and In, results in reduction to the group 13 metal. Assignment of the meso isomer is based on NMR data and an X-ray crystal structure determination. Crystals of **2b** are triclinic, space group $P\bar{1}$, with a = 9.811 (3) Å, b = 15.252 (8)Å, c = 15.266 (9) Å, α = 108.39 (3)°, β = 91.14 (3)°, γ = 95.95 (3)°, V = 2153 (2) Å^3, and Z = 2. Ab initio calculations at the 3-21G* level on the model metallacycle $[AlCl(C_4H_6)(NR_3)]$, R = H or Me (C_s symmetry), gives a stabilization energy of 46.11 or 45.82 kcal/mol, R = H or Me, respectively, relative to $[AlCl(C_4H_6)]$ (C_{2v}) and NR_3, and the metallacycle is favored by 33.70 or 35.62 kcal/mol, R = H or Me, relative to the chloro-bridged dimer $[\{Al(\mu\text{-}Cl)(C_4H_6)\}_2]$ (D_{2h}), and NR_3.

Introduction

Recently we reported selective dimetalation of 1,4-bis(trimethylsilyl)but-2-ene and 1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene using $Bu^nLi(TMEDA)$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine).[1] The resulting crystalline organolithium species, **1a** and **1b**, respectively, have the lithiums residing above and below the (*Z*)-but-2-ene-1,4-diyl planes in the symmetrically bridged structure.[1,2] The corresponding 1,4-diphenyl analogue has a similar structure,[3] and the magnesium derivative based on the same dianion has an η^4-but-2-ene-1,4-diyl–metal interaction.[4] For the more congested 1,1,4,4-tetraphenyl system the sodium and potassium derivatives adopt an (*E*)-configuration with polyhapto-contact ion aggregates.[5] These studies represent the limited structural work on but-2-ene-1,4-diyl complexes of the s-block elements, despite their utility as transfer reagents in organometallic[1,6] and organic synthesis.[7] Compound **1a**, for example yields (*Z*)-butene derivatives with silyl chlorides and gives a good yield of (*E,E*)-1,4-bis(trimethylsilyl)buta-1,3-diene, when oxidized with mercuric chloride.[1]



R = H, 1a
R = Me, 1b



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Herein we report some group 13 chemistry for **1a** and **1b** and related species. This includes the synthesis and structural characterization of chloroaluminacyclopent-3-enes [*meso*-$\{RC(Me_3Si)HC\}_2Al(Cl)NMe_2CH_2]_2$, R = H (**2a**) and Me (**2b**), the reduction of gallium(III) and indium(III) chlorides by **1a**, and theoretical calculations on model compounds relevant to the structures of chloroaluminacyclopent-2-enes. But-2-ene-1,4-diyl chemistry of aluminum to date deals with (i) the formation of a hexameric aggregate, $[AlCl(2,3\text{-dimethyl-2-butenediyl})]_6$, **3**, with bridging hydrocarbyl ligands, via cocondensation of 2,3-dimethylbutadiene and chloroaluminum(I),[8,9] (ii) formation of the aluminacyclopent-3-ene $[Me_2Al\{(CH_2CH)_2\}]^-$ via treating butadiene with $Na/AlMe_3$,[10] (iii) oligomerization of butadiene using organoaluminum/transition metal catalysts,[11] (iv) low-temperature generation of aluminacyclopent-3-ene from metal vapor and butadiene, and (v) ab initio MO calculations on the metallacycle in (iv) which places the aluminum atom 42° out of the butadiene plane and yields a calculated spin density of 0.88 on the metal.[12]

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Table I. Selected Structural Parameters for [*meso*-$\{MeC(Me_3Si)HC\}_2Al(Cl)NMe_2CH_2]_2$, 2b (Bond Lengths in Å and Bond Angles in deg)

molecule A		molecule B	
Al1–Cl1	2.163 (2)	Al2–Cl2	2.167 (2)
Al1–C1	1.961 (5)	Al2–C5	1.958 (5)
Al1–C4	1.963 (5)	Al2–C8	1.960 (5)
Al1–N1	2.045 (3)	Al2–N2	2.049 (4)
C1–C2	1.532 (7)	C5–C6	1.535 (7)
C2–C3	1.335 (7)	C6–C7	1.334 (6)
C3–C4	1.531 (7)	C7–C8	1.526 (8)
Cl1–Al1–C1	123.6 (2)	Cl2–Al2–C5	119.0 (1)
Cl1–Al1–C4	119.4 (2)	Cl2–Al2–C8	121.8 (2)
C1–Al1–C4	97.2 (2)	C5–Al2–C8	96.8 (2)
Cl1–Al1–N1	97.7 (1)	Cl2–Al2–N2	98.6 (2)
C1–Al1–N1	106.0 (2)	C5–Al2–N2	112.5 (2)
C4–Al1–N1	112.7 (2)	C8–Al2–N2	108.5 (2)

Table II. Non-Hydrogen Atom (and Methine Hydrogen Atom) Coordinates for [*meso*-$\{MeC(Me_3Si)HC\}_2Al(Cl)NMe_2CH_2]_2$, 2b

	x/a	*y/b*	*z/c*
Al(1)	0.0158 (1)	1.14954 (9)	0.69572 (8)
Cl(1)	0.0825 (1)	1.24281 (9)	0.61972 (8)
C(1)	–0.0879 (5)	1.1860 (3)	0.8075 (3)
Si(1)	–0.1047 (2)	1.3108 (1)	0.8715 (1)
C(11)	–0.1709 (9)	1.3643 (5)	0.7864 (5)
C(12)	–0.2342 (7)	1.3277 (4)	0.9620 (4)
C(13)	0.0618 (7)	1.3755 (4)	0.9270 (6)
C(2)	–0.0264 (5)	1.1268 (3)	0.8592 (3)
C(21)	–0.1016 (7)	1.1173 (4)	0.9430 (4)
C(3)	0.0813 (5)	1.0811 (3)	0.8295 (3)
C(31)	0.1358 (7)	1.0144 (4)	0.8744 (4)
C(4)	0.1521 (5)	1.0875 (3)	0.7428 (3)
Si(4)	0.3347 (1)	1.1411 (1)	0.7552 (1)
C(41)	0.3974 (6)	1.1232 (5)	0.6359 (4)
C(42)	0.3556 (6)	1.2686 (4)	0.8181 (4)
C(43)	0.4567 (6)	1.0881 (4)	0.8141 (4)
Al(2)	0.4117 (1)	0.68817 (9)	0.62757 (9)
Cl(2)	0.4101 (2)	0.82706 (9)	0.6185 (1)
C(5)	0.5235 (5)	0.6707 (3)	0.7271 (3)
Si(5)	0.5922 (1)	0.7762 (1)	0.82562 (9)
C(51)	0.4533 (6)	0.8425 (4)	0.8848 (4)
C(52)	0.6983 (7)	0.7487 (5)	0.9154 (4)
C(53)	0.7099 (6)	0.8517 (4)	0.7769 (4)
C(6)	0.4276 (5)	0.5954 (3)	0.7495 (3)
C(61)	0.4871 (6)	0.5493 (4)	0.8145 (4)
C(7)	0.3001 (5)	0.5707 (3)	0.7116 (3)
C(71)	0.2039 (6)	0.4941 (4)	0.7315 (5)
C(8)	0.2435 (5)	0.6147 (3)	0.6436 (3)
Si(8)	0.0809 (1)	0.6685 (1)	0.6743 (1)
C(81)	0.0841 (6)	0.7345 (5)	0.7985 (4)
C(82)	0.0517 (8)	0.7480 (8)	0.6065 (6)
C(83)	–0.0735 (6)	0.5798 (6)	0.6460 (6)
N(1)	–0.1171 (3)	1.0584 (2)	0.5953 (2)
C(1n)	–0.0659 (4)	1.0230 (3)	0.5002 (3)
C(2n)	–0.1670 (5)	0.6784 (3)	0.6282 (3)
C(3n)	–0.2368 (5)	1.1083 (4)	0.5853 (3)
N(2)	0.4798 (4)	0.6250 (2)	0.4995 (2)
C(4n)	0.4665 (7)	0.5195 (4)	0.4713 (4)
C(5n)	0.6201 (6)	0.6676 (4)	0.4914 (4)
C(6n)	0.3883 (6)	0.6405 (4)	0.4275 (3)
H(1)	–0.178 (4)	1.161 (3)	0.791 (3)
H(4)	0.157 (4)	1.026 (3)	0.702 (3)
H(5)	0.604 (4)	0.646 (3)	0.705 (3)
H(8)	0.216 (4)	0.567 (3)	0.589 (3)

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze/thaw degassed prior to use. Compounds **1a** and **1b** were prepared from the corresponding (*E*)-but-2-ene and Bu^{n}Li(TMEDA) according to our literature procedures.[1] All other reagents were obtained from Aldrich. ^{1}H NMR spectra were recorded on Bruker WM-250 or CXP-300 spectrometers in deuterated benzene and referenced to the residual ^{1}H resonances of the solvent (δ 7.15). ^{13}C NMR spectra were recorded in the same solvent on a Bruker WM-250 spectrometer operating at 62.8 MHz using broad band

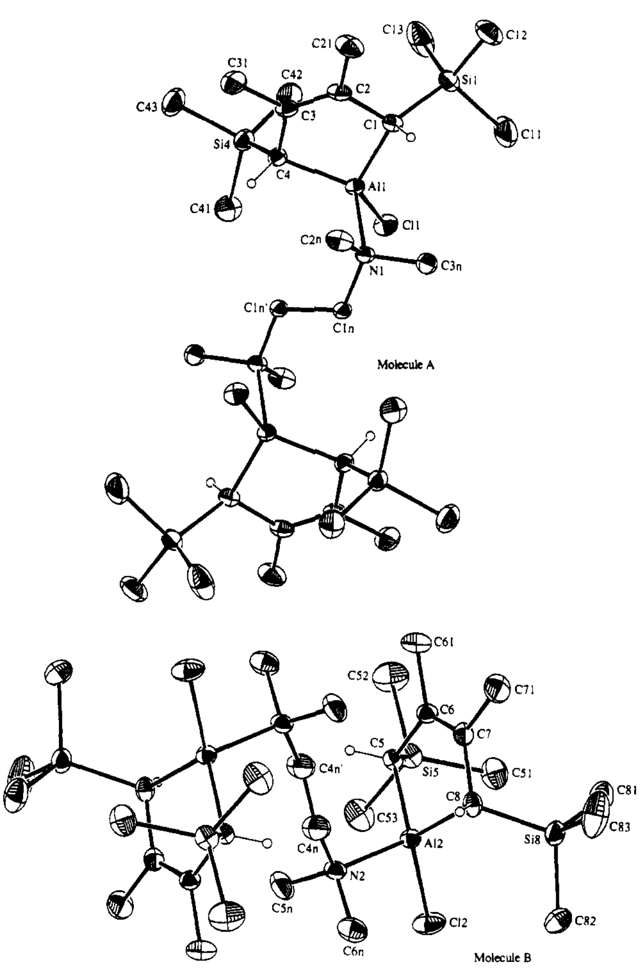

Figure 1. Molecular projections of the two crystallographic independent molecules in [*meso*-$\{MeC(Me_3Si)HC\}_2Al(Cl)NMe_2CH_2]_2$, **2b**, showing the labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity only methine hydrogens are shown.

Table III. Summary of X-ray Diffraction Data and Overall Refinement Parameters for [*meso*-$\{MeC(Me_3Si)HC\}_2Al(Cl)NMe_2CH_2]_2$, 2b

formula	$C_{30}H_{68}Al_2Cl_2N_2Si_4$
mol wt	694.1
space group	$P\bar{1}$
a, Å	9.811 (3)
b, Å	15.252 (8)
c, Å	15.266 (9)
α, deg	108.39 (3)
β, deg	91.14 (3)
γ, deg	95.95 (3)
V, Å^3	2153 (2)
Z	2
D(calcd), g cm^{-3}	1.071
F(000)	756
cryst dimens, mm	0.30 × 0.30 × 0.40
temp, °C	297
radiation	Mo Kα (0.710 73 Å, graphite monochromator)
μ, cm^{-1}	3.22
2θ limit, deg	50
no. of collcd rflns	7565
no. of obsd rflns [$I > 2.5\sigma(I)$]	4162
R	0.046
R_w	0.046
final residual, e Å^{-3}	0.20
s	1.168

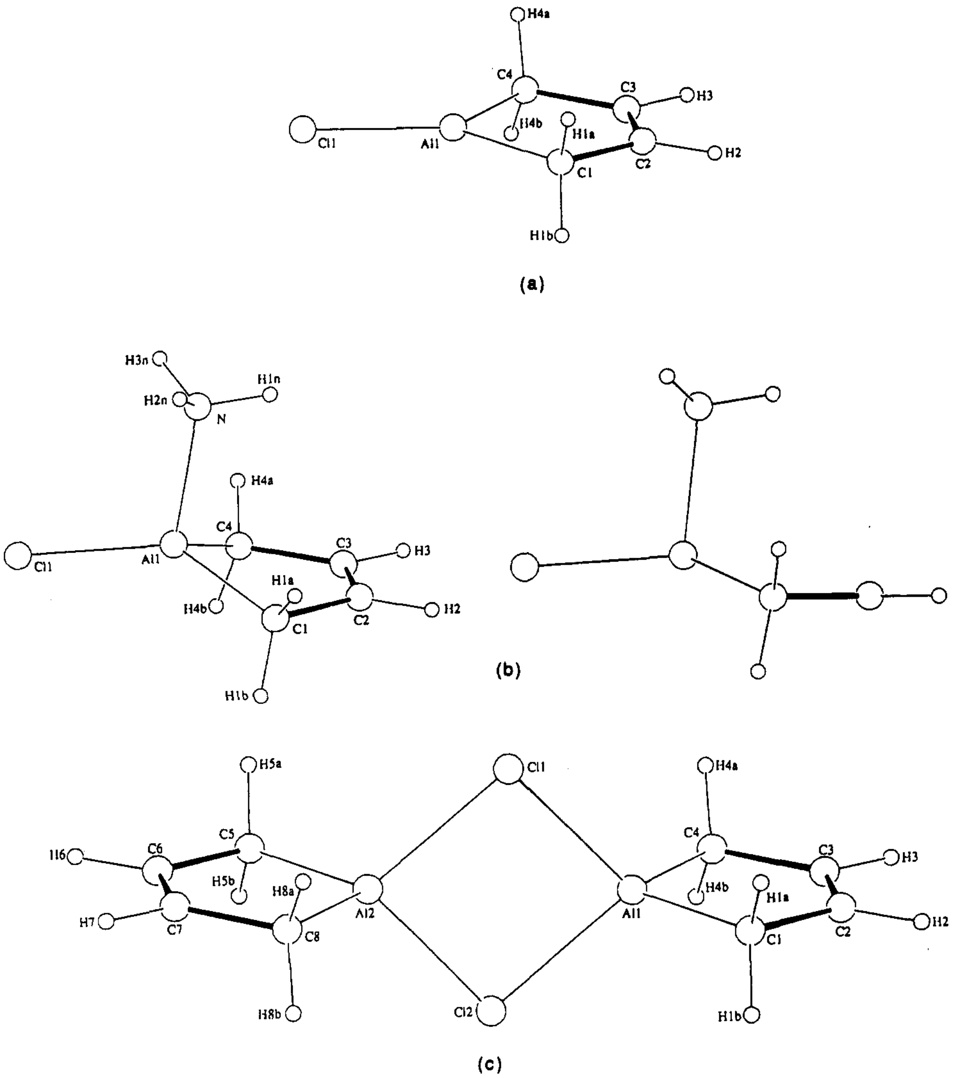

Figure 2. Optimized geometries for minima located using the 3-21G* basis set for (a) [$AlCl(C_4H_6)$], (b) [$AlCl(C_4H_6)(NH_3)$], and (c) [{$Al(\mu\text{-}Cl)(C_4H_6)$}$_2$].

proton decoupling and were referenced to the ^{13}C resonances of the deuterated solvent (δ 128.00). Elemental analyses were performed by the Canadian Microanalytical Services Ltd. Melting points were determined in sealed glass capillaries under argon and are uncorrected.

[*meso*-{HC(Me$_3$Si)HC}$_2$Al(Cl)NMe$_2$CH$_2$]$_2$, 2a. To a diethyl ether solution (10 mL) of $AlCl_3$ (0.79 g, 5.9 mmol) was added a solution of **1a** (2.59 g, 5.83 mmol) in diethyl ether (40 mL) over 10 min at −80 °C, and the resulting mixture was allowed to warm to room temperature. After 1 h the red color had dissipated. The mixture was filtered, the volatiles were removed, and the resulting oil was heated in vacuo at ca. 100 °C for 4 h affording a colorless solid. Hexane (150 mL) was added, and the solution was filtered and then concentrated (ca. 20 mL). Cooling to −30 °C gave colorless crystals of the *title compound* (1.2 g, 65%): mp 204–206 °C (dec 290 °C); ^1H NMR (250 MHz, C_6D_6) 0.33 ($SiMe_3$, s, 36H), 2.66 (CH, s, 4H), 6.21 (CH, s, 4H), 1.65 (NMe, s, 12H), 1.69 (NCH_2, s, 4H); ^{13}C NMR (62.8 MHz, C_6D_6) 0.4 ($SiMe_3$), 16.1 (CH, broad), 133.2 (CH), 44.5 (NMe), 53.5 (NCH_2). Anal. Found: C, 48.81; H, 9.57; N, 5.25. Calc: C, 48.98; H, 9.42; N, 4.40.

[*meso*-{MeC(Me$_3$Si)HC}$_2$Al(Cl)NMe$_2$CH$_2$]$_2$, 2b. To a diethyl ether solution (5 mL) of $AlCl_3$ (0.40 g, 3.0 mmol) was added a solution of **1b** (1.36 g, 4.73 mmol) in diethyl ether (20 mL) over 10 min at −80 °C, and the resulting mixture was allowed to warm to room temperature. After 1 h the red color had dissipated. The mixture was then filtered, the volatiles were removed, and the resulting oil was heated in vacuo at ca. 100 °C for 5 h affording a colorless solid. Hexane (100 mL) was added, and the solution was filtered and then concentrated (ca. 10 mL). Cooling to −30 °C gave a mixture of colorless needles and prisms of the *title compound* (0.83 g, 51%): mp 207–215 °C (dec 290 °C); ^1H NMR (250 MHz, C_6D_6) 0.34 ($SiMe_3$, s, 36H), 1.91 (CMe, s, 12H), 2.74 (CH, s, 4H), 1.67 (NMe, s, 12H), 1.90 (NCH_2, s, 4H); ^{13}C NMR (62.8 MHz, C_6D_6) 0.3 ($SiMe_3$), 17.1 (CH, broad), 18.4 (C*Me*) 135.2 (*C*Me), 44.7 (NMe), 53.5 (NCH_2). Anal. Found: C, 51.39; H, 9.72; N, 4.05. Calc: C, 52.22; H, 9.35; N, 4.06.

Structure Determination. Suitable prismatic crystals of **2b** were grown from hexane solutions at −30 °C. A unique diffractometer data set was measured on a prismatic crystal using an Enraf-Nonius CAD4 diffractometer. Reflections with $I > 2.5\sigma(I)$ were considered "observed" and used in full-matrix least-squares refinement, minimizing $\Sigma w\Delta^2$ after solution of the structure by direct methods. Anisotropic thermal parameters were refined for non-hydrogen atoms. Methine H-atoms were refined in x, y, z; allylic methyl H-atoms were located in difference Fouriers and constrained in x, y, z, and U_{iso}, and other H-atoms were constrained at estimated values, C–H = 1.0 Å. Temperature factors for methyl H-atoms were estimated at ca. $1.5U_{ii}$(av) of the attached carbon atom and $1.25U_{ii}$(av) for other H-atoms. Conventional residuals on $|F|$ at convergence are quoted as R and R' $[(\Sigma w\|F_o| - |F_c\|^2/\Sigma w|F_o|^2)^{1/2}]$. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed;[13] computation used the XTAL program system,[14] implemented on a SUN SPARCStation 2. Molecular core geometries, atom coordinates, and crystal data are given in

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[13] *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

Table IV. Selected Non-Hydrogen Experimental, [*meso*-{MeC(Me_3Si)HC}$_2$Al(Cl)NMe_2CH_2]$_2$, 2b, and Theoretical (3-21G*), [AlCl(C_4H_6)], [{Al(μ-Cl)(C_4H_6)}$_2$], [AlCl(C_4H_6)(OH_2)], [AlCl(C_4H_6)(NH_3)], and [AlCl(C_4H_6)(NMe_3)], Geometries of the Various Aluminacyclopent-3-enes Featured in This Study

	molecule[b] (symmetry)					
quantity[a]	AlCl(C_4H_6) (C_{2v})	{Al(μ-Cl)(C_4H_6)}$_2$ (D_{2h})	AlCl(C_4H_6)(OH_2) (C_s)	AlCl(C_4H_6)(NH_3) (C_s)	AlCl(C_4H_6)(NMe_3) (C_s)	**2b**
energy	−852.222 916	−1704.479 260	−927.879 301	−908.168 605	−1024.606 203	
Al1–Cl1	2.109	2.324	2.161	2.161	2.177	2.165
Al1–C1	1.959	1.957	1.976	1.981	1.985	1.961
C1–C2	1.536	1.536	1.535	1.536	1.534	1.531
C2–C3	1.327	1.327	1.330	1.330	1.328	1.333
Al1–N(O)			1.912	2.02	2.011	2.047
Cl1–Al1–C1	130.4	117.7	126.6	125.8	120.9	121.0
C1–Al1–C4	99.1	99.9	96.0	96.0	96.4	97.0
Al1–C1–C2	97.8	97.2	97.0	97.1	98.9	99.1
C1–C2–C3	122.6	122.8	121.5	121.7	122.1	121.6
N(O)–Al1–Cl1			95.2	99.9	101.3	98.2
N(O)–Al1–C1			104.5	102.6	108.4	109.9
Al1–Cl1–Al2		92.3				
Cl1–Al2–Cl2		87.7				
Cl1–Al1–C1–C2	180.0	−128.6	168.1	165.1	142.5	144.2
C4–Al1–C1–C2	0.0	0.0	22.6	21.8	10.5	11.4
Al1–C1–C2–C3	0.0	0.0	−17.6	−17.0	−8.2	−8.9
C1–C2–C3–C4	0.0	0.0	0.0	0.0	0.0	1.2
N(O)–Al1–C1–C2			−84.0	−82.7	−101.4	−102.7
C1–Al1–Cl2–Al2		120.2				
Fold angle[c]	0.0	0.0	26.6	25.6	12.2	13.3

[a] Energy = hartrees, bond lengths = angstroms, and bond angles = degrees. Averaged experimental quantities are given for **2b**. [b] Refer to Figure 4 for atom labeling of theoretical structures. Geometry of H_2O (C_{2v}, −75.585 960 hartrees): O–H, 0.967 Å; H–O–H, 107.7°. Geometry of NH_3 (C_{3v}, −55.872 204 hartrees): N–H, 1.003 Å; H–N–H, 112.4°. Geometry of NMe_3 (C_{3v}, −172.310 270 hartrees): N–C, 1.464 Å; C–Ha,Hb, 1.093, 1.083 Å; C–N–C, 113.1°; N–C–Ha,Hb, 112.8, 109.4°; Ha–N–C–Hb, 120.7°. [c] Complementary angle to the dihedral angle defined by Al1–C4–C1–C2.

Tables I–III, and molecular projections showing numbering schemes are given in Figure 1.

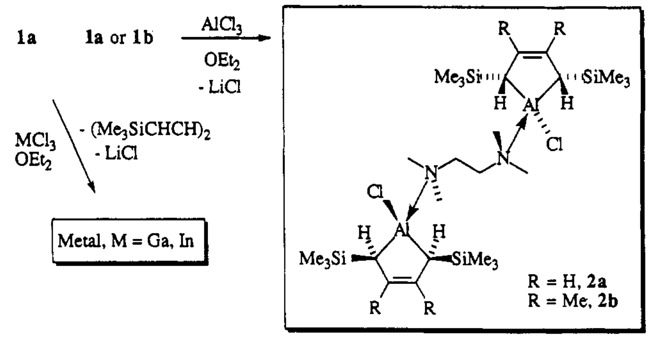
A second weak data set was obtained for compound **2b** on a needle which yielded an inaccurate polymorphic structure, with high discrepancy factors, showing severe disorder of one of the trimethylsilyl groups. Nevertheless, the structure was similar to that of molecule A, for the structure of compound **2b** based on the above refinement (see below).

Theoretical Structures. Ab initio molecular orbital calculations were carried out on [AlCl(C_4H_6)(NR_3)], R = H or Me, [AlCl(C_4H_6)(OH_2)], [AlCl(C_4H_6)], and [{Al(μ-Cl)(C_4H_6)}$_2$] (and NR_3 and H_2O) using Gaussian 90[15] on IBM RISC 6000 and Sun SPARCStation 2 computers. Structures were computed using the 3-21G* basis set. This level of theory has been widely used in calculations on aluminum/organic molecule species.[16] Computed structures and molecular core geometries are given in Figure 2 and Table IV. All optimized structures were found to be true minima by frequency analysis.

Discussion

Syntheses. The synthesis of **2a,b** in modest yields and the reduction of MCl_3, M = Ga and In, to metal are summarized in Scheme I. Isolated crystalline organolithium reagents were used; the use of crude reaction mixtures derived from treating (*E*)-1,4-bis(trimethylsilyl)but-2-enes with Bu^{n}Li(TMEDA) in hexane gave intractable oils in reactions with $AlCl_3$. Assignment of structure of **2a,b** was based on ^1H and ^{13}C NMR data and the crystal structure of the later. NMR equivalence of the trimethylsilyl groups and of the methine groups is consistent with meso diastereoisomers, viz. both of the trimethyl silyl groups directed to the same side of the but-2-ene-1,4-diyl ligand planes. Whether they are on the same side as the chloro or amine group in each case comes from the X-ray structure determination.

Scheme I



Heating **2a,b** in vacuo up to their decomposition temperatures (290 °C) failed to remove the TMEDA ligands and generate monomeric species or chloro-bridged dimers (see Theoretical Studies). Such dimers are common for alkylhaloaluminum species, e.g., [{Al(μ-Cl)Bu$^t_2$}$_2$].[17] Interestingly, this compound condenses with TMEDA to yield a compound related to **2a,b**, [AlClBu$^t_2$-{N(Me_2)$CH_2CH_2NMe_2$}], where TMEDA is attached to only one metal center, and ionic compounds possessing chelate ring systems attached to four coordinate cationic metal centers, [AlBu$^t_2$(TMEDA)]$^+$Cl$^-$ or [$AlCl_2$Bu$^t_2$]$^-$.[17] In this context, similar ionic species may be present as insoluble residues in the reaction mixtures yielding **2a,b**.

The formation of aluminacycles is consistent with the (*Z*)-structure of the planar organolithium species; viz., the product is kinetically controlled and there is stereospecific formation of the meso diastereoisomers of the alumina-

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(14) XTAL User's Manual-Version 3.0. Hall, S. R., Stewart, J. M., Eds.; The Universities of Western Australia and Maryland, 1990.

(15) Gaussian 90. Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990.

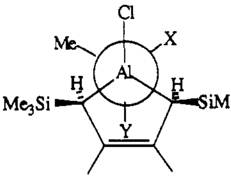
(16) E.g.: Tse, J. *J. Am. Chem. Soc.* **1990**, *112*, 5061.

(17) Uhl, W.; Wagner, J.; Fenske, D.; Baum, G. *Z. Anorg. Allg. Chem.* **1992**, *612*, 25.

cycles. The *rac*-isomer may be thermodynamically and sterically feasible, but its formation would be inconsistent with kinetic control for a planar (*Z*)-dianion present in **1a**,**b**. This has precedence in the synthesis of a wide range of exclusively *meso*-metallacycles based on the related ligands *o*-$C_6H_4(CHSiMe_3)_2$[2,18] and 1,8-$C_{10}H_6(CHSiMe_3)_2$.[2,19]

Compound **1a** reduced MCl_3, M = Ga and In, to metal, but further investigations are being pursued since changing the conditions may disfavor reduction as the primary process. The ability of **1a** to act as a potent reducing agent in yielding (*E*,*E*)-butadiene has been noted previously in the context of Ca(II) → Ca and Hg(II) → Hg[1] and is consistent with the well-established reducing ability of organolithium reagents, in particular the ability of the analogous reagent $[o\text{-}C_6H_4(CHSiMe_3)_2][\{Li(TMEDA)\}_2]$ to reduce Zr(IV) → Zr(III), Hg(II) → Hg, Pt(II) → Pt, and Sn(IV) → Sn(II).[18] Both **2a** and **2b** can be viewed as containing trapped chloroaluminum(I), and in this context we note that above 290 °C the compounds decompose, yielding Al metal, presumably via AlCl, which then disproportionates to metal and $AlCl_3$.

Structural Commentary. Compound **2b** crystallizes with two half-molecules as the asymmetric unit, the other halves of the "dimers" being generated by inversion centers at 0, 1, 0.5 (molecule A) and 0.5, 0.5, 0.5 (molecule B) (Figure 1). Important internuclear distances and angles are given in Table I, with mean values being in Table IV along with geometries of relevant computed structures. The only significant differences between the two molecules is with respect to torsion along the Al–N bond. In molecule A, the *N*-methylene group is anti to one of the two carbons bearing the trimethylsilyl groups, whereas in molecule B, the same N-group is gauche to the same carbon centers and the chlorine, as shown in the Newman projections, **4**, down the Al–N bond. While the results of the second crystal modification on compound **2b** are inaccurate, the molecular core geometries are comparable within experimental error with those found in the first modification, and like in this structure the molecules are centrosymmetric, albeit with only one half-molecule in the asymmetric unit. The conformation about the Al–N linkage is the same as molecule A for **2b**; see **4**. In both structures the metallacycle adopts the meso diastereoisomer with the trimethyl silyl groups on the same side of the ligand plane as the chloro group, presumably for steric reasons, with the methine-H atoms on the same side as the TMEDA ligand. While steric hindrance of the trimethylsilyl groups may block chelation of the tertiary amine as part of a monomeric five-coordinate metal species, any chelation is likely to yield four-coordinate ionic species, cf. $[AlBu^t_2(TMEDA)]^+Cl^-$ or $[AlCl_2Bu^t_2]^-$ (see above).[17]



Molecule A, X = CH_2, Y = Me
Molecule B, X = Me, Y = CH_2

4

Four-fold coordination is achieved by complexation of one tertiary amine center of TMEDA, which arises from the lithium-bound TMEDA in the starting material (see above). In the related compound, **3**, bridging chloro groups result in 4-fold coordination. Formation of chloro-bridged species in the present study is possible but is energetically unfavorable with respect to amine complexation (see Theoretical Studies). Any unsolvated species are likely to exist as dimeric species possessing bridging chloro groups rather than form higher aggregates like that found for **3**, because of the large steric hindrance of the silyl groups. Moreover, the hydrocarbyl group is likely to retain its chelating mode, rather than bridging two metal centers, like in **3**. This is based on analogy with the extensive chemistry established for the related *o*-xylenediyl ligands. Here the absence of trimethylsilyl groups bound to the ipso-carbon centers can result in metallacycles[18] or a bridging mode, e.g. $[\{Mg(\mu\text{-}CH_2C_6H_4CH_2\text{-}o)(THF)_2\}_3]$,[20] and possibly arises from relief of otherwise unfavorable steric strain, whereas the trimethylsilyl-substituted ligand exclusively results in the formation of metallacycles.[18] The metallacycle is approximately symmetrical in molecules A and B such that, ignoring substituents on the N atoms, the substituted aluminacycles have C_s symmetry.

A useful parameter in describing the disposition of the butadiene unit relative to the metal center is the fold angle, defined as the dihedral angle between the AlC_2 and C_6 planes, θ, noting that the C_6 atoms in the present structure are essentially coplanar. Any deviation of the atom from the plane in consequence of ring strain and/or metal–ligand π interaction will be reflected in adopting an envelope structure (C_s symmetry) and a folding of the two planes. An extreme case of folding for butadiene complexes in general is in transition metal π-complexes, e.g. W(butadiene)$_3$.[21] In the absence of a π-interaction and accommodation of a small metal such as aluminum the folding is expected to be small. Indeed, θ values for the two molecules are relatively low at 17.0 (2) and 12.4 (2)°, respectively, for molecules A and B. The difference between the two values may reflect that θ is sensitive to other factors such as crystal packing forces, different conformations, and the geometrical requirements of incorporating aluminum in a five-membered ring system which is in the vicinity of a shallow minimum. The θ value for the computed structure $[Al(C_4H_6)]$[12] is larger at 42°, which is in accordance with the geometrical requirements of incorporating a longer Al–C distances (1.997 Å) compared to those in **2b** (1.961 Å) in a five-membered ring system.

The metal cores are considerably distorted from tetrahedral coordination. The mean C–Al–C angle is less than the tetrahedral value, 97.0°, a manifestation of the relatively small ligand "bite", but the greatest deviation from tetrahedral geometry is associated with the Cl–Al–C angles, mean value 121.0 Å. This is not in consequence of the closer proximity of the silyl substituents to the halogen, since the computed angles for the model compounds are close to experimental values (see below). Metal–C distances, mean value 1.961 Å, are similar to those in **3**, 1.952 (7) Å,[8] and are within the realms established for terminal Al–C(sp^3) distances.[22] The C–C distances within the ring are unexceptional for a (*Z*)-but-2-ene

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[18] Lappert, M. F.; Leung, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1992**, 775 and references therein.

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structure, C–C = 1.531 and C=C = 1.333 Å (mean), with the double bond being in close agreement with the corresponding C=C linkage in **1a**, 1.34 (3) Å,[2] and also for the computed structure of [$Al(C_4H_6)$][12] and those discussed below; vide infra. Geometries for the trimethylsilyl substituents are normal. The Al–Cl distances, mean value 2.165 Å, are as expected shorter than for bridging chlorides in compound **3**, 2.292 (1) Å, as borne out in the computed Al–Cl distance of 2.324 Å for [$Al(\mu\text{-}Cl)C_4H_6]_2$, yet are significantly longer than the terminal Al–Cl bond distances in Al_2Cl_6, 2.06 Å.[23] The Al–N distances, mean value 2.047 Å, are similar to those in the gas-phase structure of the trimethylamine adduct of $AlMe_3$.[24]

Computed ab initio structures for the model compound [$AlCl(C_4H_6)(NH_3)$] at the 3-21G* level give reasonable agreement with the structure of **2b**, having angles and dihedral angles about the aluminum center which are expected to be influenced by N-substituents (Table IV and Figure 2). Understandably then, agreement is improved for calculations incorporating methyl substituents on the N-center, [$AlCl(C_4H_6)(NMe_3)$] (Figure 2b). Thus, the 3-21G* level of theory is seemingly appropriate for species based on Al, Cl, C, and H, and the finding substantiates that any component of the tetrahedral distortion around the metal center (see above) arising from the bulky trimethylsilyl groups is minimal. Complexation of NH_3 and NMe_3 to the monomeric chloroaluminacyclopent-3-ene species, C_{2v} symmetry (Figure 2a), is favored by 46.11 and 45.82 kcal/mol, respectively, and is energetically more favored than dimerization to the chloro-bridged species possessing the minimized D_{2h} symmetry structure (Figure 2c). Indeed, dimerization gives a stabilization energy of only 10.49 kcal/mol. (The starting geometry of the monomeric chloroaluminacyclopent-3-ene species was C_s but convergence was on C_{2v} symmetry.) In the light of the structure of the hexamer of AlCl($C_4H_4Me_2$), **3**, higher aggregates are also possible, and with hydrocarbyl bridging metal centers rather than forming metallacycles. However, for comparative purposes this was not explored since for compounds featuring trimethylsilyl substitution at the carbon attached to the metal center, as in **2a,b**, association is unlikely on steric grounds (see above).

Model species [$AlCl(C_4H_6)(NR_3)$], R = H or Me, and [$\{Al(\mu\text{-}Cl)(C_4H_6)\}_2$] possess 4-fold coordination for aluminum, and no minima on the potential energy surface are likely with π-ligand–metal interaction. However, for the electron-deficient species [$AlCl(C_4H_6)$], folding of the ligand plane with respect to the AlC_2 plane with concomitant formation of a π-interaction is conceivable. This type of interaction is well documented for transition metal–butadiene complexes. Thus, starting geometries for both the metallacycle and a π-complex were used, but the structures converged on the metallacycle with C_{2v} species (Figure 2a).

Ab initio calculations on the compound [AlCl(C_4H_6)(OH_2)] were also investigated as a model system for complexation of chloroaluminacyclopen-3-enes by diethyl ether, noting this was the solvent of choice in the synthesis of compounds **2a,b**. The stabilization energy of the water adduct is 44.19 kcal/mol, marginally less than the amine adducts. This is consistent with prevalence of the TMEDA binding over diethyl ether in the reaction workups to isolate **2a,b**. Geometries of the water adduct are also given in Table IV.

Overall, we have been able to rationalize the formation of metallacyclopent-3-enes **2a,b** using ab initio calculations at the 3-21G* level of theory. Moreover, the geometry of the experimentally determined structure can be reasonably predicted using the same theory.

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council, and we thank Colin Kennard and Karl Byriel for collecting the X-ray diffraction data.

Supplementary Material Available: For **2b**, lists of U_{ij} values, hydrogen atom parameters, and bond distances and angles (4 pages). Ordering information is given on any current masthead page.

OM920467L

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