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TRIS(TRIMETHYLSILYLMETHYL)ALUMINIUM

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Summary

Tris(trimethylsilylmethyl)aluminium, made from bis(trimethylsilylmethyl)mercury and aluminium foil, is a colourless inflammable liquid, which appears to give a mixture of monomeric and dimeric species in benzene. It reacts with methylamine to yield the dimeric amido derivative $[(Me_3SiCH_2)_2AlNHMe]_2$.

Trimethylsilylmethyl derivatives of transition metals, in which the metal atom shows an unusual coordination number, have been isolated [1]. The enhanced thermal stability of these compounds compared with their methyl or ethyl analogues, has been attributed to kinetic restraints imposed by the bulky alkyl groups and by the absence of β-hydrogen atoms. It was felt that an examination of the structure and reactions of tris(trimethylsilylmethyl)aluminium and its derivatives would be worthwhile, to discover whether these also showed aluminium atoms with unusual coordination numbers. Trineopentylaluminium is largely monomeric in dilute solution [2] whereas tri-n-alkylaluminiums are associated to dimers.

Tris (trimethylsilylmethyl) aluminium was obtained from the mercury derivative [3] and aluminium foil in boiling toluene. It was isolated as a colourless liquid, spontaneously inflammable in air, and reacting violently with water.

$$3(Me_3SiCH_2)_2Hg + 2\,Al/Hg \xrightarrow[14\text{ days}]{110^\circ} 2(Me_3SiCH_2)_3Al + 3\,Hg$$

Cryoscopic measurements in benzene showed some molecular association. The apparent molecular weight, like that of tri-n-propylaluminium [4], decreased with dilution, but the results were insufficiently precise for the derivation of an accurate equilibrium constant. The NMR spectrum showed sharp resonances with intensities in the ratio 9/2 (assigned to the methyl and methylene protons) with the methylene resonance at higher field, as expected for a compound with the trimethylsilylmethyl groups adjacent to an electropositive element [5]. Small satellites were attributed to coupling with ^{13}C and ^{29}Si nuclei and values of coupling constants were comparable with those in similar compounds [6]. The spectrum showed little variation with temperature down to the freezing point of the liquid or to —40° in toluene-d_8; there was no separation of resonances from bridge and terminal groups in associated species.

Infrared and Raman spectra of trimethylsilylmethyl derivatives of metals have been well characterised [7] and assignments of bands in the aluminium compound are straightforward. There was only one peak at 502 cm^{-1} in the Raman spectrum in the region between 430 and 550 cm^{-1} which is normally free from bands associated with the Me_3SiCH_2 group. This peak could be associated with vibration of the AlC_3 skeleton but, because Al—C and Si—C vibrations are expected to interact strongly, it does not seem at present possible to draw any more certain conclusions about the molecular framework.

Tris(trimethylsilylmethyl)aluminium reacted with a stoichiometric amount of methylamine to give tetramethylsilane quantitatively and a compound $[(Me_3SiCH_2)_2AlNHMe]_2$, which probably has a structure based on four-membered $(AlN)_2$ rings. The NMR spectrum of the amido derivative showed a

$$(Me_3SiCH_2)_3Al + NH_2Me \rightarrow Me_4Si + \tfrac{1}{2}[(Me_3SiCH_2)_2AlNHMe]_2$$

sharp doublet attributed to *N*-methyl protons, and sharp singlets assigned to the methyl and methylene protons of the *Al*-alkyl groups. The molecular configuration is thus *trans* (the *cis* isomer would show *Al*-alkyl groups in two different environments). A weak doublet, upfield from the main *N*-methyl doublet may indicate a small proportion of the *cis* isomer in solution, but this has not been separated as a pure solid. The methylene resonance is much broader (7.5 Hz at half height) than the *Si*-methyl resonance (2 Hz at half height), probably because the two methylene protons are not quite in the same chemical environment. Splitting of resonances from methylene protons adjacent to Al—N or Al—O rings has been observed in several other compounds [8, 9].

The mass spectrum of tris(trimethylsilylmethyl)aluminium at 70 eV showed a weak but clearly identifiable peak corresponding to the parent ion and a very strong peak from the fragment $(Me_3SiCH_2)_2Al^+$. No peaks from associated species were observed by reducing the source temperature or exciting potential. The breakdown pattern follows that observed for trimethylaluminium [10], with even-electron fragments predominating, but with additional fragmentation from breaking of silicon—carbon bonds [11]. The most abundant ion in the mass spectrum of bis(trimethylsilylmethyl)mercury was $[Me_3SiCH_2HgCH_2SiMe_2]^+$ from breaking of silicon—carbon rather than mercu-

TABLE 1

NMR SPECTRA[a]

	$\tau(Me_3SiCH_2)$ (ppm)	$\tau(Me_3SiCH_2)$ (ppm)	$^1J(^{13}CH)$[b] (Hz)	
$(Me_3SiCH_2)_3Al$	9.66	10.22	118	$^2J(^{29}SiCH)$[b], 6.5 Hz
$(Me_3SiCH_2)_2Hg$	9.71	9.66	116	$^2J(^{199}HgCH)$, 128 Hz
$[(Me_3SiCH_2)_2AlNHMe]_2$	9.70	10.73		τ(NMe), 7.68 ppm ^3J(HNCH), 7.2 Hz

[a] In toluene τ(TMS) = 10 ppm. [b] In Me_3Si group.

TABLE 2

MASS SPECTRA[a]

$(Me_3SiCH_2)_3Al$: 288(1), *P*; 273(2), *P*—Me; 201(35), *P*—CH_2SiMe_3; 185(5), 201—CH_4; 145(2); 129(10), 201—Me_2SiCH_2; 113(2), 201—Me_4Si; 73(100), Me_3Si^+. metastable peak: 140.3 (288 → 201);

$(Me_3SiCH_2)_2Hg$: 376(17), *P*; 361(100), *P*—Me; 289(6), *P*—CH_2SiMe_3; 202(17), Hg^+; 87(14), $Me_3SiCH_2^+$; 73(75), Me_3Si^+; 59(75) Me_2SiH^+.

$[(Me_3SiCH_2)_2AlNHMe]_2$: 447(11), *P*—Me; 375(77), *P*—CH_2SiMe_3; 359(4), 375—CH_4; 344(2), 375—NH_2Me; 328(2) 344—CH_4; 303(2), 375—Me_2SiCH_2; 288(25), 375—CH_2SiMe_3; 287(17), 375—Me_4Si; 256(20), 287—NH_2Me; 231(10), M; 216(37), M—Me; 200(27), 216—CH_4; 159(27); 144(47), M—CH_2SiMe_3; 139(20); 115(20); 73(100), Me_3Si^+.

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[a] *m/e* values with intensities, as % strongest, in parentheses, and probable assignments. Parent ion, *P*; $(Me_3SiCH_2)_2AlNHMe$ monomer M. Only peaks for ^{28}Si and ^{202}Hg given.

ry—carbon bonds. Parent ions, the ions $[Me_3SiCH_2]^+$ and mercury ions Hg^+, were also observed; the ions $[Me_3SiCH_2Hg]^+$ appeared much less strongly. The breakdown of the amido compound $[(Me_3SiCH_2)_2AlNHMe]_2$ followed the usual pattern [9,12], with the strongest peak from the dimer minus CH_2SiMe_3 and with methane, methylamine, and Me_2SiCH_2 recognisable among the neutral species eliminated.

It seems that the large trimethylsilylmethyl group does not completely prevent molecular association in tris(trimethylsilylmethyl) aluminium, but in the amido derivatives $(R_2AlNHMe)_n$ the molecular complexity *n* is 2 for $R = Me_3SiCH_2$ (as for R = Ph [13]) compared with 3 for R = Me [12] or Et [9]. In both trimethylsilylmethylaluminium compounds described here, aluminium achieves a coordination number of four, as usual in organometallic compounds.

Experimental

Liquids and solids were transferred under nitrogen in a drybag and volatile materials were measured and manipulated by vacuum line.

Tris(trimethylsilylmethyl)aluminium

Aluminium foil (10.8 g, 0.4 mole), amalgamated with one drop of mercury, was heated under reflux with bis(trimethylsilylmethyl)mercury (22.5 g, 0.06 mole) in toluene (100 ml) for 14 days. The reaction mixture was distilled on a Vigreux column at atmospheric pressure to remove solvent, and then at reduced pressure, giving tris(trimethylsilylmethyl)aluminium, b.p. 51° at 0.08 mm, m.p. —22°. Yield 7.8 g, 67%. (Found: C, 49.8; H, 11.6. $C_{12}H_{33}AlSi_3$ calcd.: C, 49.9; H, 11.5%.) Molecular weights, measured cryoscopically in benzene, were 434(13.4 wt.%) 364 (4.5 wt.%) 346 (0.6 wt.%) (calcd.: monomer, 288; dimer, 576). IR: 2949s, 2891m, 1420w(br), 1342w, 1260m, 1250s, 959s, 922s, 854s, 826s, 757s, 729m, 686m, 651m. Raman: 2941s, 2884s, 1400w(br), 1344w, 1255w, 744w, 694m, 619s, 502m, 250w, 220w, 178w, 140w cm^{-1}.

An attempt to make tris(trimethylsilylmethyl)gallium by a similar reaction was not successful. 56% of the starting bis(trimethylsilylmethyl) mercury was recovered after heating under reflux in toluene for 23 days, and no volatile gallium derivative was isolated from the brown tarry residue.

Cyclodi-μ-methylamidobis[bis(trimethylsilylmethyl)aluminium]

Methylamine (7.7 mmole) was condensed slowly at −78° on to tris(trimethylsilylmethyl)aluminium (2.21 g, 7.7 mmole), and the resulting liquid complex was heated for 3 h at 110°. Tetramethylsilane (7.5 mmole) was collected in the vacuum line and identified by its IR and NMR spectra, and the methylamido derivative, m.p. 82°, was recrystallised from n-heptane. Yield after recrystallisation 1.8 g, 80%. [Found: C, 46.2; H, 11.2, N, 5.95; mol. wt. (2.4 wt.% soln.), 465. $C_{18}H_{52}Al_2N_2Si_4$ calcd.: C, 46.7; H, 11.3; N, 6.05%; mol. wt., 462.] IR (Nujol): 3300w, 1258m, 1246s, 1135w, 1063w, 1026m, 967s, 934m, 857s, 824s, 804s, 740-751s, 681m cm^{-1}.

Other samples of the compound $[(Me_3SiCH_2)_2AlNHMe]_2$ were obtained by the reaction between methylamine and the etherate $(Me_3SiCH_2)_3Al \cdot OEt_2$, b.p. 82° at 0.8 mm, made from the Grignard reagent Me_3SiCH_2MgCl and aluminium chloride in diethyl ether. (This etherate has been made independently by other workers [14]). The ether was displaced quantitatively (found 94%) by methylamine at 20°, and was pumped away from the methylamine adduct before this was heated. $[(Me_3SiCH_2)_2AlNHMe]_2$ sublimed at about 90° at 0.1 mm, but an attempt to separate isomers, like those of the analogous $(Me_2AlNHMe)_3$ [12] by fractional sublimation was not successful. When $[(Me_3SiCH_2)_2AlNHMe]_2$ (0.207 g, 0.446 mmole) was treated with 2 *N* sulphuric acid (5 ml), Me_4Si (1.75 mmole) was collected in the vacuum system. The aqueous solution was made up to 100 ml and aliquots treated with 8-hydroxyquinoline to precipitate aluminium and with 30% sodium hydroxide solution in a Markham still to liberate methylamine. Al^{3+} (0.890 mmole) and $MeNH_2$ (0.884 mmole) were found: thus the hydrolysis of the amido derivative is clean and quantitative and its chemical composition is confirmed.

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