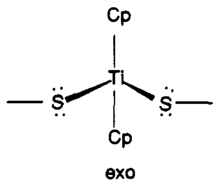
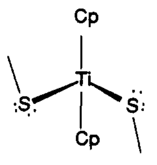
$[(Cp_2Zr(\mu\text{-}SCH_2CH_2CH_2S)_2ZrCp_2)Ag]^+$.[11,12] In addition, FHMO calculations for Zr or Nb thiolato-bridged models show that as the second row metal d orbitals are lower in relative energy compared to Ti, larger overlap populations despite longer M–M′ distances, are observed. In addition, both σ and π components comprise the interactions between Zr or Nb and the late metals. Similar results were observed for the models $Cp_2Zr(\mu\text{-}PH_2)_2ML_n$.[22]

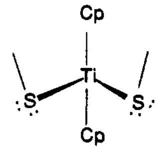
Conformational Considerations. Three conformers are possible for the free metalloligands; *cisoid-endo*, *transoid-endo*, and *exo*. Structural data reveal that free titanocenedithiolates $Cp_2Ti(SR)_2$ (R = Me, Et) adopt the *endo–transoid* conformation. This preference has been rationalized on the basis of both electronic and steric arguments.[2] In contrast, Darensbourg et al.[23] have shown that the *exo* conformation is preferred by d^1 and d^2 complexes of the form $Cp_2M(SR)_2$. On binding to the late-metal center, only *endo* conformations of the titanocenedithiolate moieties are geometrically and sterically permitted. The structural data for 2 show that the ethyl substituents adopt a *cisoid–endo* conformation. Restricted MMX calculations were performed for 2 in which the metal atom geometries were held constant and only the organic substituents on S and P were allowed to vary. The results confirm a qualitative energetic preference for the *cisoid–endo* over the *transoid–endo* conformer. In contrast, related qualitative, restricted MMX calculations for 2 in which the TiS_2Cu core was constrained to be planar, shows an energetic preference for the *transoid–endo* conformer. Thus, it seems that the fold in the TiS_2Cu core, which accommodates Ti–Cu bonding, enhances the preference for a *cisoid* conformation.



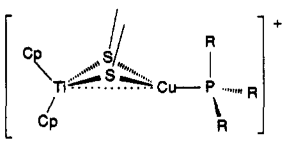
exo

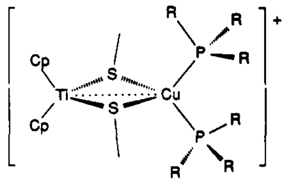


endo-transoid



endo-cisoid





A similar result is also seen for 7. In contrast to 2 and 7, the pseudotetrahedral coordination spheres of Cu(I) and Ni(0) in 5 and 6, respectively, requires a *transoid–endo* sulfur substituent conformation and thus planar MS_2M' cores are observed. This is also true for the trimetallic species with central d^{10} metal centers.[4,9]

Summary. The EHMO and FHMO calculations establish that a weak, dative, metal–metal interaction exists in these thiolato-bridged heterobimetallics. Generally, for Ti species the interaction is weak and σ bonding in character, although for Zr there is an indication of an additional π component. When the coordination sphere of the late-metal center is trigonal or square planar, these interactions result in a MS_2M' core folding and an *cisoid–endo* conformation of the substituents on the bridging S atoms is adopted. Alternatively, a *transoid–endo* conformation and a planar MS_2M'core are seen when the late-metal center requires a pseudotetrahedral coordination geometry. In any case, the approach of the metal centers is affected by steric factors. The ramifications of such metal–metal interactions on the chemistry of ELHB species is the subject of on-going study.

Acknowledgment. Financial support from NSERC of Canada is gratefully acknowledged. The University of Windsor is thanked for the award of a Research Professorship (D.W.S.).

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(23) Darensbourg, M. Y.; Bischoff, C. J.; Houliston, S. A.; Pala, M.; Reibenspies, J. *J. Am. Chem. Soc.* **1990**, *112*, 6905.

(24) (a) Cameron, T. S.; Prout, K. C.; Rees, G. V.; Green, M. L. H.; Joshi, K. K.; Davies, G. R.; Kilbourn, B. T.; Braterman, P. S.; Wilson, V. A. *J. Chem. Soc., Chem. Commun.* 1971, 14. (b) Davies, G. R.; Kilbourn, B. T. *J. Chem. Soc. D* 1971, 87.

(Trialkylsiloxy)dialkylaluminum Dimers

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Summary: **Trimethylaluminum reacts with cyclic siloxane oligomers or poly(siloxanes) to generate the primary member of a family of dimeric dialkylaluminum trialkylsiloxanes, (trimethylsiloxy)dimethylaluminum, $[Me_2Al(OSiMe_3)]_2$. The X-ray crystal structure of this primary siloxalane has been redetermined with use of modern crystallographic techniques. It crystallizes in the space group *C*2/*m* (No. 12) with unit cell dimensions a = 11.350 (5) Å, b = 13.101 (2) Å, c = 6.918 (4) Å, and β = 111.60 (2)°.**

There has been considerable work demonstrating that alkylaluminum reagents modified by reaction with a wide variety of siloxanes are useful in the preparation of Ziegler–Natta catalysts[1] and catalysts for olefin metathesis.[2] The polymerization catalysts display high activity for ethylene polymerization and high activity and stereospecificity in the polymerization of propene. In one remarkable issue of *Chemical Abstracts Selects*[3] there were

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[‡] Contribution No. 5653.

(1) For good examples of commercial use applications, see: (a) Schmidt, M.; Schmidbaur, H. (Wasag-Chemie AG). U.S. Patent 3,373,178, 1968. (b) Gloriod, P.; Levresse, B.; Machon, J.-P. (Ethylene Plastique). U.S. Patent 3,969,332, 1976. (c) Piekarski, G.; Hundmeyer, A.; Kippe, D.; Maier, S. (Wacker Chemie GmbH). U.S. Patent 3,755,274, 1973. (d) Miyanishi, H.; Shimada, T.; Hayashi, S.; Matsuura, M.; Fujita, T.; Matsui, R.; Kageyama, Y. (Mitsubishi). U.K. Patent Appl. GB 2,057,468, 1980. (e) Machon, J. P.; Hermant, R.; Houzeaux, J. P. *J. Polym. Sci., Polym. Symp.* **1975**, *52*, 107. (f) Hamilton, M. A.; Harbourne, D. A.; Russell, C. G.; Zboril, V. G.; Mulhaupt, R. (Du Pont Canada). EP131,420, 1988.

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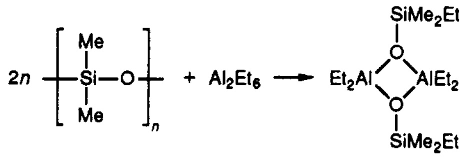
no less than thirteen abstracts of papers and patents citing the use of seven different Si–O compounds in the formulation of polymerization catalysts. Several of these involve the formation of Al–O–Si linkages through reactions of alkylaluminum compounds with polysiloxanes or cyclic siloxane oligomers.[4]

In the course of his studies to better understand the reaction of alkylaluminum compounds with silicone grease, Barron discovered a synthesis of siloxalanes[5] similar to that which was being practiced commercially. A similar reaction has been reported to be a convenient and safe method for deactivation of alkyllithium compounds prior to disposal.[6] The commercial process for the preparation of these compounds generally involves direct reaction of neat alkylaluminums with neat, polymeric siloxanes.[7-9] The least expensive and most widely used siloxalane is (ethyldimethylsiloxy)diethylaluminum, which is prepared by reaction 1. This material is available commercially



(1)

from both Ethyl Corp. and Sherex (Schering AG) as a viscous liquid, or it can be prepared conveniently as needed in a small, plug-flow reactor in line with the polymerization unit. The reaction can also be carried out with trimethylaluminum rather than triethylaluminum, but the product is a waxy, white crystalline compound unsuitable for most olefin polymerization processes. We have determined the structure of the crystalline permethyl compound using modern diffractometer techniques. The synthesis and structure are reported here.

Experimental Section

General Procedures. All solvents were purified and dried by standard techniques.[10] Alkylaluminums were used as received from Texas Alkyls. Siloxanes were obtained from Aldrich and Petrarch and were used as received. All glassware used in synthetic work was either flame- or oven-dried. NMR spectra were recorded in toluene-d_8 on NT Series GE spectrometers at 300- or 360-MHz proton frequencies. Chemical shifts (ppm) were referenced to residual protic solvent peaks or internal TMS. Spectra were recorded in standard pulsed FT mode at constant temperature, which was calibrated with a precalibrated thermocouple. Infrared spectra were recorded on a Perkin-Elmer Model 983G optical null spectrophotometer using an O-ring-sealed IR cell and standard salt plates. Spectra were run either as neat liquid samples or as Nujol mulls as appropriate. Elemental analyses and vapor pressure osmometry molecular weight determinations were performed by Galbraith Laboratories, Knoxville, TN. Mass spectra were determined on a VG 70-SE mass spectrometer using electron impact and a probe temperature rising at 50 °C/min.

Synthesis of $[Et_2Al(OSiMe_2Et)]_2$. Octamethyltetrasiloxane (7.42 g, 25 mmol) and triethylaluminum (11.42 g, 100 mmol) were mixed in an air-heated quartz Fisher–Porter tube equipped with an internal thermocouple for temperature control. There was a slight exotherm upon mixing. The mixture was then heated to 180 °C for a period of 24 h. There was a slight pressure buildup. Upon cooling, the contents of the tube were found to be the desired dimer; no impurities were detected by any of the analytical techniques used. This material is a viscous oil.

Warning: One reviewer has pointed out that high temperatures are required to initiate the reaction but that the heat generated from this exothermic reaction can lead to a runaway reaction if larger quantities of reagents are used without adequate heat-transfer surface. Addition of alkylaluminums to preheated polysiloxane reduces this problem.

Warning: Alkylaluminum compounds react with a number of elastomeric materials used in O-rings and this can lead to leaks and resulting fires as pressure develops in the apparatus. Kalrez is a preferred material. It is also obvious from this work that silicone rubbers and greases are to be avoided.

When the reaction was repeated with low molecular weight trimethylsilyl end-capped dimethylsiloxane polymers, the isolated products were of sufficient purity for use as activators in Ziegler–Natta catalysts for olefin polymerization, but NMR signals resulting from the trimethylsilyl polymer end caps and other unknown impurities could be detected. ^{1}H NMR: CH_3CSi, 1.23 (t, 8 Hz, 6 H); CH_3CAl, 0.86 (t, 8 Hz, 3 H); CCH_2Al, 0.64 (q, 8 Hz, 2 H); CH_3Si, 0.16 (s, 6 H); CCH_2Al, 0.10 (q, 8 Hz, 4 H). ^{13}C NMR: CH_3CSi, 9.93 (1); CH_3CAl, 9.16 (2); CCH_2Si, 6.91 (1); CCH_2Al, 1.8 (br, 2); Me, −0.68 (2). ^{29}Si NMR: 20.45 (s). IR (neat, cm^{-1}, intensity): 1409, w; 1258, m; 1197, w; 1075, w; 993, w; 960, w; 904, w; 830, s; 797, s; 711, w; 651, m; 634, m; 606, m. Anal. Calcd for $(C_8H_{21}AlSiO)_2$: C, 51.02; H, 11.24. Found: C, 51.2; H, 11.2. MW (C_6H_6 dimer: calcd, 376.6; found, 380. Mp: viscous liquid. None observed. Attempts to obtain subambient melting points were unsuccessful, presumably because the material formed a glassy phase. MS: m/z 347 ($M^+ - C_2H_5$); characteristic pattern of decreasing intensities at 319, 291, and 263 (additional loss of 1, 2, and 3 C_2H_4).

Synthesis of $[Me_2Al(OSiMe_3)]_2$. Octamethyltetrasiloxane (7.42 g, 25 mmol) and trimethylaluminum (7.21 g, 100 mmol) were mixed in a quartz Fisher–Porter tube. There was a slight exotherm upon mixing. The mixture was then heated to 180 °C for a period of 24 h. The resulting pressure was 28 psig. Upon cooling, the contents of the tube crystallized to a waxy solid. Yield was almost quantitative. This solid is readily purified by vacuum distillation (78 °C (10 mmHg)), recrystallization from cold pentane, or vacuum sublimation. Final yield was 90% due to mechanical losses. ^{1}H NMR: CH_3Si, 0.1 (s, 9 H); CH_3Al, −0.67 (s, 6 H). ^{13}C NMR: CH_3Si, 1.75 (3 C); CH_3Al, −7.8 (br, 2 C). ^{29}Si NMR: 19.0. IR (Nujol, (cm^{-1}, intensity): 1412, w; 1378, w; 1323, w; 1225, s; 1196, s; 1093, m; 1056, w; 910, sh; 849, s; 825, s; 761, s; 696, m; 604, s; 544, m; 408, m; 361, s. Anal. Calcd for $(C_5H_{15}AlSiO)_2$: C, 41.06; H, 10.34. Found: C, 41.3; H, 10.2. MW (C_6H_6) dimer: calcd, 292.5; found, 290. Mp: 45 °C. MS: m/z 277 ($M^+ - CH_3$).

The reaction was repeated with linear, higher molecular weight trimethylsilyl-end-capped polysiloxanes. There was little difference in the outcome of the reaction. When the polysiloxanes were of sufficiently low molecular weight to see the end caps by NMR prior to reaction, several additional resonances of unknown origin could be detected by NMR in the crude reaction mixtures. These species had no effect on subsequent Ziegler–Natta polymerizations.

Attempted Exchange of Alkylsiloxalanes. Equimolar quantities of $[Me_2Al(OSiMe_3)]_2$ and $[Et_2Al(OSiMe_2Et)]_2$ were mixed in a toluene solution, and the resultant mixture was heated to reflux. The mixture was then cooled to room temperature with no apparent change. NMR was indistinguishable from that of an unheated 1:1 mixture of $[Me_2Al(OSiMe_3)]_2$ and $[Et_2Al(OSiMe_2Et)]_2$. The mass spectrum showed peaks attributable to $[Me_2Al(OSiMe_3)]_2$ (m/z 277) and $[Et_2Al(OSiMe_2Et)]_2$ (characteristic m/z 347, 319, 291, and 263), but there were no additional peaks attributable to mixed products. Identical results were obtained when a mixture of the two neat components was heated to 150 °C for 24 h.

Synthesis of (Mixed alkyl)siloxalanes. Octamethyltetrasiloxane (7.42 g, 25 mmol), triethylaluminum (5.71 g, 50

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(2) Slaugh, L. H.; Johnson, T. H.; Hoxmeier, R. J. (Shell). U.S. Patent 4,925,822, 1990.

(3) Catalysis (Applied and Physical Aspects). *CA Selects* 1987, *23* (Nov. 16); *Chem. Abstr.* 1987, *107*, 176530q–177155h.

(4) For leading references on heterosiloxanes, see: (a) Schmidbaur, H. *Angew. Chem, Int. Ed. Engl.* 1965, *4*, 201. (b) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: New York; 1972.

(5) Apblett, A. W., Barron, A. R. *Organometallics* 1990, *9*, 2137.

(6) Suzuki, T. *C&EN* 1991, *Feb. 11*, 2.

(7) Jenkner, H. Z. *Naturforsch.* 1959, *146*, 133.

(8) Aishima, I.; Sakurai, H.; Takashi, Y.; Monita, H.; Hirotsu, Y.; Hamada, T. U.S. Patent 3,661,878, 1972.

(9) Russell, C. G. (Du Pont Canada). U.S. Patent 4,612,382, 1986.

(10) Shriver, D. F. *The Manipulation of Air-sensitive Compounds*; McGraw-Hill: New York; 1969.

mmol), and trimethylaluminum (3.61 g; 50 mmol) were mixed in a quartz Fisher–Porter tube. There was a slight exotherm upon mixing. The mixture was then heated to 180 °C for a period of 24 h. The contents of the tube were cooled, resulting in a clear liquid. The NMR was virtually indistinguishable from a 1:1 mixture of $[Me_2Al(OSiMe_3)]_2$ and $[Et_2Al(OSiMe_2Et)]_2$. The mass spectrum showed peaks attributable to $[Me_2Al(OSiMe_3)]_2$ (m/z 277) and $[Et_2Al(OSiMe_2Et)]_2$ (characteristic decreasing m/z 347, 319, 291, and 263) and, in addition, peaks attributable to the five intermediate alkyl combinations (m/z 277, 291, 305, 319, 333, 347). The lighter components volatilized first, and it was possible to distinguish clearly between base peaks and subsequent fragmentation of higher ions by observing spectra as a function of increasing probe temperature.

Crystal Structure Determination. Solution of the structure of $[Me_2Al(OSiMe_3)]_2$ by direct methods (MULTAN) was complicated by a disorder. The asymmetric unit consists of one-fourth of the molecule lying on the $2/m$ site. It is canted with respect to the mirror, yielding two superimposed images. The refinement model is sensitive even to the presence of the disordered methyl hydrogen atoms, suggesting a static averaging as opposed to a thermal smearing of the atoms. Hydrogen atoms were idealized with C–H = 0.95 Å. The refinement was full-matrix least squares on F; scattering factors[11] included anomalous terms for Si and Al. Weighting was proportional to $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. All nonhydrogen atoms were refined anisotropically.

Results and Discussion

Synthetic Studies. The compounds $[R_2Al(OSiR'_2R)]_2$ are readily prepared from the reaction of alkylaluminum compounds, AlR_3, with polysiloxanes, $(-SiR'_2O-)_x$. Syntheses have generally been carried out in solution, but the reaction is greatly accelerated if it is carried out with neat reactants. Reaction of neat $(Me_2SiO)_4$ with neat $(AlEt_3)_2$ yields neat $[Et_2Al(OSiMe_2Et)]_2$. The insertion reaction is clean enough that the product needs no further purification for most applications.

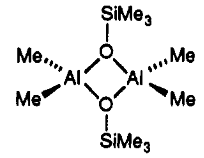
This approach is general because in most cases the reactants are liquids. Many of the products are low-melting solids or viscous liquids due to the mixed alkyls on the silyl groups. It is therefore often convenient to avoid the use of a solvent. It is even possible to prepare these materials in a continuous, pipeline reactor, feeding them directly into the end-use application. This is, in fact, the preferred method of preparation if large quantities are to be required. If the reaction were carried out in a solvent, much longer times and a solvent removal step would be required.

$[Me_2Al(OSiMe_3)]_2$ can be prepared in a similar manner and is isolated as a crystalline solid. It is easily purified by vacuum sublimation or distillation (78 °C (10 mmHg)) or by recrystallization from toluene. Other more symmetrical analogues such as $[Et_2Al(OSiMe_3)]_2$ or $[Me_2Al(OSiPh_3)]_2$, which are prepared by reaction of alkylaluminum halides with sodium siloxides, are also crystalline solids, but $[Me_2Al(OSiEt_3)]_2$ is a liquid at room temperature and $[Et_2Al(OSiEt_3)]_2$ melts at 26–7 °C.[12] The bis(siloxide) $[MeAl(OSiMe_3)_2]_2$ can be prepared by reaction of sodium trimethylsiloxide with methylaluminum dichloride.[13]

The dimeric nature of $[Me_2Al(OSiMe_3)]_2$ in solution is indicated by molecular weight measurements.[14] In the solid state, the compound is isostructural with $[Me_2AlOCMe_3]_2$[4a,15] and $[Me_2AlOGeMe_3]_2$,[16] and the X-ray diffraction pattern is very similar to that of $[Me_2SiNSiMe_3]_2$.[17] For these reasons, the structure was assigned as the oxygen-bridged dimer, 1. By analogy, the other mixed-alkyl products are presumed to be dimerized through oxygen bridges.

Table I. Summary of X-ray Diffraction Data for $[Me_2Al(OSiMe_3)]_2$

formula	$Si_2Al_2O_2C_{10}H_{30}$
fw	292.49
space group	$C2/m$ (No. 12)
a, Å	11.350 (5)
b, Å	13.101 (2)
c, Å	6.918 (4)
β, deg	111.60 (2)
V, Å^3	956.4
Z	2
D(calcd), g cm^{-3}	1.015
cryst dimens, mm	0.37 × 0.13 × 0.47
temp, °C	–70
radiation	Mo Kα (0.71069 Å, graphite monochrometer)
λ, cm^{-1}	2.61
diffractometer	Enraf-Nonius CAD4
2θ limits, deg	5–48
max hkl	12,14,7 (+++,–++)
ω scan, deg	1.30–1.90 at 1.7–5.0°/min
no. of unique observns	886
absorption	DIFABS, transmissn 0.70–2.31
no. of data, $I > 3\sigma(I)$	501
final no. of variables	307
final residual (e Å^{-3})	0.28 (near Si)
R	0.059
R_w	0.057



1

Mixtures of mixed-alkyl dimers are readily prepared by mixing alkylaluminums prior to reaction with the siloxane. Thus, all components of the distribution $Al_2Si_2O_2Me_{10-x}Et_x$ (x = 0–6) were observed when trimethylaluminum and triethylaluminum were reacted simultaneously with octamethyltetrasiloxane. This is not readily detected by NMR because the shifts of the various peaks are relatively insensitive to the substitution located three atoms away. Mass spectroscopy provides clear characterization of the mixture. The two extreme compounds (x = 0, 6) have very characteristic mass spectra. Mixtures of these two compounds display the two characteristic spectra. A mixture of all components prepared by mixed synthesis is clearly different, displaying peaks for each of the intermediate species. The different volatilities of the various components mean that they will appear at different times as the temperature of the MS probe is increased with time.

Having developed a technique for differentiating between the various homologues, it was of interest to investigate the scrambling of trialkylsiloxy groups. Heating a mixture of $[Et_2Al(OSiMe_2Et)]_2$ and $[Me_2Al(OSiMe_3)]_2$ produced no evidence of scrambling whether it was done in refluxing toluene solution or in neat mixtures at 150 °C.

Discussion of the Structure. We undertook a full structural analysis of $[Me_2Al(OSiMe_3)]_2$ employing modern

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(11) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K.; 1974; Vol. IV.

(12) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam: 1972; p 222.

(13) Schmidbaur, H.; Armer, B.; Bergfeld, M. *Z. Chem.* **1968**, *8*, 254.

(14) Schmidbaur, H. *J. Organomet. Chem.* **1963**, *1*, 28.

(15) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 201.

(16) Armer, B.; Schmidbaur, H. *Chem. Ber.* **1967**, *100*, 1521.

(17) Wheatley, P. J. *J. Chem. Soc.* **1962**, 1721; **1963**, 2562.

Table II. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for Non-Hydrogen Atoms in $[Me_2Al(OSiMe_3)]_2$

atom	x	y	z	B_{iso}, Å^2
Si(1)	2362 (2)	5000	2234 (3)	3.0 (1)
Al(1)	5114 (3)	5990 (2)	4426 (4)	3.0 (1)
O(1)	3907 (3)	5000	3738 (5)	2.6 (1)
C(1)	1453 (8)	4698 (11)	3904 (14)	5.9 (6)
C(2)	1967 (16)	3707 (14)	1081 (20)	5.1 (5)
C(3)	2110 (17)	4004 (12)	209 (21)	5.2 (5)
C(4)	4590 (10)	7113 (8)	5735 (16)	5.1 (4)
C(5)	5763 (9)	6293 (8)	2247 (15)	5.2 (4)

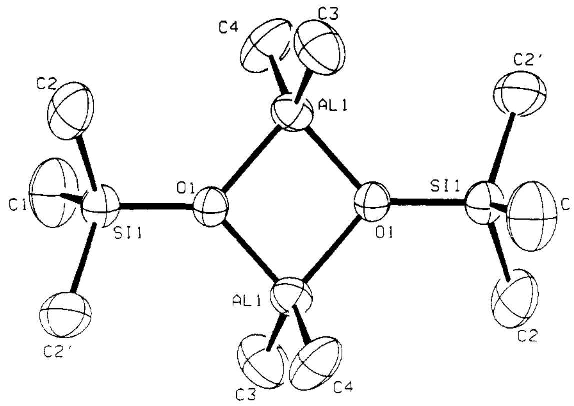


Figure 1. Perspective view of $[Me_2Al(OSiMe_3)]_2$ with atom-labeling scheme. Thermal ellipsoids are drawn at the 40% level, and hydrogen atoms are omitted for clarity.

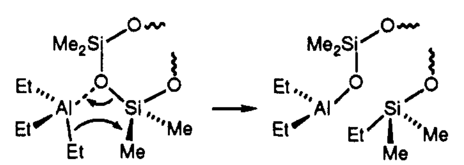
diffractometer techniques because of the commercial importance of this class of compounds and the crystallinity of this particular homologue.[18] A summary of crystallographic details is presented in Table I, and results of the crystal structure determination are presented in Table II. The space group for the structure is *C*2/*m* as opposed to *P*2$_1$/*n* chosen for the earlier structure. As a result of the disorder, there are two images of the molecule. The results of the structural determination (excluding hydrogen atoms) and a table of important bond distances and angles given in the supplementary materials. The structure and atom-labeling scheme are depicted in Figure 1.

The structure consists of discrete, dimeric units with tetrahedral, four-coordinate aluminum centers and the expected planar Al_2O_2 ring system as the inner core of atoms. The planes defined by the aluminum atoms and their pendant methyl groups are perpendicular to the AlO_2 planes. All distances are within previously reported ranges and correspond very closely to those reported for the phenyl analogue.[4] The two silicon atoms are essentially coplanar with the inner ring, and the plane defined by the silicon methyl groups is essentially perpendicular to the inner core, minimizing steric interactions with the aluminum methyl groups. The Al–O distances (1.868 (4), 1.818 (4) Å) are in the middle of the normally accepted range of 1.7–2.0 Å,[19] as are the observed Al–C (1.933 (10), 1.947 (10) Å) distances (compare 1.90–2.01 Å).[20] The Si–O bond lengths (1.677 (4) Å) are not significantly different from those reported for alkoxysilanes and disiloxanes.[21]

Conclusions

The utility of oxygen-functionalized alkylaluminum compounds as activators in Ziegler–Natta-catalyzed olefin polymerization has been discussed elsewhere.[22] It is presumed that the catalyst is less likely to be overreduced to inactive $TiCl_2$ species when the reduction potential of the alkylaluminum promoter has been lowered by oxygen coordination. It is this phenomenon that drives the polyolefin industry to include alkoxy and siloxy species in their formulations, but to date, this has often been done with little regard for the actual chemistry going on.

The reaction of alkylaluminum compounds with polysiloxanes results in cleavage of the Si–O bond with alkylation at silicon and formation of an Al–O bond. The reaction presumably starts with coordination of aluminum to siloxane oxygen atoms,[4,5,23] bringing the alkylaluminum in close initial contact with the Si–O bond. Consecutive metatheses of the type shown in eq 2 ultimately generate the desired product. The alkyl group and the dialkylaluminum from any given trialkylaluminum molecule end up in different siloxalane molecules as demonstrated in the mixed-alkyl experiments and by earlier work.[7] The resulting dimeric species is remarkably stable as indicated by its distillation as a dimer and inertness to exchange as indicated by the lack of exchange of siloxy groups from one aluminum to the next through the bridged structure.



(2)

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Supplementary Material Available: Listings of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, hydrogen atom parameters, bond distances and angles, and symmetry operation codes and a perspective view of $[Me_2Al(OSiMe_3)]_2$ (6 pages); a table of calculated and observed structure factors (2 pages). Ordering information is given on any current masthead page. Inquiries may also be directed to the indicated author.

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[18] The original assignment of the structure of $[Me_2Al(OSiMe_3)]_2$ was made on the basis of the similarity of the film data to the previously determined structure of $[Me_2SiNSiMe_3]_2$.[17] We find that the space group was incorrectly assigned.

(19) (a) Zaworotko, M. J.; Rogers, R. D.; Atwood, J. L. *Organometallics* **1982**, *1*, 1179. (b) Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 302.

(20) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Eds.; Pergamon Press: Oxford, U.K., 1986; Vol. 1, Chapter 6.

(21) (a) Almenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M. *Acta Chem. Scand.* **1963**, *17*, 2455. (b) Airey, W.; Glidewell, C.; Rankin, D. W. H.; Robiette, A. G.; Sheldrick, G. M.; Cruickshank, D. W. J. *Trans. Faraday. Soc.* **1970**, *66*, 551. (c) Airey, W.; Glidewell, C.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1971**, *8*, 413. (d) Morosin, B.; Harrah, L. A. *Acta Crystallogr., Sect B* **1981**, *37*, 579. (e) Healy, M. D.; Barron, A. R. *J. Organomet. Chem.* **1990**, *381*, 165.

(22) Goodall, B. L. *J. Chem. Educ.* **1986**, *63*, 191.

(23) Vahasarja, E.; Pakkanen, T. T.; Pakkanen, T. A.; Iiskola, E.; Sormunen, P. *J. Polym. Sci., Polym. Chem.* **1987**, *25*, 3241.