Sodium–Potassium Alloy for the Reduction of Monoalkyl Aluminum(III) Compounds

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Monoalkylaluminum(III) compounds of the type $RAlX_2$ {R = Cp* (C_5Me_5), X = Cl, Br, I (1–3); $(BisAlCl_2)_2$ (5) (Bis = $(Me_3Si)_2CH$); TrisSi [$(Me_3Si)_3Si$], X = Cl, Br, I (6–8); CycTris [$(CycMe_2Si)(Me_3Si)_2C$], X = Me, F, Cl, Br, I (11–15)} were prepared and characterized by NMR-, IR-, and mass spectroscopy as well as elemental analysis. The single-crystal X-ray structures of $Cp*AlBr_2$, $TrisSiAlX_2 \cdot THF$ (X = Cl, Br, I), $CycTrisAlX_2 \cdot THF$ (X = Me, Cl, Br, I), and $[CycTrisAl(\mu\text{-}O(CH_2)_3CH_2)]_2$ are reported. The monoalkylaluminum(I) compound $(Cp*Al)_4$ (4) was isolated after the reduction of $Cp*AlX_2$ (X = Cl, Br, I) using a Na/K alloy. The yield of $(Cp*Al)_4$ has been improved compared to the previously reported method. However, completely different products were obtained when the THF adducts of $TrisSiAlI_2 \cdot THF$ and $CycTrisAlI_2 \cdot THF$ were used for the reduction with Na/K alloy. In the former case, the cleavage of the Si–Al bond was observed with the formation of elemental aluminum and $(TrisSi)_2$, while in the latter the THF ring opening reaction occurred. $CycTrisAlF_2 \cdot THF$ was prepared by reacting $CycTrisAlMe_2 \cdot THF$ with Me_3SnF. © 2001 Elsevier Science

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INTRODUCTION

Recently, tremendous progress was achieved in the synthesis of group 13 organometallic compounds with metals in low oxidation states. Indium and thallium derivatives have been known for a long time and large numbers of them have been prepared (1). However, compounds of the lighter congeners have been prepared much later and in lower numbers. A reductive dehalogenation of $t\text{-}BuBF_2$ results in the formation of $[t\text{-}BuB]_4$ (2). Schnöckel *et al.* reported on the structural characterization of the stable compound

$(Cp*Al)_4$ with aluminum (1) which was prepared by reacting AlCl with $Cp*_2Mg$ (3). These examples show two reliable routes for the preparation of compounds with low valent elements of group 13: first the reduction of the organometallic M(III)halide, second the salt elimination using M(I)halides. The second route seems to be disadvantageous due to the difficult preparation of AlCl from aluminum and HCl at 1200 K (3,4). Previously $(Cp*Al)_4$ was also prepared by reacting $(Cp*AlCl_2)_2$ with potassium (5). Herein, we report on the high yield synthesis of $(Cp*Al)_4$ by reacting $(Cp*AlCl_2)_2$, $(Cp*AlBr_2)_2$, and $(Cp*AlI_2)_2$, respectively, with Na/K alloy.

The tris(trimethylsilyl)methyl group (Tris ligand) is an example for a sterically demanding ligand showing stabilizing electronic properties (6). The cluster $[TrisM]_4$ of gallium (7), indium (8), and thallium (9) was prepared by reacting $Ga_2Br_4 \cdot dioxane$, InBr, and CpTl with TrisLi, respectively. The analogous aluminum compound $(TrisAl)_4$ was previously prepared by reacting $TrisAlI_2 \cdot THF$ with Na/K alloy (10). Herein, we report on the preparation and reduction of various Tris–aluminum compounds.

EXPERIMENTAL

All reactions were performed in deoxygenated argon or dinitrogen atmosphere using glove-box and high-vacuum techniques. The starting materials Me_3SnCl, Me_2AlCl, $CycMe_2SiCl$, Br_2, I_2, and KF were purchased from Aldrich. Me_3SnF (11), $(Tris)_4Si$ (12), $(Me_3Si)_2CHLi$ (13), and $(Cp*AlCl_2)_2$ (14) were prepared according to the literature methods. Aromatic, hydrocarbon, and etherated solvents were dried over Na/K alloy and vacuum transferred to the reaction flasks prior to use. NMR spectra were recorded on a Bruker AM 200 or Bruker AM 250 instruments. Chemical shifts are reported in δ scale with reference to an external standard: $SiMe_4$ for ^{1}H and ^{13}C, CCl_3F for ^{19}F, and $AlCl_3$ for [27]Al nuclei. Mass spectra were obtained on Finnigan

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MAT system 8230 and a Varian MAT CH5 mass spectrometer. FT-IR spectra were measured on Bio-Rad FTS-7 instrument as nujol mulls or as KBr-tablet. Melting points were obtained on a HWS-SG 3000 apparatus. Elemental analyses were performed by the Analytical Laboratory of the Institute of Inorganic Chemistry University of Göttingen (X-ray Data Collection and Refinement). Crystal data are summarized in Table 5. Data were collected on a Stoe AED2 four-circle diffractometer (**7**, **8**, **11**, **13**, **14**, and **15**) or on a Stoe-Siemens-Huber four-circle diffractometer (**2**, **6**, and **16**) equipped with a Siemens SMART area detector. Monochromated MoKα radiation ($\lambda = 0.71073$ Å) was used. Semiempirical absorption correction using psi-scans (**7**, **8**, **14**, and **15**) or using equivalents (**2**, **6**, and **16**) were employed. The structures were solved by direct methods (15a). All nonhydrogen atoms were refined anisotropically (15b). For the hydrogen atoms the riding model was used. The structures were refined against F^2. In nearly all THF structures the THF group was disordered. It was refined with distance restraints and restraints for the anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC-157206–157214.[2]

$[Cp^*AlBr(\mu\text{-}Br)]_2$ (**2**)

A suspension of $AlBr_3$ (5.3 g, 20.0 mmol) in *n*-hexane (80 ml) was treated dropwise with a solution of Cp^*SiMe_3 (4.0 g, 20.0 mmol) in *n*-hexane (50 ml) at room temperature. After refluxing for 3 h the warm solution was decanted. The solvent was removed *in vacuo* and the title compound was isolated (4.5 g, 7.0 mmol) in 68% yield as a slightly violet solid (dec 122°C). ^{1}H NMR (200 MHz, C_6D_6) δ 1.71 (s, Cp*-$\underline{H}$, 15 H); ^{13}C NMR (101 MHz, C_6D_6) δ 10.79 ($\underline{C}H_3$), 117.13 ($\underline{C}_5Me_5$); ^{27}Al NMR (104 MHz, C_6D_6) δ -45.50 ($w_{1/2} = 437.85$ Hz); MS (70 eV) *m/z* (%), 322 (M/2, 23), 241 (M/2-Br, 6), 135 (Cp*, 100); IR (KBr) $\tilde{v}$ 1622 (st), 1547 (st), 1423 (vst), 1262 (st), 1222 (st), 1169 (st), 1097 (st), 1067 (st), 1022 (st), 979 (m), 843 (m), 817 (m), 798 (st), 724 (m), 589 (m), 554 (m), 493 (vst), 381 (vst) cm^{-1}. Anal Calcd. for $C_{20}H_{30}Al_2Br_4$ (644.04): C, 37.30; H, 4.70; Al, 8.38; Br, 49.63: Found: C, 36.7; H, 4.6; Al, 8.6; Br 49.8.

$[Cp^*AlI(\mu\text{-}I)]_2$ (**3**)

Following the preparation procedure of compound **2**, AlI_3 (8.2 g, 20.0 mmol) was reacted with Cp^*SiMe_3 (4.0 g, 20.0 mmol) to give compound **3** (4.9 g, 5.9 mmol, 59%) as

[2] Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+ 44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

a violet solid (mp 98°C). ^{1}H NMR (200 MHz, C_6D_6) δ 1.54 (s, $C_5C\underline{H}_3$, 15 H); ^{13}C NMR (100 MHz, C_6D_6) δ 11.4 ($\underline{C}H_3$), 118.3 ($\underline{C}_5Me_5$); MS (70 eV) *m/z* (%) 416 (M/2, 20), 289 (M/2-I, 100); IR (KBr) $\tilde{v}$ 1307 (st), 1266 (st), 1247 (st), 1168 (m), 1065 (m), 1017 (st), 975 (m), 838 (vst), 818 (m), 780 (m), 723 (st), 622 (m), 588 (st), 512 (st), 469 (m), 451 (vst) cm^{-1}. Anal Calcd. for $C_{20}H_{30}Al_2I_4$ (832.04): C, 28.87; H, 3.63; Al, 6.48. Found C, 29.0; H, 3.9; Al, 6.4.

An Improved Preparation of $[Cp^*Al]_4$ (**4**)

A Na/K alloy prepared from sodium (0.32 g, 14.0 mmol) and potassium (1.00 g, 26.0 mmol) in toluene (10 ml) was treated with a solution of $[Cp^*AlX(\mu\text{-}X)]_2$ ($X =$ Cl, Br, I) in toluene (30 ml) and stirred for 15 h at room temperature. The obtained yellow solution was filtered and the solid extracted with toluene (3 × 10 ml). The solvent was removed *in vacuo* until incipient crystallization began. Storage at 0°C afforded the crystalline compound **4**. The analytical data of compound **4** are in agreement with those reported in literature (5). Yields are given in Table 1.

$[(Me_3Si)_2CHAlCl(\mu\text{-}Cl)]_2$ (**5**)

A suspension of $AlCl_3$ (1.58 g, 12.0 mmol) in *n*-hexane (50 ml) at room temperature was treated dropwise with $[(Me_3Si)_2CH]_2Zn$ (1.94 g, 5.0 mmol). After stirring for 48 h the solution was filtered using celite. The filtrate was concentrated to 10 ml and the product was crystallized at 0°C (1.86 g, 3.6 mmol, 72%) as colorless crystals (mp 103°C). ^{1}H NMR (200 MHz, C_6D_6) δ -0.57 (s, $\underline{H}CSiMe_3$, 2 H), 0.18 (s, $SiC\underline{H}_3$, 18 H); ^{13}C NMR (126 MHz, C_6D_6) δ 5.8 (H$\underline{C}SiMe_3$), 3.2 (Si$\underline{C}H_3$); ^{29}Si NMR (79 MHz, C_6D_6) δ -1.3 ($\underline{Si}Me_3$); MS (70 eV) *m/z* (%) 497 (M-Me, 5), 241 (M/2-Me, 22), 129 (($Me_3Si)_2C$-2 Me, 100).

$(Me_3Si)_3 SiAlCl_2 \cdot THF$ (**6**)

A suspension of $AlCl_3$ (1.33 g, 10.0 mmol) in *n*-hexane (10 ml) was treated with a solution of $(Me_3Si)_3SiK \cdot 2THF$ (3.34 g, 7.7 mmol) in *n*-hexane (20 ml) at room temperature. After stirring for 12 h, the KCl was filtered off using celite and the amount of solvent was reduced to 5 ml. Compound **6** was recovered after crystallization from toluene at 0°C as a colorless solid (2.68 g, 6.36 mmol, 80%) (mp 181°C).

TABLE 1
Comparison of the Yields of Compound 4

Educt	g	mmol	Yield (%)
$[Cp^*AlCl(\mu\text{-}Cl)]_2$ (**1**)	4.66	10.0	35
$[Cp^*AlBr(\mu\text{-}Br)]_2$ (**2**)	6.44	10.0	48
$[Cp^*AlI(\mu\text{-}I)]_2$ (**3**)	8.32	10.0	53

^{1}H NMR (200 MHz, C$_6$D$_6$) δ 0.42 (s, SiCH$_3$, 27 H), 0.93 (m, OCH$_2$CH$_2$, 4 H), 3.78 (m, OCH$_2$CH$_2$, 4 H). ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 3.6 (SiCH$_3$), 24.5 (OCH$_2$CH$_2$), 72.9 (OCH$_2$CH$_2$). ^{29}Si NMR (79 MHz, C$_6$D$_6$) δ -81.2 (SiSiMe$_3$), -8.6 (SiMe$_3$); MS (70 eV) m/z (%) 416 (M, 12), 401 (M-Me, 15), 309 (M-THF, -Cl, 35), 232 ((Me$_3$Si)$_3$Si-Me, 100); IR (KBr) $\tilde{v}$ 1350 (m), 1304 (m), 1258 (vst), 1244 (vst), 1170 (m), 1156 (m), 1067 (m), 1044 (m), 997 (st), 918 (m), 836 (sst), 746 (st), 736 (st), 723 (m), 686 (sst), 622 (sst), 486 (st), 444 (m), 405 (sst), 356 (sst) cm^{-1}. Anal Calcd. for C$_{13}$H$_{35}$AlCl$_2$OSi$_4$ (416.10): C, 37.38; H, 8.44; Al, 6.46. Found: C, 37.2; H, 8.3; Al, 6.3.

(Me$_3$Si)$_3$SiAlBr$_2$·THF (7)

Colorless crystals of the title compound **7** (6.22 g, 12.2 mmol, 81%) were prepared from AlBr$_3$ (5.2 g, 19.5 mmol) and (Me$_3$Si)$_3$SiK·2THF (6.51 g, 15.0 mmol) by adopting a method similar to that which was used for the preparation of **6**. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 0.42 (s, SiCH$_3$, 27 H), 1.00 (m, OCH$_2$CH$_2$, 4 H), 3.82 (m, OCH$_2$CH$_2$, 4 H). ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 3.5 (SiCH$_3$), 24.6 (OCH$_2$CH$_2$), 73.4 (OCH$_2$CH$_2$); ^{29}Si NMR (79 MHz, C$_6$D$_6$) δ -81.1 (SiSiMe$_3$), -8.5 (SiMe$_3$); MS (70 eV) m/z (%) 506 (M, 8), 491 (M-Me, 12), 354 (M-THF, -Br, -H, 35), 73 (Me$_3$Si, 100); IR (KBr) $\tilde{v}$ 1349 (st), 1303 (m), 1257 (vst), 1234 (vst), 1180 (m), 1044 (m), 994 (vst), 955 (m), 917 (m), 836 (vst), 746 (vst), 736 (vst), 685 (vst), 622 (vst), 476 (st), 453 (m), 443 (m), 401 (vst), 364 (vst), 353 (st) cm^{-1}. Anal Calcd. for C$_{13}$H$_{35}$AlBr$_2$OSi$_4$ (506.57): C, 30.82; H, 6.96; Al, 5.32; Br, 31.54; Si, 22.17. Found: C, 30.3; H, 6.9; Al, 5.1; Br, 31.3; Si, 21.9.

(Me$_3$Si)$_3$SiAlI$_2$·THF (8)

As described above, AlI$_3$ (5.30 g, 13.0 mmol) was treated with (Me$_3$Si)$_3$SiK·2THF (4.34 g, 10.0 mmol) to yield compound **8** (4.83 g, 8.0 mmol, 80%) as a colorless solid (mp 191°C). ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 0.43 (s, SiCH$_3$, 27 H), 0.99 (m, OCH$_2$CH$_2$, 4 H), 3.90 (m, OCH$_2$CH$_2$, 4 H); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 3.6 (SiCH$_3$), 24.7 (OCH$_2$CH$_2$), 74.5 (OCH$_2$CH$_2$); ^{29}Si NMR (79 MHz, C$_6$D$_6$) δ -80.8 (SiSiMe$_3$), -8.1 (SiMe$_3$); MS (70 eV) m/z (%) 600 (M, 28), 513 (M-THF,-Me, 35), 400 (M-THF,-I,-H, 40), 232 ((Me$_3$Si)$_3$Si-Me, 100); IR (KBr) $\tilde{v}$ 1348 (st), 1306 (m), 1257 (vst), 1243 (vst), 1177 (m), 1043 (m), 998 (st), 954 (m), 918 (m), 835 (vst), 746 (st), 736 (st), 685 (vst), 621 (vst), 466 (st), 450 (m), 441 (st), 338 (vst) cm^{-1}. Anal Calcd. for C$_{13}$H$_{35}$AlI$_2$OSi$_4$ (600.55): C 26.00, H 5.87, Al 4.49; Found: C 25.9, H 5.9, Al 4.5.

(CycMe$_2$Si)(Me$_3$Si)$_2$CH (9)

A solution of (Me$_3$Si)$_2$CHLi (3.32 g, 20.0 mmol) in THF (50 ml) was reacted at 0°C with CycMe$_2$SiCl (3.53 g,

20.0 mmol). After stirring for 12 h, the solvent was removed *in vacuo* and the residue was extracted with *n*-pentane (3 × 50 ml) and filtered. Distillation of the filtrate gave the desired product **9** (4.61 g, 15.2 mmol, 76%) as a colorless liquid (bp 75°C, 0.01 mbar). ^{1}H NMR (200 MHz, C$_6$D$_6$) δ -0.67 (s, HCSi$_3$, 1 H), 0.10 (s, SiCH$_3$, 6 H), 0.16 (s, SiCH$_3$, 18 H), 0.75 (m, CH C1 Cyc, 1 H), 1.00 (m, CH$_2$ C4 Cyc, 2 H), 1.20, 1.70 (m, CH$_2$ C2, C3 Cyc, 8 H); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ -1.0 (SiCyc(CH$_3$)$_2$), 0.2 (HCSi$_3$), 3.7 (Si(CH$_3$)$_3$), 27.4 (C4 Cyc), 27.5 (C1 Cyc), 28.1 (C3 Cyc), 28.7 (C2 Cyc); ^{29}Si NMR (79 MHz, C$_6$D$_6$) δ -0.2 (SiMe$_3$), 2.0 (SiCycMe$_2$). Anal Calcd. for C$_{15}$H$_{36}$Si$_3$ (300.71): C, 59.91; H, 12.07; Found: C, 59.6; H, 11.8.

(CycMe$_2$Si)(Me$_3$Si)$_2$CLi·THF (10)

To a solution of (CycMe$_2$Si)(Me$_3$Si)$_2$CH (4.61 g, 15.2 mmol) in THF (30 ml) was added methyllithium (11.4 ml, 1.6 M in ether, 18.2 mmol). After removing the ether under vacuum the reaction mixture was refluxed for 5 h and stirred for additional 12 h at room temperature. All volatile components were removed *in vacuo* and the resulting residue was recovered (5.30 g, 14.0 mmol, 92%) as a colorless solid (mp 48°C). ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 0.28 (s, SiCH$_3$, 6 H), 0.43 (s, SiCH$_3$, 18 H), 0.90 (m, CH C1 Cyc, 1 H), 1.10 (m, CH$_2$ C4 Cyc, 2 H), 1.30 (m, OCH$_2$CH$_2$, 4 H), 1.44, 2.00 (m, CH$_2$ C2, C3 Cyc, 8 H), 3.41 (m, OCH$_2$CH$_2$, 4 H); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 3.7 (SiCyc(CH$_3$)$_2$), 8.2 (Si(CH$_3$)$_3$), 25.3 (OCH$_2$CH$_2$), 28.0 (C1 Cyc), 29.4 (C3 Cyc), 29.5 (C2 Cyc), 30.8 (C4 Cyc), 68.3 (OCH$_2$CH$_2$); ^{29}Si NMR (79 MHz, C$_6$D$_6$) δ -10.3 (SiMe$_3$), -5.6 (SiCycMe$_2$); ^{7}Li NMR (97 MHz, C$_6$D$_6$) δ 0.5 (w$_{1/2}$ = 15 Hz).

(CycMe$_2$Si)(Me$_3$Si)$_2$CAlMe$_2$·THF (11)

To a solution of Me$_2$AlCl (1.68 g, 18.2 mmol) in *n*-hexane (10 ml) at 0°C was added dropwise a solution of (CycMe$_2$Si)(Me$_3$Si)$_2$CLi·THF (5.30 g, 14.0 mmol) in THF (50 ml). After stirring for 15 h at room temperature all volatile components were removed *in vacuo* and the residue was dissolved in *n*-hexane (30 ml). After filtration, the amount of solvent was reduced to 10 ml. Compound **11** was recovered as colorless crystals after storage of the above solution at 0°C (5.28 g, 12.3 mmol, 88%) (mp 66°C). ^{1}H NMR (200 MHz, C$_6$D$_6$) δ -0.36 (s, AlCH$_3$, 6 H), 0.35 (s, SiCH$_3$, 6 H), 0.42 (s, SiCH$_3$, 18 H), 0.95 (m, CH C1 Cyc, 1 H), 1.06 (m, OCH$_2$CH$_2$, 4 H), 1.13 (m, CH$_2$ C4 Cyc, 2 H), 1.32, 1.90 (m, CH$_2$ C2, C3 Cyc, 8 H), 3.54 (m, OCH$_2$CH$_2$, 4 H); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ -8.1 (AlCH$_3$), 2.8 (SiCyc(CH$_3$)$_2$), 7.0 (Si(CH$_3$)$_3$), 24.6 (OCH$_2$CH$_2$), 27.4 (C4 Cyc), 27.8 (C1 Cyc), 29.4 (C3 Cyc), 30.4 (C2 Cyc), 71.4 (OCH$_2$CH$_2$); ^{29}Si NMR

(79 MHz, C_6D_6) δ − 4.6 ($\underline{Si}Me_3$), − 0.7 ($\underline{Si}CycMe_2$); MS (70 eV) m/z (%) 345 (M-Cyc, 5), 273 (M-THF, -Cyc, 100). IR (KBr) $\tilde{\nu}$ 1348 (m), 1296 (m), 1255 (vst), 1192, (st), 1169 (m), 1089 (m), 1036 (m), 1005 (vst), 961 (m), 910 (m), 853 (vst), 843 (vst), 769 (st), 700 (st), 671 (vst), 629 (st), 566 (m), 504 (m), 436 (m) cm^{-1}. Anal Calcd. for $C_{21}H_{49}AlOSi_3$ (428.85): C, 58.81, H, 11.51, Al, 6.29: Found: C, 58.3; H, 11.4; Al, 6.1.

(CycMe$_2$Si)(Me$_3$Si)$_2$CAlF$_2$·THF (12)

A mixture of $(CycMe_2Si)(Me_3Si)_2CAlMe_2$·THF (2.00 g, 4.66 mmol) and Me_3SnF (1.70 g, 9.32 mmol) in THF (20 ml) was stirred for 12 h at room temperature. After removing all volatile components under vacuum the residue was dissolved in THF/hexane (20 ml:10 ml). Crystallization at − 20°C afforded the colorless compound **12** (1.44 g, 3.3 mmol, 71%) (mp 108°C). ^{1}H NMR (250 MHz, C_6D_6) δ 0.40 (s, SiC$\underline{H}_3$, 6 H), 0.45 (s, SiC$\underline{H}_3$, 18 H), 0.90 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H), 1.15 (m, C$\underline{H}$ C1 Cyc, 1 H), 1.35 (m, C$\underline{H}_2$ C4 Cyc, 2 H), 1.80, 2.15 (m, C$\underline{H}_2$ C2, C3 Cyc, 8 H), 3.80 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H); ^{19}F NMR (250 MHz, C_6D_6): δ − 156.5 (s); ^{29}Si NMR (99 MHz, C_6D_6) δ − 3.2 ($\underline{Si}Me_3$), 0.5 ($\underline{Si}CycMe_2$); MS (70 eV) m/z (%) 217 (($Me_3Si)_2(CycMe_2Si)C$- Cyc, 100); IR (KBr) $\tilde{\nu}$ 2957 (st), 2920 (st), 2849 (m), 1448 (m), 1254 (st), 1097 (m), 1045 (m), 1011 (m), 852 (vst), 816 (vst), 718 (m), 673 (st), 616 (m) cm^{-1}. Anal Calcd. for $C_{19}H_{43}AlF_2OSi_3$ (436.78): C, 52.25, H, 9.92; Al, 6.18, F, 8.70. Found: C, 51.5; H, 9.7; Al, 5.9; F, 8.4.

(CycMe$_2$Si)(Me$_3$Si)$_2$CAlCl$_2$·THF (13)

To a solution of $(CycMe_2Si)(Me_3Si)_2CAlMe_2$·THF (2.14 g, 5.0 mmol) in THF (30 ml) was added slowly a solution of Me_3SnCl (2.00 g, 10.0 mmol) in THF (20 ml). After stirring for 15 h at room temperature all volatile components were removed under vacuum. The residue was dissolved in toluene (5 ml) and crystallization at 0°C afforded the colorless compound **13** (1.76 g, 3.8 mmol, 75%) (mp 110°C). ^{1}H NMR (200 MHz, C_6D_6) δ 0.43 (s, SiC$\underline{H}_3$, 6 H), 0.48 (s, SiC$\underline{H}_3$, 18 H), 0.88 (m, C$\underline{H}$ C1 Cyc, 1 H), 0.97 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H), 1.10 (m, C$\underline{H}_2$ C4 Cyc, 2 H), 1.30, 1.90 (m, C$\underline{H}_2$ C2, C3 Cyc, 8 H), 3.97 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H); ^{13}C NMR (126 MHz, C_6D_6) δ 2.6 (SiCyc($\underline{C}H_3$)$_2$), 6.7 (Si($\underline{C}H_3$)$_3$), 24.2 (OCH$_2\underline{C}H_2$), 27.3 (C4 Cyc), 27.3 (C1 Cyc), 29.3 (C3 Cyc), 30.4 (C2 Cyc), 75.4 (O$\underline{C}H_2$CH$_2$); ^{29}Si NMR (79 MHz, C_6D_6) δ − 3.4 ($\underline{Si}Me_3$), 0.6 ($\underline{Si}CycMe_2$); MS (70 eV) m/z (%) 313 (M-THF,-Cyc, 50), 201 (($Me_3Si)_2(CycMe_2Si)C$-Cyc, -Me, 100); IR (KBr) $\tilde{\nu}$ 1305 (st), 1263 (vst), 1169 (m), 1155 (m), 1076 (m), 1032 (m), 972 (m), 878 (vst), 853 (vst), 813 (vst), 676 (st), 566 (m), 509 (m) cm^{-1}. Anal calcd. for $C_{19}H_{43}AlCl_2OSi_3$ (469.68): C, 48.59; H, 9.23; Al, 5.74; Cl, 15.10. Found: C, 48.6; H, 9.0; Al, 6.1; Cl, 15.1.

(CycMe$_2$Si)(Me$_3$Si)$_2$CAlBr$_2$·THF (14)

To a solution of compound $(CycMe_2Si)(Me_3Si)_2$ $CAlMe_2$·THF (2.14 g, 5.0 mmol) in toluene (20 ml) was added dropwise bromine (1.60 g, 10.0 mmol) at 0°C. After stirring for 15 min the byproduct methylbromide was removed *in vacuo*. The resultant solution was concentrated to 5 ml and stored at 0°C to yield compound **14** (2.18 g, 3.9 mmol, 78%) as colorless solid (mp 136°C). ^{1}H NMR (200 MHz, C_6D_6) δ 0.45 (s, SiC$\underline{H}_3$, 6 H), 0.50 (s, SiC$\underline{H}_3$, 18 H), 0.95 (m, C$\underline{H}$ C1 Cyc, 1 H), 1.00 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H), 1.10 (m, C$\underline{H}_2$ C4 Cyc, 2 H), 1.35, 1.95 (m, C$\underline{H}_2$ C2, C3 Cyc, 8 H), 4.06 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H); ^{13}C NMR (126 MHz, C_6D_6) δ 2.8 (SiCyc($\underline{C}H_3$)$_2$), 6.9 (Si($\underline{C}H_3$)$_3$), 25.1 (OCH$_2\underline{C}H_2$), 27.2 (C4 Cyc), 27.3 (C1 Cyc), 29.2 (C3 Cyc), 30.5 (C2 Cyc), 76.2 (O$\underline{C}H_2$CH$_2$); ^{29}Si NMR (79 MHz, C_6D_6) δ − 3.4 ($\underline{Si}Me_3$), 0.7 ($\underline{Si}CycMe_2$); MS (70 eV) m/z (%) 403 (M-THF, -Cyc, 50), 201 (($Me_3Si)_2(CycMe_2Si)C$-Cyc,-Me, 100); IR (KBr) $\tilde{\nu}$ 1349 (st), 1296 (m), 1254 (vst), 1185 (m), 1169 (m), 1088 (m), 1070 (m), 1035 (m), 998 (st), 986 (st), 955 (m), 919 (m), 884 (st), 852 (vst), 802 (vst), 774 (vst), 724 (st), 706 (m), 669 (st), 644 (m), 624 (m), 464 (m), 419 (m), 404 (vst), 343 (st) cm^{-1}. Anal Calcd. for $C_{19}H_{43}AlBr_2OSi_3$ (558.60): C, 40.85; H, 7.76, Al, 4.83. Found: C, 40.5; H, 7.7; Al, 4.6.

(CycMe$_2$Si)(Me$_3$Si)$_2$CAlI$_2$·THF (15)

A solution of $(CycMe_2Si)(Me_3Si)_2CAlMe_2$·THF (4.28 g, 10.0 mmol) in toluene (30 ml) was reacted with a solution of iodine (5.08 g, 20 mmol) in toluene (50 ml) at room temperature. After adding 25 ml of the iodine solution, the color of the reaction mixture turned violet. After subsequent stirring for 15 h and filtration, the byproduct methyliodide was removed *in vacuo*. The amount of solvent was reduced to 25 ml and crystallization at 0°C afforded compound **15** (5.16 g, 7.9 mmol, 79%) (mp 140°C). ^{1}H NMR (200 MHz, C_6D_6) δ 0.48 (s, SiC$\underline{H}_3$, 6 H), 0.53 (s, SiC$\underline{H}_3$, 18 H), 0.99 (m, C$\underline{H}$ C1 Cyc, 1 H), 1.01 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H), 1.15 (m, C$\underline{H}_2$ C4 Cyc, 2 H), 1.38, 2.00 (m, C$\underline{H}_2$ C2, C3 Cyc, 8 H), 4.15 (m, OC$\underline{H}_2$C$\underline{H}_2$, 4 H); ^{13}C NMR (126 MHz, C_6D_6) δ 3.1 (SiCyc($\underline{C}H_3$)$_2$), 7.4 (Si($\underline{C}H_3$)$_3$); 24.0 (OCH$_2\underline{C}H_2$), 26.9 (C4 Cyc), 27.2 (C1 Cyc), 29.1 (C3 Cyc), 30.5 (C2 Cyc), 77.4 (O$\underline{C}H_2$CH$_2$); ^{29}Si NMR (79 MHz, C_6D_6) δ − 3.1 ($\underline{Si}Me_3$), 0.8 ($\underline{Si}CycMe_2$); MS (70 eV) m/z (%) 497 (M-THF, -Cyc, 60), 201 (($Me_3Si)_2(CycMe_2Si)C$-Cyc, -Me, 100); IR (KBr) $\tilde{\nu}$ 1348 (st), 1296 (m), 1253 (vst), 1167 (m), 1088 (st), 1034 (m), 986 (m), 954 (m), 918 (m), 884 (st), 850 (vst), 799 (vst), 773 (vst), 721 (st), 667 (st), 642 (st), 466 (m), 403 (st), 322 (vst) cm^{-1}. Anal Calcd. for $C_{19}H_{43}AlI_2OSi_3$ (652.58): C, 34.97; H, 6.64; Al, 4.13. Found: C, 35.3; H, 6.5; Al, 3.8.

[(CycMe$_2$Si)(Me$_3$Si)$_2$CAl(μ-O(CH$_2$)$_3$CH$_2$)]$_2$ (16)

To a suspension of Na/K alloy (Na, 0.08 g, 3.5 mmol; K, 0.25 g, 6.5 mmol) in toluene (10 ml) was added dropwise

$$2 \; Cp^*SiMe_3 \; + \; 2 \; AlX_3 \quad \xrightarrow[- \; 2 \; Me_3SiX]{}$$

X = Br, I **2 , 3**
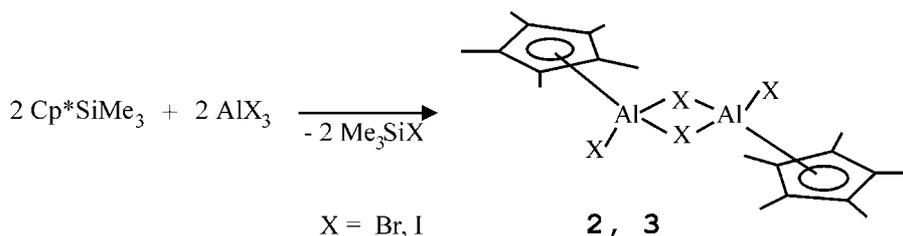
SCHEME 1.

a solution of $(CycMe_2Si)(Me_3Si)_2CAlI_2 \cdot THF$ (3.26 g, 5.0 mmol) in toluene (30 ml) at room temperature. After stirring for 78 h the solution was filtered and the solvent removed *in vacuo*. The yellow residue was dissolved in *n*-hexane (5 ml) and at 0°C compound **16** (1.36 g, 1.7 mmol, 68%) crystallized as a colorless solid (mp 233°C). ^1H NMR (200 MHz, C_6D_6) δ 0.35 (s, $SiCH_3$, 12 H), 0.43 (s, $SiCH_3$, 36 H), 0.49–0.61 (m, $OCH_2CH_2CH_2CH_2Al$, 4 H), 0.90 (m, CH C1 Cyc, 2 H), 1.10 (m, CH_2 C4 Cyc, 4 H), 1.43, 2.10 (m, $OCH_2CH_2CH_2CH_2Al$, 8 H), 1.30, 1.90 (m, CH_2 C2, C3 Cyc, 16 H), 3.45–4.20 (m, $OCH_2CH_2CH_2CH_2Al$, 4 H); ^{29}Si NMR (79 MHz, C_6D_6) δ − 4.2 ($SiMe_3$), − 0.4 ($SiCycMe_2$). MS(70 eV) m/z (%) 797 (M, 8), 781 (M-Me, 18), 713 (M-Cyc, 38), 315 (M/2-Cyc, 100); IR (KBr) $\tilde{v}$ 1295 (m), 1259 (vst), 1254 (st), 1166 (m), 1123 (m), 1093 (st), 1024 (st), 999 (m), 910 (m), 889 (m), 847 (vst), 800 (vst), 739 (m), 722 (st), 669 (st), 653 (st), 636 (m), 587 (m), 553 (st), 503 (m), 469 (m) cm^{-1}. Anal Calcd. for $C_{38}H_{86}Al_2O_2Si_6$ (797.57): C, 57.23; H, 10.87, Found: C, 57.6; H, 10.5.

RESULTS AND DISCUSSION

a. Cp*AlX₂ Compounds

The pentamethylcyclopentadienyl ligand is an important substituent due to its steric bulk and variable bonding modes in main group chemistry (16). Monoorganylaluminumhalides incorporating the Cp* ligand are valuable precursors for aluminum(I) compounds (5). $[Cp^*AlCl(\mu\text{-}Cl)]_2$ (**1**) was prepared from Cp^*SiMe_3 and $AlCl_3$ (14). We followed the same strategy (Scheme 1) for the synthesis of $[Cp^*AlBr(\mu\text{-}Br)]_2$ (**2**) and $[Cp^*AlI(\mu\text{-}I)]_2$ (**3**).

Compounds **2** and **3** were prepared in good yields. The analytical data of these compounds are listed under Experimental. Crystals of compound **2** suitable for a single-crystal X-ray structural analysis were obtained by slow cooling of the reaction mixture in toluene to room temperature. The molecular structure of **2** is shown in Fig. 1 and characteristic bond lengths and angles are displayed in Table 2.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell. Each aluminum atom provides a tetrahedral environment with two bridging and one terminal bromine atom and an η^5-Cp*-ligand. The average Al–C bond distance is 2.223 Å. The bridging bromine atoms have longer bond distances (2.513 and 2.516 Å) in comparison to the terminal bromine atoms (2.311 Å). For comparison, $Al_2Br_6 \cdot C_6H_6$ provides similar bond distances (bridging, 2.50 Å; terminal, 2.39 Å) (17).

Previously, we reported on the reaction of compound **1** with potassium to give $(Cp^*Al)_4$ (**4**) in 20–28% yield (5). Herein we performed the reduction of compounds **1**–**3** with a Na/K alloy, which results in the formation of $(Cp^*Al)_4$ in 35, 48, and 53% yields, respectively. Advantageously, the preparation using Na/K alloy avoids thermal stress in comparison to the procedure using potassium alone. This result indicates an increased yield (35% versus 20–28%) in the case of the chloride compared to the previously reported method. The decreasing aluminum–halide bond energy in the series AlCl (331 kJ/mol) > AlBr (256 kJ/mol) > AlI (172 kJ/mol) (18) results in higher yields of the product using the iodides in the reduction process. The spectroscopic data for **4** are in agreement with those in the literature (Scheme 2) (5).

b. (Me₃Si)₂CHAlX₂ Compounds

Aluminum halides providing sterically demanding substituents are interesting starting materials for the synthesis of organometallic compounds with aluminum in low oxidation state. Uhl *et al.* prepared $[((Me_3Si)_2CH)_2Al]_2$ with an aluminum–aluminum bond from the reaction of $((Me_3Si)_2CH)_2AlCl$ and potassium (19). Analogous compounds of gallium and indium are also reported (19). According to the literature compound $((Me_3Si)_2CH)_2AlCl$ was prepared from $((Me_3Si)_2CH)_3Al$ and $AlCl_3$ (20). We obtained compound **5** in high yield from the reaction of $AlCl_3$ and $((Me_3Si)_2CH)_2Zn$. The analytical data for this compound are in agreement with those reported in the literature (Scheme 3) (20).

Compound **5** was reacted with Na/K alloy, which results immediately in the formation of metallic aluminum due to a disproportionation reaction.

The ^1H NMR spectrum shows resonances for both the products given in Scheme 4 and is consistent with the reported one (20).
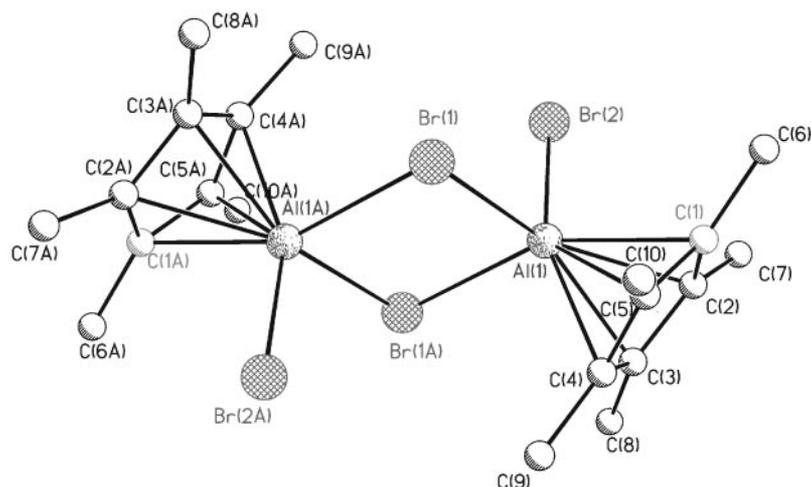
FIG. 1. Single-crystal X-ray structure of **2**. The hydrogen atoms have been omitted for clarity.

c. (MeSi)₃SiAlX₂ Compounds

Gilman and Smith used the TrisSi ligand (21) for the stabilization of extraordinary main group (22) and transition metal (23) compounds. We prepared the monosubstituted aluminum halides by a salt elimination reaction of the aluminum halide and the potassium salt of the ligand in good yield as shown in Scheme 5.

TrisSiK·2THF can easily be prepared from $(Me_3Si)_4Si$ and KOtBu (24). For the synthesis of compounds **6–8**, it is necessary to use the potassium instead of the lithium salt of the ligand, otherwise a LiCl adduct of the type $[Li(THF)_4][(Me_3Si)_3SiAlCl_3]$ (25) is formed.

The ^1H, ^{13}C, and ^{29}Si NMR data of the compounds **6, 7**, and **8** are listed in Table 3. The chemical shift values differ only slightly among the halides.

For the preparation of (Cp*Al)₄, the diiodide was found to be the best precursor, consequently, we used derivative **8**. The preparation of the analogous gallium compound $[(Me_3Si)_3SiGa]_4$ was also successful (26). However, when we reacted **8** with Na/K alloy at room temperature in toluene we observed the formation of hexakis(trimethylsilyl)disilane $[(Me_3Si)_3Si]_2$. Obviously the Al–Si bond was cleaved and the formation of the disilane and metallic aluminum is observed (Scheme 6).

d. (CycMe₂Si)(Me₃Si)₂CAlX₂ Compounds

The tris(trimethylsilyl)methyl substituent was modified by introducing one cyclohexyl group. The new ligand is not symmetric anymore and therefore better properties for the crystallization can be expected compared to compounds bearing the Tris ligand. In addition, the new ligand will be even more sterically demanding than the Tris ligand. Therefore it was interesting to prove whether the chemistry established with the Tris ligand can be improved using the CycTris ligand. We prepared $(CycMe_2Si)(Me_3Si)_2CH$ (**9**) from $(Me_3Si)_2CHLi$ and CycMe₂SiCl. The reaction of **9** with methyllithium yielded the lithium salt $(CycMe_2Si)(Me_3Si)CLi·THF$ (**10**). Finally compound **10** was reacted with Me₂AlCl to give CycTrisAlMe₂·THF (**11**) (Scheme 7).

We used the methyl derivative as a precursor for the preparation of the halides. The fluorides and chlorides were prepared by reacting **11** with Me₃SnF and Me₃SnCl, respectively (Scheme 8).

The methyl fluoride metathesis is a reliable route for the preparation of aluminum fluorides (27). Examples for a methyl chloride exchange using Me₃SnCl for aluminum compounds are reported in the literature (28).

TABLE 2
Selected Bond Lengths (Å) and Angles (°) for $[Cp^*AlBr(\mu\text{-}Br)]_2$ (2)

Al(1)–Br(1)	2.516 (2)	Br(1)–Al(1)–Br(1A)	85.6 (1)
Al(1A)–Br(1A)	2.513 (2)	Br(1)–Al(1)–Br(2)	97.4 (1)
Al(1)–Br(2)	2.311 (2)	Br(1A)–Al(1)–Br(2)	96.9 (1)
		Al(1)–Br(1)–Al(1A)	94.4 (1)

TABLE 3
^1H, ^{13}C, and ^{29}Si NMR Data of the Compounds 6, 7, and 8

Compound:	6	7	8
^1H NMR δ (Si$\underline{Me}_3$)	0.42	0.42	0.43
THF	0.93/3.78	1.00/3.82	0.99/3.90
^{13}C NMR δ ($\underline{C}H_3$)	3.6	3.5	3.6
THF	24.5/72.9	24.6/73.4	24.7/74.5
^{29}Si NMR δ (Si$\underline{Me}_3$)	−8.6	−8.5	−8.1
$\underline{Si}(SiMe_3)_3$	−81.2	−81.1	−80.8

X = Cl, Br, I   4

SCHEME 2.

$$[(Me_3Si)_2CH]_2Zn \ + \ 2 \ AlCl_3 \ \xrightarrow[- \ ZnCl_2]{} \ (Me_3Si)_2CH \diagdown \underset{Cl}{\overset{Cl}{Al}} \diagup \underset{Cl}{\overset{Cl}{Al}} \diagdown CH(SiMe_3)_2$$

5

SCHEME 3.

$$9 \ [(Me_3Si)_2CHAlCl_2]_2 \ \xrightarrow{Na/K} \ 4 \ Al \ + \ 2 \ [(Me_3Si)_2CH]_3Al \ + \ 12 \ K[(Me_3Si)_2CHAlCl_3]$$

SCHEME 4.

$$(Me_3Si)_3SiK \cdot 2 \ THF \ + \ AlX_3 \ \xrightarrow[- \ THF]{- \ KX} \ (Me_3Si)_3SiAlX_2 \cdot THF$$

6 - 8

X = Cl, Br, I

SCHEME 5.

$$2 \ (Me_3Si)_3SiAlI_2 \cdot THF \ + \ Na/K \ \xrightarrow[\substack{- \ THF \\ - \ Al}]{- \ NaI/KI} \ (Me_3Si)_3Si\text{-}Si(SiMe_3)_3$$

SCHEME 6.

$$Me_3Si\!-\!\underset{SiMe_2Cyc}{\overset{SiMe_3}{\underset{|}{\overset{|}{C}}}}\!-\!Li \cdot THF \ + \ Me_2AlCl \ \xrightarrow[- \ LiCl]{THF} \ Me_3Si\!-\!\underset{SiMe_2Cyc}{\overset{SiMe_3}{\underset{|}{\overset{|}{C}}}}\!-\!AlMe_2 \cdot THF$$

11

SCHEME 7.

$$Me_3Si\!-\!\underset{SiMe_2Cyc}{\overset{SiMe_3}{\underset{|}{\overset{|}{C}}}}\!-\!AlMe_2 \cdot THF \ + \ 2 \ Me_3SnX \ \xrightarrow[- \ 2 \ Me_4Sn]{toluene} \ Me_3Si\!-\!\underset{SiMe_2Cyc}{\overset{SiMe_3}{\underset{|}{\overset{|}{C}}}}\!-\!AlX_2 \cdot THF$$

X = F, Cl   **12, 13**

SCHEME 8.

TABLE 4
Comparison of the ¹H NMR Data of the Compounds 9–15

Compound:	9	10	11	12	13	14	15
¹H NMR δ Me₃Si	0.16	0.43	0.42	0.45	0.48	0.50	0.53
CycSiMe₂	0.10	0.28	0.35	0.40	0.43	0.45	0.48
²⁹Si NMR δ Me₃Si	−0.2	−10.3	−4.6	−3.2	−3.4	−3.4	−3.1
CycSiMe₂	2.0	−5.6	−0.7	0.5	0.6	0.7	0.8

The bromine and iodine derivatives (**14** and **15**) were prepared by reacting CycTrisAlMe₂·THF (**11**) with the corresponding elements (Scheme 9).

Compounds **9–15** were characterized by multinuclear NMR-, mass-, and IR spectroscopy as well as elemental analysis. The NMR data are compiled in Table 4.

e. X-Ray Structural Investigations

Crystallization of the compounds TrisSiAlX_2 (X = Cl, Br, I; **6–8**) and CycTrisAlX_2 (X = Me, Cl, Br, I; **11, 13–15**) from *n*-hexane at 0°C gave crystals suitable for a single crystal X-ray structural analysis. The three TrisSi deriva-
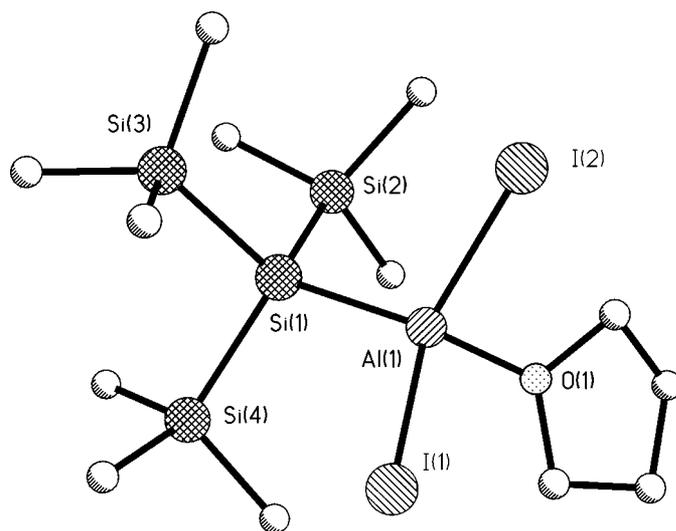
FIG. 2. Single-crystal X-ray structure of **8**. The hydrogen atoms have been omitted for clarity.

tives crystallize in the same triclinic space group $P\bar{1}$ with four molecules per unit cell. Compounds **11**, **13**, and **14** crystallize in the orthorhombic space group $P2_12_12_1$ with

TABLE 5
Crystal Data for Compounds 4, 6, 7, 8, 11, 13, 15, and 16

Compound:	2	6	7	8	11
Empirical formula	$C_{20}H_{30}Al_2Br_4$	$C_{13}H_{35}AlCl_2OSi_4$	$C_{13}H_{35}AlBr_2OSi_4$	$C_{13}H_{35}AlI_2OSi_4$	$C_{21}H_{49}AlOSi_3$
fw	644.04	417.65	506.57	600.55	428.85
Color of crystal	Pale violet	Colorless	Colorless	Colorless	Colorless
Temp (K)	133(2)	133(2)	153(2)	203(2)	150(2)
Crystal size (mm)	0.4 × 0.3 × 0.2	0.8 × 0.5 × 0.5	1.0 × 0.5 × 0.1	1.0 × 0.4 × 0.3	0.5 × 0.5 × 0.4
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a (Å)	11.433(2)	9.584(2)	9.614(5)	9.738(3)	9.356(1)
b (Å)	12.791(3)	15.574(3)	15.621(9)	16.058(5)	11.871(1)
c (Å)	8.567(3)	18.073(4)	18.396(10)	18.951(7)	23.283(5)
α (Degrees)	90	66.88(3)	66.51(3)	66.22(2)	90
β (Degrees)	111.28(3)	79.94(3)	79.62(3)	79.19(2)	90
γ (Degrees)	90	86.93(3)	87.03(3)	87.00(2)	90
Cell vol (Å)	1167.4(5)	2442.5(9)	2492(2)	2662.8(15)	2585.9(7)
Z	2	4	4	4	4
ρ_c (g mm⁻³)	1.832	1.136	1.350	1.498	1.102
μ (mm⁻¹)	6.974	0.496	3.497	2.574	0.226
F(000)	632	896	1040	1184	952
2θ Range (degrees)	5–56	4–50	7–45	7–50	7–50
No. of data measured	6354, 2628	42884, 8599	8050, 6044	13644, 9417	9512, 4545
Unique	(R_{int} = 0.0328)	(R_{int} = 0.0293)	(R_{int} = 0.0377)	(R_{int} = 0.0749)	(R_{int} = 0.0398)
$R,^a$ $wR2^b$ ($I > 2\sigma(I)$)	0.0508, 0.1219	0.0280, 0.0657	0.0353, 0.0874	0.0395, 0.0895	0.0290, 0.0729
R, wR2 (all data)	0.0572, 0.1264	0.0352, 0.0676	0.0453, 0.0951	0.0506, 0.0980	0.0309, 0.0745
Goodness of fit, S^c	1.136	1.074	1.062	1.060	1.039
Extinction coefficient	—	0.0020(3)	—	0.00302(16)	—
No. of refined parameters	123	435	416	408	265
Largest difference Peak/hole (e Å⁻³)	1.909/ −1.132	0.289/ −0.278	0.517/ −0.563	1.022/ −0.875	0.398/ −0.163
Absolute structure Parameter (32)	—	—	—	—	0.41(9)

TABLE 5—*Continued*

Compound:	**13**	**14**	**15**	**16**
Empirical formula	$C_{19}H_{43}AlCl_2OSi_3$	$C_{19}H_{43}AlBr_2OSi_3$	$C_{19}H_{43}AlI_2OSi_3$	$C_{38}H_{86}Al_2O_2Si_6$
fw	469.68	558.60	652.58	797.57
Color of crystal	Colorless	Colorless	Colorless	Colorless
Temperature (K)	203(2)	203(2)	200(2)	133(2)
Crystal size (mm)	$0.8 \times 0.3 \times 0.3$	$0.8 \times 0.7 \times 0.5$	$0.7 \times 0.6 \times 0.5$	$0.3 \times 0.3 \times 0.2$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$C2/c$
a (Å)	9.227(2)	9.464(2)	9.948(1)	16.622(3)
b (Å)	11.845(3)	11.816(2)	11.983(2)	9.033(2)
c (Å)	23.445(7)	23.256(5)	22.694(16)	30.390(6)
α (Degrees)	90	90	90	90
β (Degrees)	90	90	91.88(3)	94.10(3)
γ (Degrees)	90	90	90	90
Cell vol (Å)	2562.4(11)	2600.6(9)	2704(2)	4551(2)
Z	4	4	4	4
ρ_c (g mm^{-3})	1.218	1.427	1.603	1.164
μ (mm^{-1})	0.436	3.297	2.500	0.253
$F(000)$	1016	1160	1304	1760
2θ Range (degrees)	7–50	7–50	7–45	5–45
No. of data measured,	4369, 3871	3681, 3294	3554, 3522	40397, 2971
Unique	($R_{int} = 0.0189$)	($R_{int} = 0.0365$)	($R_{int} = 0.0418$)	($R_{int} = 0.0910$)
R,^{a} $wR2^b$ ($I > 2\sigma(I)$)	0.0306, 0.0782	0.0468, 0.1025	0.0356, 0.0932	0.0667, 0.1161
R, $wR2$ (all data)	0.0329, 0.0811	0.0591, 0.1113	0.0396, 0.0964	0.0949, 0.1242
Goodness of fit, S^c	1.078	1.067	1.097	1.177
No. of refined parameters	262	243	262	225
Largest diff Peak/hole (e Å^{-3})	0.286/ − 0.274	0.487/ − 0.555	0.859/ − 0.618	0.292/ − 0.230
Absolute structure Parameter (32)	0.02(7)	− 0.017(15)	—	—

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

four molecules in the unit cell. In contrast, the iodine derivative crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell (Table 5). Figures 2 and 3 display the structures of the iodine derivatives with TrisSi- and CycTris ligands, respectively.

In all the cases, the aluminum center exhibits a tetrahedral environment and is surrounded by a silicon (or carbon), an oxygen, and two iodine atoms. In Table 6 a selection of bond lengths (Å) and angles (°) of TrisSiAlX_2, CycTrisAlX_2, and TrisAlX_2 is listed for comparison reason.

The Al–X bond length (X = Cl, Br, I) is similar to that of compounds with the same halide and different ligands. For example, the Al–Cl bond length of compounds **6**, **13**, and TrisAlCl$_2$·THF is 2.15 Å. In agreement with the expected result, the Al–X bond length increases from the chloride to the iodide. Compounds with the TrisSi fragment have a 0.4-Å longer Al–Si bond length compared to the corresponding carbon analog (C–Al). The Al–R and Al–O bond lengths are constant in all halide derivatives provided that they have the same ligand, except for compound **11**, in which the Al–R and Al–O bond lengths are enlarged by 0.05 and 0.07 Å, respectively. The X–Al–X angle decreases with the heavier congeners of X. Consequently the longer Al–Si bond length compared to the Al–C one leads to a wider X–Al–X angle of

$$\text{Me}_3\text{Si}-\overset{\overset{\displaystyle \text{SiMe}_3}{|}}{\underset{\underset{\displaystyle \text{SiMe}_2\text{Cyc}}{|}}{\text{C}}}-\text{AlMe}_2 \cdot \text{THF} \quad + \quad 2\,X_2 \quad \xrightarrow[\text{- 2 MeX}]{\text{toluene}} \quad \text{Me}_3\text{Si}-\overset{\overset{\displaystyle \text{SiMe}_3}{|}}{\underset{\underset{\displaystyle \text{SiMe}_2\text{Cyc}}{|}}{\text{C}}}-\text{Al}X_2 \cdot \text{THF}$$

$$X = \text{Br, I} \qquad\qquad \textbf{14, 15}$$
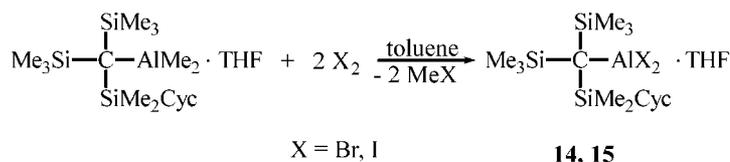
SCHEME 9.
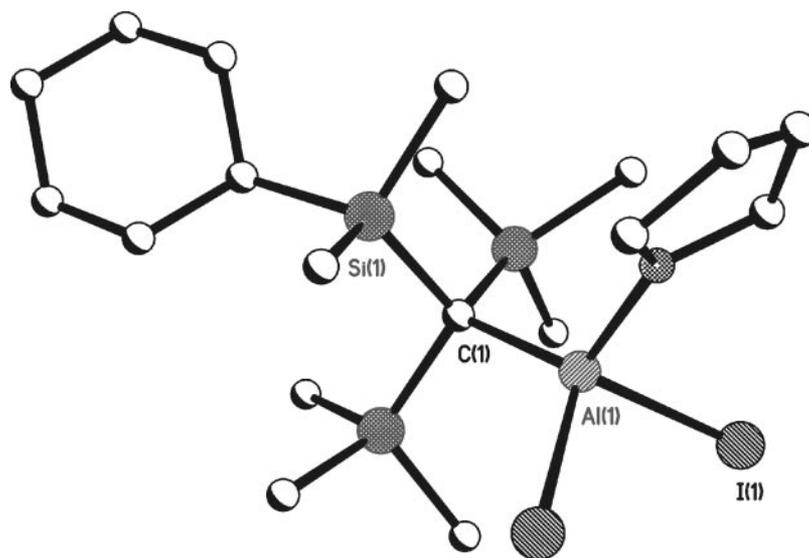
FIG. 3. Single-crystal X-ray structure of **15**. The hydrogen atoms have been omitted for clarity.

$5°$. The more sterically demanding CycTris-, in comparison to the Tris ligand, results in a $1°$ smaller X–Al–X angle.

Compounds TrisAlCl$_2$·THF and TrisAlI$_2$·THF both have been treated with Na/K alloy to give the THF ring-opened product [TrisAl(μ-O(CH$_2$)$_3$CH$_2$)]$_2$ in the first case and (TrisAl)$_4$ in the second case (10). A similar THF ring opening product was obtained in the reaction using 2,4,6-i-Pr$_3$C$_6$H$_2$AlCl$_2$·THF and Na/K alloy (30). From our experience in this field, the best results and yields for the reduction reaction have been achieved using the iodides. However, the reaction of CycTrisAlI$_2$·THF (**15**) with Na/K alloy resulted in the THF ring opening product [CycTrisAl(μ-O(CH$_2$)$_3$CH$_2$)]$_2$ (**16**) (Scheme 10).

We obtained the same product when compound **15** was reacted with SmI$_2$ in toluene at elevated temperature. Compound **16** was fully characterized by NMR, mass, and IR spectroscopy and elemental analysis. The data are listed under Experimental. Crystals of **16** suitable for single-crystal X-ray diffraction measurements were obtained from a solution in toluene at $0°$C. The molecular structure of **16** is shown in Fig. 4 and characteristic bond distances and angles are displayed in Table 7.

Compound **16** crystallizes in the monoclinic space group $C2/c$. The molecule is built up by a four-membered Al$_2$O$_2$-ring that is bridged by four CH$_2$ groups on two sides. The two Alμ-O(CH$_2$)$_3$CH$_2$ rings take up a *cis* conformation toward the Al$_2$O$_2$ plane. Compound [TrisAl(μ-O(CH$_2$)$_3$CH$_2$)]$_2$ provides also a *cis* conformation (10), while [2,4,6-i-Pr$_3$C$_6$H$_2$Al(μ-O(CH$_2$)$_3$CH$_2$)]$_2$ exhibits a *trans* arrangement (31).

TABLE 6
Comparison of Selected Bond Lengths (Å) and Angles (°) of Tris Si Al X$_2$, Cyc Tris Al X$_2$, and Tris Al X$_2$

Compounds	Al–X bond	Al–R bond	Al–O bond	X–Al–X angle
TrisSiAlCl$_2$·THF(**6**)	2.15	2.42	1.87	110.3
TrisSiAlBr$_2$·THF(**7**)	2.32	2.42	1.86	109.5
TrisSiAlI$_2$·THF(**8**)	2.55	2.42	1.87	107.9
CycTrisAlMe$_2$·THF(**11**)	1.98	2.05	1.98	109.3
CycTrisAlCl$_2$·THF(**13**)	2.15	2.00	1.90	105.8
CycTrisAlBr$_2$·THF(**14**)	2.31	1.98	1.91	104.4
CycTrisAlI$_2$·THF(**15**)	2.55	1.99	1.91	101.9
TrisAlCl$_2$·THF	2.15	1.98	1.88	106.8
TrisAlBr$_2$·THF	2.31	1.98	1.89	105.5
TrisAlI$_2$·THF	2.56	1.98	1.89	102.8

Note. TrisAlX$_2$·THF (29); Tris = (Me$_3$Si)$_3$C.

TABLE 7
Selected Bond Lengths (Å) and Angles (°) for [(CycMe$_2$Si)(Me$_3$Si)$_2$ CAl(μ-O(CH$_2$)$_3$CH$_2$)]$_2$ (16)

Al(1)–C(1)	2.036(4)	O(1)–C(5)	1.453(5)
Al(1)–O(1)	1.869(3)	C(5)–C(4)	1.520(6)
Al(1)–O(1A)	1.882(3)	C(4)–C(3)	1.513(7)
Al(1)–C(2)	1.987(4)	C(3)–C(2A)	1.534(6)
C(1)–Al(1)–C(2)	116.7(2)	C(2)–Al(1)–O(1)	114.9(2)
C(2)–Al(1)–O(1A)	95.3(2)	C(1)–Al(1)–O(1)	115.9(2)
C(1)–Al(1)–O(1A)	130.5(2)	O(1)–Al(1)–O(1A)	77.4(2)
Al(1)–O(1)–Al(1A)	100.1(2)	Al(1)–O(1)–C(5)	125.3(3)
Al(1A)–O(1)–C(5)	121.3(3)		

FIG. 4. Single-crystal X-ray structure of **16**. The hydrogen atoms have been omitted for clarity.

16

SCHEME 10.

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