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Tris-Triphenylsiloxy Compounds of Aluminium

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Tris-Triphenylsiloxy Compounds of Aluminium[†]

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The reaction of $AlMe_3$ with three equivalents of $HOSiPh_3$ in THF results in the formation of the solvent complex $Al(OSiPh_3)_3(THF)$ (1). Hydrolysis of 1 yields the stable water complex $Al(OSiPh_3)_3(H_2O)(THF)_2$ (2) in which the THF molecules are hydrogen bonded to the coordinated water ligand. Compounds 1 and 2 have been fully characterized by ^1H, ^{13}C, ^{17}O, ^{27}Al and ^{29}Si NMR and IR spectroscopy. In addition, variable temperature ^1H NMR of 2 has been employed to investigate the steric interactions between the phenyl rings of adjacent siloxide ligands. The molecular structures of the solvates 1.(THF) and 2.(THF)$_{1.25}$ have been determined by X-ray crystallography. 1.(THF): Monoclinic $P2_1/c$, $a = 10.03$ (1), $b = 23.758$ (6), $c = 23.294$ (7) Å, $\beta = 101.13$ (6)°, Z = 4, R = 0.084, R_w = 0.094. 2.(THF)$_{1.25}$: Cubic $Pa\bar{3}$, $a = 23.034$ (3) Å, Z = 4, R = 0.093, R_w = 0.099.

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[†] Dedicated to the memory of Tom Birchall, for his many contributions to main group inorganic chemistry.

Introduction

Recent work in our laboratory has been concerned with the synthesis and structural characterization of siloxy-substituted alumoxanes (1,2,3). While alumoxanes is a term applied to organically-substituted aluminium oxygen macromolecules in general, we have determined that siloxy-substituted derivatives all have the empirical formula $[Al(O)_x(OH)_y(OSiR_3)_z]_n$ where $2x + y + z = 3$ (3). These materials were first synthesized in 1958 by Andrianov $et.\ al.$, via the hydrolysis of trisiloxy compounds of aluminium (Equation 1) (4).

$$Al(OSiR_3)_3 \xrightarrow[- HOSiR_3]{+ H_2O} [Al(O)_x(OH)_y(OSiR_3)_y]_n \qquad [1]$$
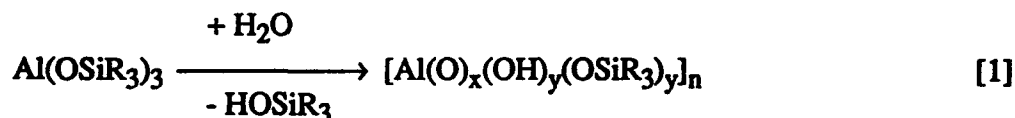
Since there are only a limited number of stable trialkylsilanols commercially available for use as precursors to these aluminium tri-siloxides, we have developed an alternative route to siloxy-alumoxanes based on the hydrolysis of dimeric dimethylaluminium mono-siloxides (2), (Equation 2), which are readily prepared from polydiorganosiloxides (Equation 3) (5).

$$n\ [AlMe_2(OSiR_3)]_2 \xrightarrow[\substack{-MeH \\ -HOSiR_3}]{+H_2O} \frac{n}{2}\ [\ Al(O)_x(OH)_y(OSiR_3)_z]_n \qquad [2]$$

$$n\ AlMe_3\ +\ (R_2SiO)_n \xrightarrow{\Delta} \frac{n}{2}\ [AlMe_2(OSiR_2Me)]_2 \qquad [3]$$
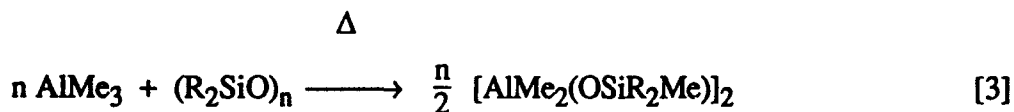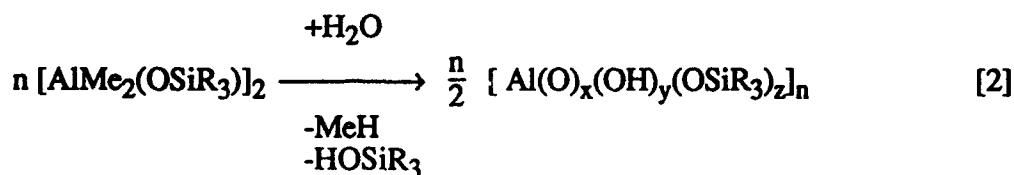
While both of the routes outlined in equations 1 and 2 lead to high molecular weight siloxy-alumoxanes, we have been unable to isolate any of the proposed intermediates in the

hydrolysis reactions; for example low molecularity species containing either coordinated water or terminal hydroxide groups (Equation 4).

$$Al(OSiR_3)_3 \xrightarrow{+H_2O} Al(OSiR_3)_3(H_2O) \xrightarrow[-HOSiR_3]{\Delta} [Al(OH)(OSiR_3)_2]_x \qquad [4]$$
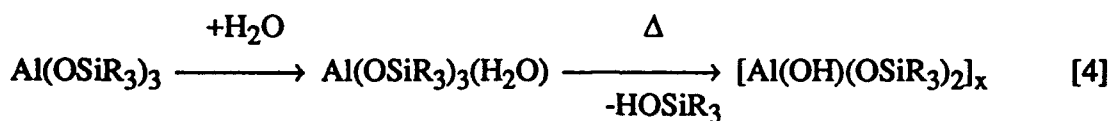
In an effort to isolate such species we have investigated the hydrolysis of the aluminium siloxide compound derived from the sterically bulky triphenyl silanol, $HOSiPh_3$. The rationale for the choice of this ligand is based on the concept that sterically demanding ligands preclude oligomerization, and thus in the present case the condensation reaction which leads to alumoxane formation is prevented.

Experimental

General

Elemental analyses were performed by Oneida Research Services, Whitesborough, NY. Melting points and thermogravometric analyses were obtained on a Seiko 200 TG/DTA instrument. IR spectra (4000-400 cm^{-1}) were recorded on a Nicolet DX-5 FTIR as Nujol or Fluorolube mulls on KBr plates. ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-500 spectrometer, and chemical shifts are reported relative to $SiMe_4$ in C_6D_6 unless otherwise stated. ^1H-^1H COSY NMR spectra were collected by use of a standard pulse sequence (6, 7) with 45° mixing pulse, a 1-2 second relaxation delay, and a resolution of *ca.* 4 Hz per point. The FID's were not weighted before Fourier transformation, and the spectral matrix was symmetrized about the diagonal. ^1H-^{13}C correlated 2D NMR spectra were obtained using a standard pulse sequence (8), a spectrum width of 250 Hz and 300 Hz, and 1000 and 256 data points in the F2 (^{13}C) and F1 (^1H) domains, respectively. The latter domain was zero filled to 512K and Lorentzian line-broadening functions equal to the digital resolution (*ca.* 4 Hz) were applied to each axis.

^{17}O, ^{27}Al and ^{29}Si NMR spectra (see Table I) were recorded on a Bruker WM-300 spectrometer and chemical shifts were reported versus H_2O, $[Al(H_2O)_6]^{3+}$ and $SiMe_4(CDCl_3)$, respectively.

AlMe$_3$ as a 2M solution in hexane (Aldrich), HOSiPh$_3$ (Huls) and ClSiPh$_3$ (Aldrich) were commercial samples and were used without further purification. Unless otherwise stated all manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried, distilled and degassed before use. Water was doubly distilled and deionized.

Al(OSiPh$_3$)$_3$(THF) .(1):

A solution of AlMe$_3$ (10.6 mL, 2 M solution in hexane, 21.2 mmol) in THF (50 mL) was added dropwise to a stirred solution of HOSiPh$_3$ (17.53 g, 63.4 mmol) in THF (50 mL) at 0°C. After 12 hours all gas evolution had ceased and the volatiles were removed in vacuo, 50°C, to afford a powdery white solid in quantitative yield (21.06 g, 99.9%). Crystals of 1.(THF) suitable for X-ray structural analysis were obtained by cooling a solution of 40 g of the crude material in 30 mL.THF to -25°C. mp 353°C (dec. without melting). Anal. Calcd. for C$_{62}$H$_{61}$AlO$_5$Si$_3$: C, 74.66; H, 6.16. Found: C, 74.60; H, 5.99. IR (Fluorolube and Nujol, cm^{-1}) 3182 (w), 3083 (w), 3064 (m), 3047 (m), 3020 (w), 3010 (w), 2975 (s), 2876 (s), 1588 (w), 1566 (vw), 1428 (s), 1304 (w), 1261 (m), 1187 (w), 1114 (vs), 1070 (vs), 1025 (w), 999 (m), 918 (w), 871 (m), 787 (s), 765 (w), 743 (s), 709 (vs), 701 (vs), 501 (vs), 484 (w), 475 (w), 433 (m). NMR (CDCl$_3$) ^{1}H 7.55 [18H, d, J(H-H) = 6.7 Hz, o-C$\underline{H}$], 7.32 [9H, t, J(H-H) = 7.5 p-C$\underline{H}$] 7.17 [18H, dd, J(H-H) = 6.7 Hz, J(H-H) = 7.5 Hz, m-C$\underline{H}$], 3.76 [4H, t, J(H-H) = 6.7 Hz, OC$\underline{H}_2$], 1.52 [4H, t, J(H-H) = 6.7 Hz, OCH$_2$C$\underline{H}_2$]. ^{13}C 138.4 (Si-$\underline{C}$), 135.0 (o-$\underline{C}$H), 128.9 (p-$\underline{C}$H), 127.5 (m-$\underline{C}$H), 70.5 (O$\underline{C}$H$_2$), 25.1 (OCH$_2$$\underline{C}H_2$).

Al(OSiPh₃)₃(H₂O)(THF)₂ (2):

Degassed water (100 mg, 0.56 mmol) was added to a solution of **1** (5.0 g, 5.01 mmol) in THF (30 mL). The solution was swirled momentarily to mix the reagents. Upon sitting, the solution gradually deposited large, colorless cube-shaped crystals. After 12 hours the solution was decanted and the crystals were dried in vacuo. A further crop of crystals of $2 \cdot (THF)_{1.25}$ were obtained upon cooling the mother liquor to -30°C. Drying the crystals (50°C) resulted in the removal of excess solvated THF and the formation of pure **2**. Yield: 5.02 g, 98%. mp 182°C (dec.) Anal Calcd. for $C_{62}H_{63}AlO_6Si_3$: C, 73.34; H, 6.25. Found: C, 73.42; H, 6.28. IR (Fluorolube and Nujol, cm^{-1}) 3659 (br s, ν O-H), 3071 (m), 3046 (m), 2948 (m), 2926 (s), 2858 (s), 1582 (w), 1478 (m), 1451 (m), 1412 (vs), 1304 (m), 1262 (m), 1186 (m), 1113 (vs), 1071 (vs), 1026 (s), 997 (s), 916 (w), 882 (m), 743 (s), 708 (vs), 644 (m), 606 (m), 517 (vs). NMR (CDCl₃) ¹H 7.72 [6H, d, J(H-H) = 6.7 Hz, *o*-C$\underline{H}$], 7.65* [12H, d, J(H-H) = 6.8 Hz, *o*-C$\underline{H}$], 7.48 [3H, t, J(H-H) = 7.3 Hz, *p*-C$\underline{H}$], 7.43 [6H, t, J(H-H) = 7.4 Hz, *p*-C$\underline{H}$], 7.36* [6H, dd, J(H-H) = 7.5 Hz, *m*-C$\underline{H}$], 7.19* [12H, dd, J(H-H) = 7.6 Hz, *m*-C$\underline{H}$], 3.86 (2H, s, O$\underline{H}_2$), 3.74 [8H, t, J(H-H) = 6.5 Hz, OC$\underline{H}_2$] 1.80 [8H, t, J(H-H) = 6.5 Hz, OCH₂C$\underline{H}_2$], ¹³C 138.6*, 135.5 (Si-$\underline{C}$), 135.0*, 134.9 (*o*-$\underline{C}$H), 129.9, 128.8* (*p*-$\underline{C}$H), 127.8, 127.4* (*m*-$\underline{C}$H), 68.3 (O$\underline{C}$H₂), 25.4 (OCH₂$\underline{C}$H₂).

Preparation of H¹⁷OSiPh₃:

Water (0.54 g, 40 mmol) enriched in ¹⁷O (22.3 %) was added dropwise via syringe to a stirred solution of ClSiPh₃ (11.79 g, 40 mmol) in THF (20 mL). After 8 hours, the volatiles were stripped off, in vacuo, to yield a pale-yellow solid. Crystallization from 50 mL of 50:50 ether: pentane, at -25°C, yielded colorless crystals. isolated yield: 10.17 g, 92%.

Crystallography.

A crystal data summary is given in Table II, fractional atomic coordinates for **1** and **2** are listed in Tables III and IV respectively. X-ray data was collected on a Nicolet R3m/V four-circle diffractometer equipped with a LT-1 low temperature device. Crystal of **1** and **3** were mounted directly onto the goniometer with silicon grease. Unit-cell parameters and intensity data were obtained by following previously detailed procedures, using a Nicolet R3m/V diffractometer operating in the θ-2θ scan mode. Data collection was controlled by using the Nicolet P3 program (9).

The structure of **1.**(THF) was solved using the direct methods program XS (10), which revealed the position of most of the heavy atoms. Standard difference map techniques were used to find the remaining non-hydrogen atoms. The crystallographic identification of the oxygen atom in the uncoordinated THF molecule was assigned on the basis of the atom thermal parameters. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed some but not all of the hydrogen atoms. Hydrogens were, therefore, included as fixed atom contributors in the final cycle, d(C-H) = 0.96 Å, U_{eq} = 0.08 Å^3. Refinement was performed to convergence (Δ/δ (max) < 0.001) with this model. The weighting scheme was w = $[\sigma^2 (|F_o|) + 0.0274 (|F|)^2]^{-1}$.

The structure of **2.**(THF)$_{1.25}$ was solved by direct methods (XS), which revealed the position of the Al, O and Si atoms. The atoms Al(1) and O(2) lie on a three-fold rotation axis at x, y, z, where x = y = z; thus their site-occupancy-factors were fixed at $^1/_3$, and their positions were allowed to freely refine along the three-fold rotation axis. Standard difference map techniques were used to find the remaining non-hydrogen atoms, including the presence of a THF molecule, the site occupancy of which was freely refined to a value of 0.99, and was, therefore, fixed at 1.0 in the final refinement. After all the non-hydrogen atoms were located and refined anisotropically, a difference map revealed some but not all of the hydrogen atoms. Hydrogens were therefore included as fixed atom contributors in the final cycle, d(C-H) = 0.96 Å, U_{eq} = 0.08 Å^3. Since the bound H_2O ligand can only be

hydrogen-bonded to two of the three symmetry-related THF molecules, it is therefore probably disordered, and the site occupancy factor for H(2B) was therefore set at $^2/_3$. After the $Al(OSiPh_3)_3(H_2O)(THF)_3$ unit was refined a peak of significant electron density remained, which generated a highly distorted six-membered ring by symmetry. Based on NMR and TGA data it is likely this is a disordered THF molecule. Refinement of this peak as oxygen (site occupancy $^1/_6$) and carbon (site occupancy $^4/_6$ with no hydrogens) led to convergence of the entire structure (Δ/δ (max) < 0.001) and a significant lowering of the R factor. The weighting scheme was $w = [\sigma^2 (|F_o|) + 0.0124 (|F|)^2]$.

Although both structures refined to a satisfactory level the weighted R factor in each case remained high. However, since the bond length and angle e.s.d.'s are acceptable and atom connectivity is entirely consistent with analytical and NMR spectral characterization the solutions are adequate and undoubtedly correct.

Results and Discussion

The interaction of three equivalents of triphenylsilanol with trimethylaluminium in THF results in the formation of the solvated tri-siloxide complex, $Al(OSiPh_3)(THF)$,1, with the concomitant liberation of methane (Equation 5).

$$AlMe_3(THF) + 3\ HOSiPh_3 \xrightarrow[\text{THF}]{} \underset{(1)}{Al(OSiPh_3)_3(THF)} + 3\ MeH \qquad [5]$$

Hydrolysis of a THF solution of 1 does not result in the hydrolytic cleavage of the aluminium-siloxide bonds and the formation of an alumoxane, as is observed for the triethylsiloxide analogue (3), but instead allows for the isolation of the water complex, $Al(OSiPh_3)_3(H_2O)(THF)_2$, 2, (Equation 6).

$$Al(OSiPh_3)_3(THF) \xrightarrow[\text{THF}]{+H_2O} Al(OSiPh_3)_3(H_2O)(THF)_2 \qquad [6]$$

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The molecular structure of the THF solvates **1**.(THF) and **2**.(THF)$_{.25}$ have been determined by X-ray crystallography and are shown in Figures 1 and 2 respectively. Selected bond lengths and angles are given in Tables V and VI.

The structure of **1**.(THF) consists of a discrete monomeric $Al(OSiPh_3)_3(THF)$ units with a second THF present in the crystal lattice as a molecule of solvation, this uncomplexed THF is, however, only removed from the crystal lattice at elevated temperatures, $>50°C$. The structure of **2**.(THF)$_{1.25}$ consists of an $Al(OSiPh_3)_3(H_2O)$ unit situated on a three-fold rotation axis. There are three symmetry related THF molecules suitably positioned for hydrogen bonding to the coordinated water molecule. Since the site occupancy of these THF molecules is unity but only two can be hydrogen bonded to the H_2O at the same time, the H_2O hydrogens must be disordered over the three symmetry related sites, and the presence of three, rather than two, THF molecules is a function of the crystal packing. Thus the structure is best considered as consisting of **2** with a molecule of THF present in the crystal lattice. In addition to the three THF situated around the water the electron density map and crystal cell packing indicate the presence of a severely disordered THF molecule in the center of the unit cell. Thus, 3 and $^1/_4$ THF's are required per aluminium. The thermogravometric analysis of a freshly crystallized sample of **2** indicates the loss of slightly more than three equivalents of THF per aluminium consistent with the presence of a further molecule of solvation. Therefore, a highly disordered THF molecule was included in the final refinement (see Experimental). The excess THF molecules are removed on prolonged drying in vacuo leaving the two molecules hydrogen-bonded to the coordinated water molecule. Although these hydrogen bonded THF molecules are, intern, removed upon high temperature thermolysis of **2**, the water ligand remains complexed.

As is commonly observed for four-coordinate Lewis acid base complexes of aluminium (11, 12) the geometry around each aluminium is distorted from tetrahedral, with the angles associated with the THF (**1**) and H_2O (**2**) ligands being the most acute. The similarity in aluminium coordination geometries in these compounds is illustrated by

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comparing the sums of interligand angles associated with the siloxide ligands [342.5(2)°
(1), 343.2(2)° (2)]. This similarity is perhaps unsurprising since we have previously
observed that the geometry around aluminum is primarily dependent on the steric bulk of
substituent ligands (11, 13), and in the case of compounds 1 and 2 the coordination
geometry is dominated by the sterically bulky siloxide ligands.

Whereas the THF (1) and H_2O (2) Al-O bond distances are within the range
usually observed (14, 15, 16), the siloxide Al-O distances [1.696 (4) - 1.709 (4) Å] are
significantly shorter. The latter are, however, close to the values found in
$Al(OSiPh_3)_2(acac)$ (17). This shortening has been previously ascribed to a possible π-type
interaction between the oxygen lone pairs and the σ^* orbitals on aluminum (16). The Si-O
bonds in 1 and 2 are also within the range observed for some π-type interaction (18).
There appears to be no correlation, however, between the Al-O-Si bond angle and either the
Al-O or Si-O bond lengths. A similar lack of correlation has been observed previously for
both main group and transition metal alkoxide and aryloxide complexes (16, 19).

The IR spectrum of 2 contains a broad resonance at 3659 cm^{-1} consistent with a
hydrogen bonded O-H group. This assignment is confirmed by the observation of an
isotope shift for the deuterated analogue of 2, $Al(OSiPh_3)_3(D_2O)(THF)_2$ [$v(O-D) = 2447$
cm^{-1}].

In Table 1, the ^{29}Si, ^{27}Al and ^{17}O NMR chemical shifts of compounds 1 and 2 are
compared with each other, those of the parent silanol, the dimeric mono-siloxide [$AlMe_2(\mu$-
$OSiPh_3)]_2$ (20), and the literature values for $Al(acac)(OSiPh_3)_2$ (acac = acetylacetonate)
(17). The ^{27}Al NMR resonances for 1 and 2 are consistent with four-coordinate aluminium
complexes with three alkoxide ligands (9). The ^{29}Si and ^{17}O NMR spectra for 1 and 2 (see
Table 1) are consistent with terminal siloxides (17) and are distinct from that observed the
bridging siloxides in the dimeric compound [$AlMe_2(\mu-OSiPh_3)]_2$ (20). It is also interesting
to note that the ^{17}O NMR spectral shifts of the terminal siloxides is close to that of the free
silanol.

The ^{1}H NMR signals for both **1** and **2** were sufficiently resolved at 500 MHz that fully interpretable first-order spectra could be obtained. Since the spectra of **2** displayed two sets of phenyl groups in a 1:2 ratio, due to restricted rotation (vide infra), it was necessary in this instance to establish ^{1}H-^{1}H connectivity using the standard COSY 2D NMR technique (Figure 3) (6, 7). The assignment of the *ortho*, *meta*, and *para* carbons of the phenyl rings was accomplished with the assistance of a standard heteronuclear-correlated (^{1}H-^{13}C) experiment (e.g., Figure 4) using delay times optimized for direct ^{1}H-^{13}C coupling (8).

Although the four-fold coordination about the aluminium center in **1.(THF)** observed in the solid state is retained in solution, as indicated by ^{27}Al NMR, there exists only a single set of resonances for the THF's indicating the presence of a rapid degenerate exchange between free and coordinated THF.(Eq 7), which does not cease on cooling (-70°C).

$$Al(OSiEt_3)_3(THF) \ + \ THF^* \ \rightleftharpoons \ Al(OSiEt_3)_3(THF^*) + \ THF \qquad [7]$$

We have previously observed that the dissociative ligand exchange for the sterically hindered aryloxide complexes AlMe(BHT)$_2$ (Eq 8), 2,6-di-*tert*-butyl-4-methylphenol, BHT-H from the trivial name butylated hydroxytoluene) readily ceases below 0°C, whereas the associative exchange for AlMe$_2$(BHT)L (Eq 9) continues down to -80°C (21).

$$AlMe(BHT)_2L \ + \ L^* \ \rightleftharpoons \ AlMe(BHT)_2L^* \ + \ L \qquad [8]$$

$$AlMe_2(BHT)L \ + \ L^* \ \rightleftharpoons \ AlMe_2(BHT)L^* \ + L \qquad [9]$$

The continued exchange at low temperatures between free and coordinated THF in **1.(THF)** suggests an associative ligand exchange is in effect. The solid state structure

lends partial credence to this proposal, since the uncomplexed THF is positioned for incipient complexation to the metal. The exchange of excess THF with those hydrogen-bonded to the water ligand in a freshly crystallized sample of 2 does not cease at low temperatures. This facile exchange is, however, consistent with the weak hydrogen-bonding as opposed to an associative exchange.

As can be seen from ^{1}H and ^{13}C NMR data (see Experimental) there are two distinct environments for the phenyl groups in 2, which may be related to the solid state structure (Figure 2) as those positioned equatorial (six phenyl groups, marked with an asterisk in the Experimental) and axial (three phenyl groups)to the Al(1)-O(2) vector. Thus the presence of distinct phenyl environment indicates that at room temperature there is no rotation about the Al-O-Si bonds. However, the phenyl groups do exhibit free rotation, since only a single set of resonance is observed for each of the *ortho* and *meta* ring protons

Heating an NMR sample of 2 results in coalescence of the signals for the phenyl rings ($T_c = 60^{\circ}C$). It is possible that this is due to the onset of dissociation of the coordinated water molecule which in turn results in a planar three coordinated aluminium, and releases the steric restraint imposed on the siloxide groups However, the activation energy (ΔG^+) for this exchange is calculated (22) from the NMR data to be 16.5($\pm$0.3) kJ/mol^{-1}, which is inconsistent with ligand bond dissociation energies (BDE) previously observed for aluminium complexes, 63 - 115 kJmol^{-1} (21, 23). A consideration of the space-filling representation of 2 in Figure 5 shows that the THF molecules are sufficiently distant from the triphenylsiloxide groups to have no significant steric effects, as can be implied from their fluxional nature in solution while the siloxides remain rigid. However, the OSiPh$_3$ groups are locked together, precluding the rotation around the Al-O-Si bonds. We propose, therefore, that the measured activation barrier is the energy required to overcome this sterically induced rigidity.

If a sample of 2 is cooled below -70°C the ^{1}H NMR spectrum indicates that not only are the siloxide groups rigid but the axially disposed phenyl rings have ceased to rotate

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($\Delta G^+ = 9.7(\pm 0.2)$ kJmol^{-1}) providing two environments for the *ortho* and *meta* ring protons. Figure 6 clearly shows the mutual steric hindrance imposed on these phenyl rings to inhibit rotation about their respective Si-C bonds. We note that both of these processes are rare measures of the steric constraints imposed on an organic substituent within a sterically hindered molecule.

Supplementary Material Available. Tables of all bond lengths and angles, anisotropic displacement coefficients, hydrogen atom coordinates, and tables of observed and calculated structure factor amplitudes may be purchased from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A OS2.

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Table 1. Heteroatom NMR Chemical Shifts[a]

Compound	^{27}Al	^{29}Si	^{17}O
$Al(OSiPh_3)_3(THF)$	57.5 (3400)	-24.6	12.9 (780), THF
			7.2 (730), $OSiPh_3$[b]
$Al(OSiPh_3)_3(H_2O)(THF)_2$	58.8 (4380)	-25.7	17.2 (660), THF
			14.5 (585), H_2O[c]
			8.8 (860), $OSiPh_3$[b]
$[AlMe_2(\mu\text{-}OSiPh_3)]_2$	57.4 (6440)	-10.8	47.8 (780)
$Al(acac)(OSiPh_3)_2$	53.0 (2300)[d]	-24.2[e]	375.0 (2200), acac
			12.9 (1400), $OSiPh_3$
$HOSiPh_3$		-12.6	8.9 (414)

[a] $W_{1/2}$ values in Hz are given in parentheses. Unless otherwise stated all spectra were obtained at ambient temperatures, in CH_2Cl_2:$CDCl_3$ (1:1).

[b] 22.3 % ^{17}O enriched $OSiPh_3$

[c] 22.3 % ^{17}O enriched H_2O

[d] Reference 17, $C_2D_2Cl_4$, 120°C

[e] Reference 17, $CDCl_3$

Table II. Crystallographic Data for **1** and **3**.

	1.(THF)	2.(THF)$_{1.25}$
Formula	$C_{62}H_{61}AlO_5Si_3$	$C_{70}H_{73}AlO_{7.25}Si_3$
Crystal system	Monoclinic	Cubic
Space group	$P2_1/c$	$Pa\bar{3}$
a, Å	10.03(1)	23.034(3)
b, Å	23.758(6)	23.034(3)
c, Å	23.294(7)	23.034(3)
β, deg	101.13(6)	
V, Å^3	5446(6)	12221(3)
Z	4	4
D(calcd), g/cm^3	1.216	1.386
cryst dimers, mm	0.43 x 0.30 x 0.26	0.27 x 0.26 x 0.27
temp, K	273	273
radiation	MoK$_\alpha$ (λ = 0.71073 Å, graphite monochromator)	
μ, mm^{-1}	0.146	0.158
2θ limits (deg)	4.0 - 45.0	4.0 - 55.0
no. of data collected	8214	11708
no. of unique data	7109	3606
no. of obsd. data	5158	2050
R	0.084	0.093
R$_w$	0.094	0.099
final residual, eÅ^{-3}	0.45	1.04

Table III. Fractional Coordinates (x 10^4) and Equivalent Isotropic Thermal Parameters (10^3 x Å^2) of the Non-Hydrogen Atoms in **1**.(THF).

	x	y	z	U(eq)
Al(1)	1783(2)	2713(1)	6394(1)	26(1)
O(1)	2618(4)	3116(2)	6950(2)	36(1)
Si(1)	2905(2)	3653(1)	7376(1)	29(1)
C(1)	2190(7)	3509(2)	8043(3)	36(2)
C(2)	1059(7)	3166(3)	8010(3)	50(3)
C(3)	460(8)	3060(4)	8502(4)	64(3)
C(4)	1071(10)	3286(4)	9024(4)	74(4)
C(5)	2200(11)	3625(3)	9082(3)	69(4)
C(6)	2783(8)	3730(3)	8588(3)	49(3)
C(7)	4792(6)	3770(2)	7586(2)	29(2)
C(8)	5337(7)	4293(3)	7809(3)	41(2)
C(9)	6719(7)	4367(3)	7972(3)	44(2)
O(2)	1600(4)	2017(2)	6548(2)	34(1)
Si(2)	1203(2)	1527(1)	6959(1)	30(1)
C(19)	886(6)	858(2)	6529(3)	32(2)
C(20)	1400(8)	770(3)	6027(3)	47(3)
C(21)	1161(8)	267(3)	5710(3)	57(3)
C(22)	413(8)	-151(3)	5902(3)	57(3)
C(23)	-137(8)	-70(3)	6383(3)	59(3)
C(24)	97(7)	425(2)	6702(3)	45(3)
C(25)	2620(7)	1418(2)	7606(2)	34(2)
C(26)	3175(8)	894(3)	7780(3)	51(3)
C(27)	4218(8)	820(3)	8240(3)	61(3)
C(28)	4768(8)	1291(4)	8562(3)	62(3)
C(29)	4284(8)	1813(3)	8393(3)	53(3)
C(30)	3228(7)	1875(3)	7927(3)	46(3)
C(31)	-408(7)	1705(2)	7215(3)	36(2)
C(32)	-1394(8)	2018(3)	6867(3)	49(3)
C(33)	-2677(8)	2103(3)	7014(3)	60(3)
C(34)	-2930(9)	1883(3)	7531(4)	65(3)
C(35)	-1980(9)	1583(3)	7872(4)	68(3)
C(36)	-721(9)	1494(3)	7733(3)	56(3)
O(3)	300(4)	2994(2)	6026(2)	33(1)
Si(3)	-639(2)	3191(1)	5420(1)	29(1)
C(37)	-1389(7)	2552(2)	5011(3)	35(2)
C(38)	-2294(7)	2585(3)	4475(3)	49(3)
C(39)	-2823(9)	2113(4)	4168(3)	69(3)
C(40)	-2479(8)	1575(3)	4410(3)	57(3)
C(41)	-1658(9)	1530(3)	4924(4)	60(3)
C(42)	-1080(7)	2021(3)	5231(3)	45(3)
C(43)	376(6)	3602(2)	4973(3)	35(2)
C(44)	849(6)	3387(3)	4493(2)	35(2)
C(45)	1734(8)	3699(3)	4220(3)	50(3)
C(46)	2169(7)	4222(3)	4435(3)	49(3)
C(47)	1732(8)	4440(3)	4897(3)	54(3)

Table III contd. Fractional Coordinates (x 10^4) and Equivalent Isotropic Thermal Parameters (10^3 x Å^2) of the Non-Hydrogen Atoms in 1.(THF).

C(48)	865(7)	4133(3)	5180(3)	44(2)
C(49)	-2004(6)	3671(2)	5571(2)	30(2)
C(50)	-2333(7)	3723(3)	6122(3)	41(2)
C(51)	-3376(7)	4077(3)	6221(3)	47(3)
C(52)	-4148(7)	4362(3)	5764(3)	44(3)
C(53)	-3860(7)	4316(2)	5205(3)	39(2)
C(54)	-2823(7)	3978(2)	5115(3)	35(2)
O(4)	2968(4)	2681(2)	5871(2)	35(1)
C(55)	3023(9)	2227(3)	5465(4)	69(3)
C(56)	3990(12)	2429(4)	5092(5)	100(5)
C(57)	4727(10)	2871(4)	5401(4)	84(4)
C(58)	3913(8)	3136(3)	5786(3)	48(3)
C(13)	2138(6)	4302(2)	7003(2)	33(2)
C(15)	2264(8)	5099(3)	6351(3)	52(3)
C(10)	7606(7)	3943(3)	7905(3)	46(3)
C(14)	2839(7)	4634(3)	6671(3)	44(2)
C(16)	931(8)	5241(3)	6360(3)	53(3)
C(17)	177(8)	4915(3)	6673(3)	57(3)
C(11)	7106(7)	3427(3)	7692(3)	49(3)
O(5)	4553(12)	994(5)	5728(8)	192(8)
C(60)	6310(17)	481(8)	6321(9)	202(12)
C(12)	5681(7)	3346(3)	7529(3)	38(2)
C(18)	788(8)	4460(3)	6987(3)	50(3)
C(61)	6480(21)	508(12)	5771(10)	322(21)
C(59)	5023(19)	691(12)	6270(9)	268(17)
C(62)	5380(25)	807(11)	5474(9)	271(18)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

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Table IV. Fractional Coordinates (x 10^4) and Equivalent Isotropic Thermal Parameters (10^3 x $Å^2$) of the Non-Hydrogen Atoms in 2.(THF)$_{1.25}$.

	x	y	z	U(eq)
Al(1)	1789(1)	1789(1)	1789(1)	32(577)
O(1)	1489(2)	2264(2)	1305(2)	51(2)
Si(1)	1017(1)	2589(1)	923(1)	41(1)
C(1)	602(3)	2068(3)	455(3)	44(2)
C(2)	866(4)	1577(3)	233(3)	64(3)
C(3)	591(4)	1200(4)	-131(4)	76(3)
C(4)	28(4)	1308(3)	-291(3)	65(3)
C(5)	-262(4)	1768(3)	-66(3)	61(3)
C(6)	22(3)	2147(3)	305(3)	50(2)
C(7)	1391(3)	3109(3)	423(3)	49(2)
C(8)	1161(5)	3277(4)	-98(4)	82(4)
C(9)	1442(6)	3656(4)	-466(4)	107(5)
C(10)	1966(5)	3884(3)	-307(4)	77(3)
C(11)	2205(4)	3740(3)	213(4)	72(3)
C(12)	1927(3)	3352(3)	569(4)	64(3)
C(13)	487(3)	2986(3)	1406(3)	50(2)
C(14)	368(4)	2782(4)	1951(4)	69(3)
C(15)	-40(4)	3056(5)	2308(4)	86(4)
C(16)	-342(4)	3520(4)	2108(5)	81(4)
C(17)	-231(4)	3727(4)	1578(5)	77(4)
C(18)	182(3)	3466(3)	1209(4)	61(3)
O(2)	2248(2)	2248(2)	2248(2)	70(577)
C(19)	2831(5)	3107(5)	1786(5)	194(7)
C(15)	2863(7)	3639(4)	2151(7)	139(7)
C(20)	3239(7)	3932(7)	1905(9)	197(12)
C(21)	3720(6)	3520(7)	1439(5)	133(7)
C(22)	3383(7)	3103(8)	1452(6)	167(10)
C(23)	4763	0	562	90
C	4763	0	562	90

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table V. Selected bond lengths (Å) and angles (°) in **1**.(THF).

Al(1)-O(1)	1.696(4)	Al(1)-O(2)	1.709(4)
Al(1)-O(3)	1.703(4)	Al(1)-O(4)	1.861(5)
O(1)-Si(1)	1.606(4)	O(2)-Si(2)	1.606(4)
O(3)-Si(3)	1.608(4)	O(4)-C(55)	1.444(9)
O(4)-C(58)	1.475(8)	Si(1)-C(1)	1.866(7)
Si(1)-C(7)	1.882(6)	Si(1)-C(13)	1.861(6)
Si(2)-C(19)	1.875(6)	Si(2)-C(25)	1.879(6)
Si(2)-C(31)	1.876(7)	Si(3)-C(37)	1.873(6)
Si(3)-C(43)	1.866(7)	Si(3)-C(49)	1.866(7)
O(1)-Al(1)-O(2)	116.3(2)	O(1)-Al(1)-O(3)	114.7(2)
O(1)-Al(1)-O(4)	103.8(2)	O(2)-Al(1)-O(3)	111.5(2)
O(2)-Al(1)-O(4)	101.9(2)	O(3)-Al(1)-O(4)	107.0(2)
Al(1)-O(1)-Si(1)	157.3(3)	Al(1)-O(2)-Si(2)	151.1(3)
Al(1)-O(3)-Si(3)	149.7(3)	Al(1)-O(4)-C(55)	124.7(5)
Al(1)-O(4)-C(58)	124.5(4)	C(55)-O(4)-C(58)	110.6(6)
O(1)-Si(1)-C(1)	108.4(3)	O(1)-Si(1)-C(7)	109.3(3)
O(1)-Si(1)-C(13)	111.2(2)	C(1)-Si(1)-C(7)	109.8(3)
C(1)-Si(1)-C(13)	110.5(3)	C(7)-Si(1)-C(13)	107.6(3)
O(2)-Si(2)-C(19)	109.4(2)	O(2)-Si(2)-C(25)	110.0(3)
O(2)-Si(2)-C(31)	110.8(2)	C(19)-Si(2)-C(25)	109.6(3)
C(19)-Si(2)-C(31)	107.1(3)	C(25)-Si(2)-C(31)	109.9(3)
O(3)-Si(3)-C(37)	108.6(2)	O(3)-Si(3)-C(43)	110.6(3)
O(3)-Si(3)-C(49)	109.8(2)	C(37)-Si(3)-C(43)	110.4(3)
C(37)-Si(3)-C(49)	110.7(3)	C(43)-Si(3)-C(49)	106.6(3)

Table VI. Selected bond lengths (Å) and angles (°) in 2.(THF)$_{1.25}$.

Al(1)-O(1)	1.708(5)	Al(1)-O(2)	1.83(1)
O(1)-Si(1)	1.586(5)	Si(1)-C(1)	1.875(7)
Si(1)-C(7)	1.871(7)	Si(1)-C(13)	1.889(7)
O(3)-C(19)	1.48(1)	O(3)-C(22)	1.48(2)
O(1)-Al(1)-O(2)	104.0(2)	O(1)-Al(1)-O(1A)	114.4(1)
Al(1)-O(1)-Si(1)	160.4(3)	O(1)-Si(1)-C(1)	111.4(3)
O(1)-Si(1)-C(7)	109.3(3)	O(1)-Si(1)-C(13)	110.2(3)
C(1)-Si(1)-C(7)	106.9(3)	C(1)-Si(1)-C(13)	108.6(3)
C(7)-Si(1)-C(13)	110.5(3)	C(19)-O(3)-C(22)	104.3(1)

Legends for Figures

Fig 1. Structure of Al(OSiPh$_3$)$_3$(THF) (1) with thermal ellipsoids drawn at the 40% level. The THF of solvation and hydrogen atoms are omitted for clarity.

Fig 2. Structure of Al(OSiPh$_3$)$_3$(H$_2$O)(THF)$_2$ (2) with thermal ellipsoids drawn at the 40% level. The THF's of solvation and hydrogen atoms not associated with the water ligand are omitted for clarity.

Fig 3. ^{1}H-^{1}H COSY spectrum of Al(OSiPh$_3$)$_3$(H$_2$O)(THF)$_2$ (2).

Fig 4. ^{1}H-^{13}C correlated 2D NMR spectrum of Al(OSiPh$_3$)$_3$(H$_2$O)(THF)$_2$ (2).

Fig 5. Space-filling representation of Al(OSiPh$_3$)$_3$(H$_2$O)(THF)$_2$ (2), and its equivalent line drawing (inset), viewed perpendicular to the Al(1)-O(2) vector, showing the steric hindrance imposed on the triphenylsiloxide groups.

Fig 6. Space-filling representation of Al(OSiPh$_3$)$_3$(H$_2$O)(THF)$_2$ (2), and its equivalent line drawing (inset), viewed along the Al(1)-O(2) vector, showing the interdependent steric hindrance of the three axial phenyl rings. The THF molecules have been omitted for clarity.

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Si(1) O(1) Al(1)