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Mild depolymerization of silicone grease using aluminum(III)chloride: high-yield synthesis and crystal structure of [{$ClSiMe_2OAlCl_2$}$_2$], and its controlled hydrolysis on aluminum surfaces

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Reaction of $AlCl_3$ with {Me_2SiO}$_n$ (Dow-Corning high-vacuum grease) at an Al : Si ratio of 1 : 1 in hexane at room temperature yielded a large crop of colorless crystals of [{$ClSiMe_2OAlCl_2$}$_2$], which were characterized by single-crystal X-ray diffraction and NMR. These crystals hydrolyzed on an aluminum surface to give a coating of silicone oil interspersed with particles of [$Al(OH_2)_6$]Cl_3, as determined by powder X-ray diffraction and X-ray photoelectron spectrometry. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: aluminum; silicon; siloxane; X-ray; XPS; depolymerization

INTRODUCTION

It has long been known that the silicone greases used as flexible sealants for ground-glass joints in chemical synthesis are not inert to Lewis acids. The commonly encountered 'joint-freezing' phenomenon has this property at its root. In the case of aluminum alkyls, the groups of Barron[1] and Ittel[2] have thoroughly investigated the area, and crystallographically characterized the dimeric siloxide product of full depolymerization, [{$Me_3SiOAlMe_2$}$_2$],[1,2] as well as many other examples and intermediate stages.[3,4] However, in these studies, clean products were most frequently available by ring-opening of small oligomeric cyclosiloxanes, such as $(Me_2SiO)_3$ or $(Me_2SiO)_4$. Also, conditions were aggressive: either a 4 day toluene reflux or a 24 h heating of neat regents at 180 °C was required.[1,2] Similar reactivity has been found with aluminum hydrides[3] and halides. Andrianov and co-workers reported in 1961 that $AlCl_3$ reacts with dimethylcyclosiloxanes to give crystalline [{$(Cl_2Al)(OSiMe_2OSiMe_2O)$}$_2AlCl$] and $\alpha\omega$-dimethylsiloxanes.[5] The aluminosiloxane product was later confirmed by X-ray crystallography to adopt the tetracyclic structure **1**[6] (for the bromo analog, see Ref. 7). The reaction was reinvestigated by Cordischi *et al.*,[8] who in 1964 published the results summarized in Scheme 1.

In contrast to these results, we have found that the total depolymerization reaction to form **2** proceeds in high yield at room temperature in hexane solvent. It has been structurally characterized, and assessed as an aluminum surface-coating agent; silanes have found application as coupling agents and protective coatings for materials ranging from glass to aluminum.[9–11] The combination of reactive silanol and aluminum centers afforded in the product **2** was thought to be of potential utility in creating a network organosiloxane aluminate primer material on aluminum surfaces.

RESULTS AND DISCUSSION

Synthesis

The siloxane source was simply high-vacuum silicone grease, which is a dimethylsiloxane polymer thickened with silica particles. When dispersed in hexane and reacted with $AlCl_3$, a solution was obtained after overnight stirring, contaminated by remaining silica particles and unidentified dark tar impurities. These could be removed by filtration to yield large rod-like crystals of the chlorosiloxaluminate **2** from the filtrate. This initially serendipitous discovery was repeated

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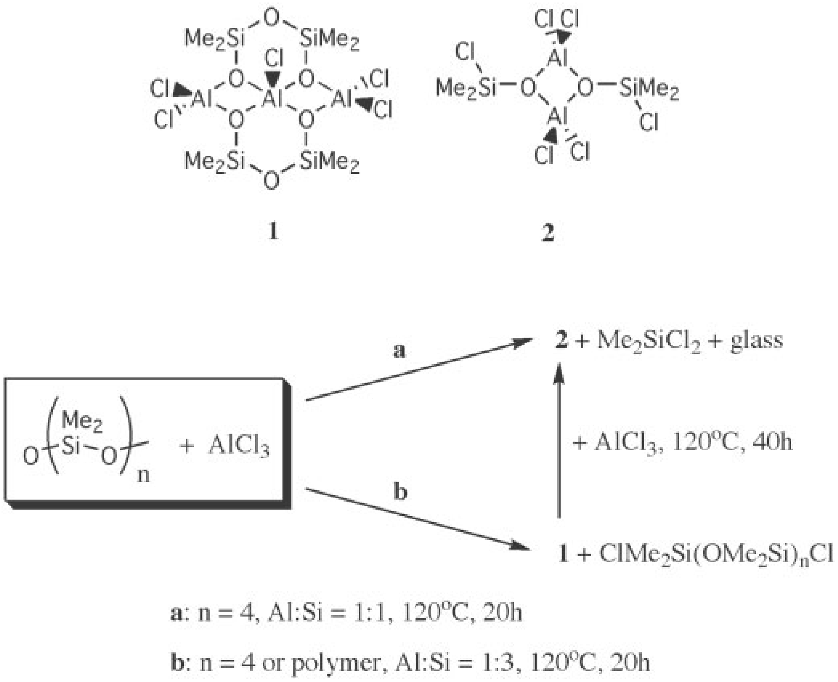


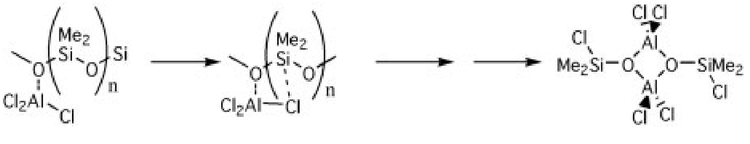
Scheme 1.

quantitatively with a yield of 84%. The yield of **2** from route **a** (Scheme 1) was half of this, although higher temperatures, a more homogeneous starting material $(Me_2SiO)_4$, and a longer reaction time were employed. It would appear that the siloxane cleavage reaction may proceed under much less forcing conditions than were hitherto assumed. (A more recently reported reaction of $(Me_2SiO)_4$ with $AlCl_3$ did proceed at room temperature, but a reaction time of 6 days was employed, and the isolated material was the product of incomplete depolymerization, **1**. No yield was given.[4]) This also contrasts with the results using $AlMe_3$, where protracted reflux or sealed-tube furnace heating regimes were employed.[1,2] That the Si–O bond is more readily cleaved by $AlCl_3$ fits with the stronger Lewis acid character of $AlCl_3$ over $AlMe_3$. Regarding mechanism, Barron has argued against the classical four-center picture of siloxide cleavage (Scheme 2), citing evidence drawn from his studies of $AlMe_3$ attack in support of a theory where one aluminum center coordinates to siloxane (confirmed by ^{1}H NMR spectroscopy)[1] while another provides the methyl group that attacks silicon.[3] The longer Al–Cl bond, coupled with the superior bridging capacity of chloride over methanide anions, sways us to favor a conventional four-center mechanism, though the necessary rate-law determinations that would decide the issue are lacking in both cases. That a higher yield is attainable in a shorter time, with less energy input and more readily accessible starting materials, could be of significance in the event of a use being found for **2**.

Structure

The crystal and molecular structure of **2** was determined by single-crystal X-ray diffraction, and is depicted in Fig. 1.

A number of dimeric aluminum siloxides have been structurally characterized;[1–3] the robustness of the bridging capacity of the siloxide group in this context has been effectively demonstrated by Ittel and co-workers,[2] whose admixture of $[(Me_2AlOSiMe_3)_2]$ and $[(Et_2AlOSiEtMe_2)_2]$ for 24 h at 150 °C resulted in no detectable exchange of alkyl or siloxide groups. Compound **2** is the first such dimer in which a chloride ligand is attached to the siloxide function. The closest structural analogy in this respect is provided by $[ClSiMe_2O(2,6\text{-}^tBu\text{-}4\text{-}Me\text{-}C_6H_2)]$ (**3**).[12] However, the bulky aryloxide employed in place of the aluminate resulted in a monomeric structure[12] in the crystal **3**. In contrast, the truly dimeric nature of the bridging siloxides in **2** is evidenced by the similarity of the distances Al(1)–O(1) and Al(1)–O(1′)



Scheme 2.

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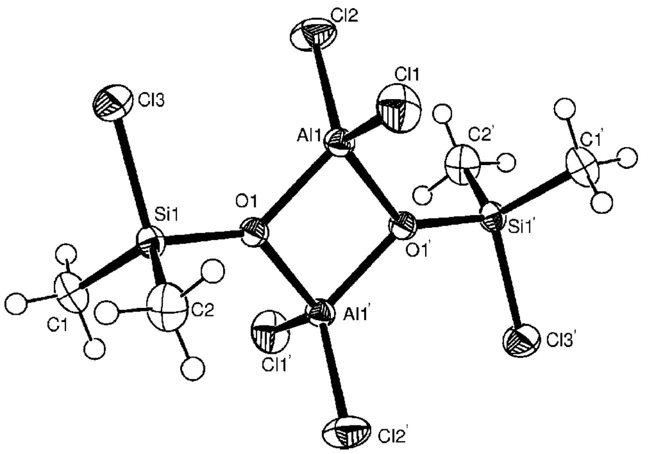

Figure 1. ORTEP plot (50%) of crystal and molecular structure of **2**.

Table 1. Selected interatomic distances (Å) and angles (°) for **2**[a]

Si(1)–O(1) 1.6851(13)	C(1)–Si(1)–C(2) 116.96(12)
Si(1)–C(1) 1.824(2)	O(1)–Si(1)–Cl(3) 103.17(5)
Si(1)–C(2) 1.827(2)	C(1)–Si(1)–Cl(3) 109.95(9)
Si(1)–Cl(3) 2.0512(7)	C(2)–Si(1)–Cl(3) 108.94(9)
Al(1)–O(1) 1.8171(13)	O(1)–Al(1)–O(1)′ 83.72(6)
Al(1)–O(1)′ 1.8282(13)	O(1)–Al(1)–Cl(2) 118.09(5)
Al(1)–Cl(1) 2.0831(8)	O(1)–Al(1)–Cl(2) 110.38(5)
Al(1)–Cl(2) 2.0809(8)	O(1)–Al(1)–Cl(1) 112.31(5)
Al(1)–Al(1)′ 2.7149(11)	O(1)–Al(1)–Cl(1) 113.23(5)
O(1)–Si(1)–C(1) 107.98(9)	Cl(2)–Al(1)–Cl(1) 115.11(3)
O(1)–Si(1)–C(2) 108.94(9)	Si(1)–O(1)–Al(1) 130.86(7)

[a] Primes indicate symmetry transformations used to generate equivalent atoms: $-x+1$, $-y$, $-z$.

(Table 1). One monomeric unit in **2** is related to the other by a crystallographic center of inversion. The primed atom labels in Fig. 1 and Table 1 denote symmetry-equivalent positions. The bond distances and angles follow expected patterns; for example, the Cl–Si, O–Si and C–Si bond lengths in dimer **2** are essentially the same as those[12] in monomer **3**. They differ, however, from those recently reported where the $ClSiMe_2$ unit is bonded to an unusual ruthenium hydride fragment.[13] In that case, additional (Ru)–H–Si contacts are present. The raised coordination number of the silicon results in expanded Cl–Si (2.11 Å, cf. 2.05 Å in **2**) and C–Si (mean 1.922(10) Å, cf. 1.826 (1) Å in **2**) bonds.[13]

The rare chlorosiloxide functionality suggests that **2** represents a structural analogy with partially hydrolyzed Me_2SiCl_2, where spontaneous condensation has been prevented by the presence of aluminum, whereas in fact the hydrolysis and polycondensation has been hemi-reversed by chlorination by $AlCl_3$. The result is a dimethylsilicone synthon with two functions of differential reactivity. The presence of the pre-formed Si–O–Al linkage, in common with reactive halides on both silicon and aluminum, prompted us to consider whether controlled hydrolysis experiments may yield materials reflecting the stability of zeolites combined with the hydrophobicity of silicones. Also, there are two types of exchangeable halide, offering the possibility of preparation of new mixed alkylsiloxalanes, of use as co-catalysts in Ziegler–Natta alkene polymerization.[2] It is the former property that motivated our experiments in aluminum surface studies. The latter property will be the subject of future synthetic work.

Adsorption to aluminum

A layer of **2** was deposited on a magnetron-sputtered aluminum surface by dip-coating in a dry hexane solution of **2** for periods of 3 and 10 min, under dry argon. The aluminum plate was then hydrolyzed, washed with hexane, and subjected to X-ray photoelectron spectrometry surface analysis. Aside from the expected background of alumina and the ubiquitous carbonaceous surface contamination,[14] some silicon incorporation was evident (2.9 at.% surface concentration after 3 min). It was slightly greater for the longer dipping time (3.4 at.%); however, the chloride levels did not tally, and a decreased surface concentration of chlorine was seen on longer dipping (1.1 at.% to 0.4 at.% respectively). This is probably because the chlorine content was lost in the washing procedure. The measured Si(2p) binding energy (102.3 eV) was consistent with that of polydimethylsiloxane.[15] It was not possible to distinguish any features in the Al(2p) region specific to the adsorbate because of the strong aluminum substrate contribution to the spectrum.

Powder X-ray diffraction of a freshly dipped sample showed some unidentified low-angle peaks (consistent with some long-range order) shortly after exposure to moist air, which decreased on prolonged exposure. After 20 min, peaks attributable to the diffraction pattern of $[Al(OH_2)_6]^{3+}\cdot 3Cl^-$ were evident.[16]

These data show that hydrolysis is fast, and that any short-lived intermediate phase quickly generates a polydimethylsiloxane phase. The aluminum separates from this phase as a hydrated cation. The polydimethylsiloxane coating produced was oily in nature, as was to be expected for such a polymer with no crosslinking. From these results it was concluded that the Si–O–Al linkage in **2** was quickly lost, and that no evidence of aluminum-crosslinked species was present. Given this finding, future experiments shall include some $MeSiCl_3$ in mixtures for hydrolysis, so as to give a more robust matrix. It remains the case that, when part of a three-dimensional network solid in zeolites, the Si–O–Al linkage is stable, just as it remains the case that better methods for anchoring siloxane coatings to aluminum are desirable.

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EXPERIMENTAL

General

High-vacuum silicone grease (Dow-Corning) and aluminum(III) chloride (Aldrich) were used as received. Hexane was freshly distilled from sodium–benzophenone ketyl. Argon was dried by passage through a column of P_2O_5 supported on vermiculite. The aluminum surfaces were prepared by magnetron sputtering onto glass microscopy slides. ^{1}H and ^{13}C NMR data were recorded on a Bruker DPX 400 spectrometer operating at 298 K.

Preparation of 2

In an argon-filled glovebox, a Schlenk tube was charged with high-vacuum silicone grease (0.73 g, 10 mmol 'Me_2SiO', assuming that the grease is pure dimethylsiloxane of infinite molecular weight) and $AlCl_3$ powder (1.33 g, 10 mmol). At room temperature, under an argon atmosphere, hexane (36 ml) was added, and magnetic stirring commenced. After 18 h of magnetic stirring at 20 °C, the mixture was composed of a straw-colored supernatant liquor over a dark tarry residue. The liquor was decanted from the dark tar, and concentrated to half its volume *in vacuo*. Crystals of **2** deposited after overnight storage at −20 °C. These were removed by filtration. When combined with a second crop isolated from the further-concentrated filtrate and washed with hexane, a high yield of colorless rods of **2** was obtained (1.72 g, 84%). The extreme moisture sensitivity of **2** prevented the UMIST micro-analytical facility from attaining accurate results; however, the X-ray data, coupled with the large crystal size and identical habit of the crystals, and clean NMR analyses, satisfied us as to the sample purity and homogeneity. $^{13}C\{^1H\}$ NMR (100 MHz, 298 K, $CDCl_3$)δ 4.09; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$)δ 0.81. M.p. 60–62 °C (hexane). Lit.[8] m.p.: 54–56 °C (benzene). IR (Nujol mull, KCl plates) λ cm^{-1} 431(s), 466(s), 517(s), 579(s), 645(s), 691(s), 746(s), 843(vs), 1073(w), 1194(w), 1264(s).

Crystallography

A crystal of **2** was selected from the mother liquor under argon, coated with perfluoropolyether oil (1800 fomblin), and placed on the end of a glass fiber in a stream of cold nitrogen on a Nonius Kappa CCD diffractometer. Data collection, processing and refinement methods were as previously described.[17] Crystal data for **2**: $C_2H_6AlCl_3OSi$, $M = 207.49$, $a = 6.6631(2)$, $b = 12.5965(5)$, $c = 10.5640(4)$ Å, $\beta = 101.433(2)°$, $U = 869.06(5)$ Å^3, $T = 150$ K, monoclinic space group $P2_1/n$ (no. 14), $Z = 4$, $\mu(\text{Mo K}_\alpha) = 1.212$ mm^{-1}, 8886 reflections measured, 2514 unique ($R_{\text{int}} = 0.0526$), which were used in all calculations. The final $wR_2(F^2)$ was 0.077 (all data), conventional $R[I > 2\sigma(I)] = 0.035$. The CIF (crystallographic information file) has been deposited at the Cambridge Crystallographic Data Centre, CCDC 206 364.

Aluminum coating and surface analysis

X-ray diffraction analysis was undertaken on a Bruker-AXS D8 Advance powder diffractometer using Göbel mirror primary beam optics producing Cu Kα radiation at 40 kV and 40 mA ($\lambda = 1.540\,60$ Å). X-ray detection was achieved using a Braun PSD detector (stage alignment and calibration were undertaken using a conventional scintillation counter). Glass microscope slides, previously magnetron-sputtered with aluminum, were immersed under argon into a dry hexane solution (0.118 M) for 10 min. After exposure to atmospheric moisture for 1 h, they were placed into the sample stage of the powder diffractometer. Height adjustments were made. Scan range: 5 to 70°; 2θ. The most intense peaks corresponded to the nine most intense[16] peaks in the JCPDS aluminum chloride hexahydrate pattern (JCPDS no. 8–453). In other runs, made immediately subsequent to dip-coating, metastable phases with low-angle reflections were observed, but these were progressively replaced by amorphous background and $Al(OH_2)_6{\cdot}3Cl$ peaks.

In separate experiments, similarly prepared aluminum slides were coated in a more dilute hexane solution of **2** (10 mM) for 3 and 10 min, hydrolyzed with deionized water for 10 s, then dried in a vacuum dessicator prior to being placed in the sample chamber of a Kratos Axis Ultra X-ray photoelectron spectrometer. The instrument used monochromated Al Kα radiation. The X-ray source was run at a power of 150 W; chemical state assignments were made from high-resolution core levels that were acquired at a pass energy of 20 eV, whereas elemental compositions were determined from survey scans acquired at 160 eV. Spectra were charge corrected to place the hydrocarbon environment of the C 1s core level at 285.0 eV.

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