

Hexamethyldisiloxane and Hexamethyldisilathiane: Reactions with Covalent Metal Halides

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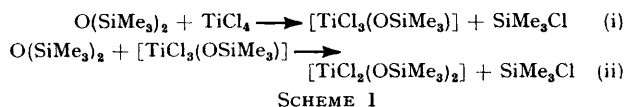
Reactions of $\text{O}(\text{SiMe}_3)_2$ (1) and $\text{S}(\text{SiMe}_3)_2$ (2) with TiCl_4 and SnCl_4 are described. For (1), Si–O cleavage and release of SiMe_3Cl , as monitored by ^1H n.m.r. spectroscopy, occurs only in the case of TiCl_4 to give $[\text{Me}_3\text{SiO}(\text{Cl})\text{TiO}]_n$. Trichloromethylstannane is the major reaction product with SnCl_4 . With (2), TiCl_4 gives monomeric complexes $\text{TiCl}_2\text{S}\cdot 2\text{L}$ ($\text{L} = \text{MeCN}$) and $\text{TiCl}_2\text{S}\cdot 3\text{L}$ [$\text{L} = \text{MeCN}$ or tetrahydrofuran (thf)] following solvation of the polymeric $(\text{Cl}_2\text{TiS})_n$ formed initially. A six-co-ordinate formulation is proposed based on spectral data. The corresponding $(\text{Cl}_2\text{SnS})_n$ formed with SnCl_4 does not give similar lattice degradation with strong donors. The lower halides $\text{MCl}_3\cdot 3\text{thf}$ ($\text{M} = \text{Ti, V, or Cl}$) react with (2) only to give SiMe_3Cl and polymeric complexes $\text{MCl}(\text{S})\cdot n\text{thf}$ ($\text{M} = \text{Ti or Cr}$) and VClS_4 .

HEXAMETHYLDISILOXANE (1) and hexamethyldisilathiane (2) are both potential σ donors but no such behaviour has been noted. Delocalisation of the lone pairs in (1), as indicated by angle $\text{SiOSi } 148^\circ$,¹ appreciably weakens the O-donor capacity relative to an aliphatic ether. $\pi_{\text{p-d}}$ bonding is less important in the Si–S bond; in fact, i.r. and Raman spectral studies indicate a bond order of 1.00 and an angle $\text{SiSSi } 104^\circ$ for (2).² Interaction of thiosilanes and disilathianes with various metal^{3,4} and non-metal⁵ halides does not give complex formation but rather alkyl or aryl mercaptides, sulphides, or sulphonium derivatives *via* fission of Si–S bonds. Reaction with alkyl halides gives alkylhalogenosilanes and organic sulphides.⁶ Compound (1) behaves similarly to give the corresponding halogenotrimethylsilane and either siloxy-derivatives or the oxide.⁷ The reactions of (1) and (2) with representative, early transition-metal chlorides and tin(IV) chloride are now described.

DISCUSSION

Recently we have shown that titanium(IV) chloride and tris(trimethylsilyl)amine react (Si–N cleavage) to give chlorotrimethylsilane and $(\text{Cl}_2\text{TiNSiMe}_3)_2$. The latter features planar dimeric titanium–nitrogen rings polymerised *via* chlorine bridges.⁸ In particular it was expected that analogous reactions with (1) (Si–O cleavage) and (2) (Si–S cleavage) would lead to discrete $(\text{Cl}_2\text{TiO})_n$ and $(\text{Cl}_2\text{TiS})_n$ cyclic systems.

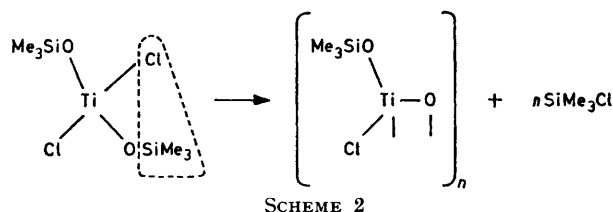
Reactions of (1).—The reaction between TiCl_4 and (1) has been reported to yield mono- and di-siloxy-derivatives (Scheme 1).⁹ In our work the reaction was conveniently



monitored by ^1H n.m.r. spectroscopy. Equimolar proportions of TiCl_4 and $\text{O}(\text{SiMe}_3)_2$ were directly mixed in an n.m.r. tube and sealed. Spectra were recorded over a period of 15 min by which time (1) had been totally consumed. The disappearance of (1) is accompanied by the appearance of a single peak at δ 0.38 due to both chlorotrimethylsilane and trichloro(trimethylsiloxy)-titanium(IV) [equation (i)].

With 1 : 2 molar proportions of TiCl_4 and $\text{O}(\text{SiMe}_3)_2$ the reaction is much slower and unchanged (1) is still present after 2 d. Initially the reaction proceeds as previously but after *ca.* 40 min the band at δ 0.38 begins to broaden and eventually splits into two singlets, *viz.* a peak at δ 0.41 due mainly to SiMe_3Cl with a contribution from $[\text{TiCl}_3(\text{OSiMe}_3)]$ and one at δ 0.33 due to $[\text{TiCl}_2(\text{OSiMe}_3)_2]$ ¹⁰ [equation (ii)]. After *ca.* 10 d a white solid (A) precipitates. The ^1H n.m.r. spectrum of the residual liquid shows a decreased intensity of the δ 0.33 signal relative to that at δ 0.41 suggestive of further reaction (Scheme 2).

A 1 : 4 mixture of TiCl_4 and $\text{O}(\text{SiMe}_3)_2$ reacts similarly but very much slower than either of the other two. Formation of tri- and/or tetra-siloxy-derivatives under these conditions is discounted since there are no new



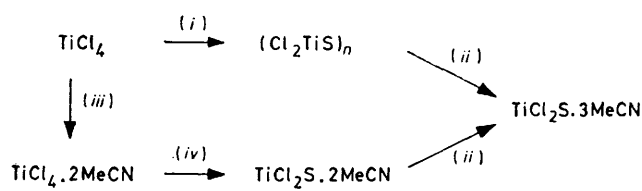
resonances. The liquid remaining after complete precipitation of (A) exhibits only two peaks due to SiMe_3Cl and unchanged (1) respectively.

The white insoluble solid (A) analyses for $[\text{TiCl}(\text{O}(\text{SiMe}_3))]_n$ and is extremely sensitive to air and moisture. The intense i.r. band at 470 cm^{-1} assigned as $\nu(\text{TiCl})$ (terminal) is indicative of a tetrahedral titanium(IV) species¹¹ so that polymerisation through bridging chlorine seems unlikely. M–O–Si systems exhibit two characteristic i.r. absorptions: an intense band ($900\text{--}950\text{ cm}^{-1}$) due to $\nu(\text{Si–O})$ and a second somewhat weaker band ($500\text{--}600\text{ cm}^{-1}$) due to $\nu(\text{M–O})$.^{12,13} Two such bands are observed at 985 and 590 cm^{-1} . The band at 755 cm^{-1} $\nu(\text{SiMe}_3)$ probably contains a significant contribution from $\nu(\text{TiOTi})$.¹⁴ The complex is completely stable with respect to further chlorotrimethylsilane elimination.

The main product obtained from reaction of (1) with SnCl_4 , even at 323 K , was trichloro(methyl)stannane.

The residual liquid shows a complex ^1H n.m.r. spectrum and further separation attempts proved inconclusive. Emphatically, no SiMe_3Cl was evolved. The same reaction, carried out at 543 K, has been briefly reported¹⁵ to yield SnMeCl_3 , chloro-derivatives of the type $\text{SiR}(\text{CH}_3)_2\text{Cl}$ ($\text{R} = \text{CH}_3$ or an extension of the siloxane chain), and methyl chloride (from decomposition of SnMeCl_3). The contrasting formation of siloxy-derivatives in the case of titanium(IV) chloride is seen as a direct result of the relative O-acceptor capacity $\text{Ti} > \text{Sn}$ whereby Ti-O bonds are preferentially formed at the expense of siloxane Si-O linkages.

Reactions of (2).—Reaction between titanium(IV) chloride and (2) proceeds extremely rapidly, even at 96 K, to yield dark brown polymeric dichlorotitanium(IV) sulphide $(\text{Cl}_2\text{TiS})_n$ contaminated with a small amount of polymeric titanium sulphide. Treatment with a strong donor solvent, *e.g.* $\text{L} = \text{CH}_3\text{CN}$, pyridine (py), or tetrahydrofuran (thf), effectively breaks down the polymeric lattice of the former to give soluble monomeric adducts $\text{TiCl}_2\text{S}\cdot 3\text{L}$. The titanium sulphide impurity is completely insoluble and can be easily removed by filtration. Alternatively, blocking the empty co-ordination sites of



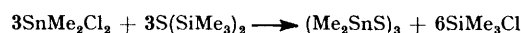
SCHEME 3 (i) $\text{S}(\text{SiMe}_3)_2$, benzene, 273 K; (ii) excess of MeCN; (iii) MeCN; (iv) $\text{S}(\text{SiMe}_3)_2$, benzene

titanium(IV) chloride by initial adduct formation, *e.g.* $\text{TiCl}_4\cdot 2\text{MeCN}$, does not appreciably affect the rate of reaction but does allow the 1 : 2 adduct $\text{TiCl}_2\text{S}\cdot 2\text{MeCN}$ to be isolated. This is easily converted to the 1 : 3 adduct in an excess of donor solvent (Scheme 3).

The $\nu(\text{TiCl})$ stretching frequencies occur at 363, 325, and 270 cm^{-1} for the tris(acetonitrile) adduct and at 365, 325, and 272 cm^{-1} for the tris(tetrahydrofuran) adduct as expected for octahedral titanium(IV) complexes.¹⁶ Those for the bis(acetonitrile) complex are of slightly higher energy but not sufficient to indicate five-co-ordination; an octahedral geometry incorporating sulphur and/or chlorine bridges is preferred. The $\nu(\text{CN})$ stretching mode increases on co-ordination, *e.g.* 2 308 cm^{-1} for $\text{TiCl}_2\text{S}\cdot 2\text{MeCN}$, 2 280 cm^{-1} for $\text{TiCl}_2\text{S}\cdot 3\text{MeCN}$, as expected,^{17,*} and in $\text{TiCl}_2\text{S}\cdot 3\text{thf}$ the C-O-C antisymmetric stretching mode shows the conspicuous frequency decrease with splitting to give two intense bands at 1 038 and 1 015 cm^{-1} .¹⁸

Tin(IV) chloride in benzene solution reacts rapidly with (2) to provide a mustard-yellow precipitate and release of SiMe_3Cl . The product which analyses for SnCl_2S is almost certainly polymeric but does not give lattice breakdown with strong donors as found with the

titanium(IV) counterpart. To confirm this point the separate reaction using dimethyltin dichloride was carried out. The products obtained were SiMe_3Cl and a white solid identified as the authentic trimer $(\text{Me}_2\text{SnS})_3$ (Scheme 4).¹⁹



SCHEME 4

Reaction of $\text{TiCl}_3\cdot 3\text{thf}$ with (2) in tetrahydrofuran solution produced the insoluble (polymeric) grey solid $\text{TiCl}(\text{S})\cdot 1.5\text{thf}$ and SiMe_3Cl . Infrared bands at 355vs, 325vs, 295s,br, and 270s,br cm^{-1} are assigned to $\nu(\text{TiCl})$ stretching modes for octahedral Ti^{III} ,¹⁶ with some contribution from $\nu(\text{TiS})$ in the latter; the two intense bands at 1 035 and 1 005 cm^{-1} [$\nu_{\text{asym}}(\text{COC})$] confirm the presence of co-ordinated solvent. Direct treatment with $\text{VCl}_3\cdot 3\text{thf}$ in tetrahydrofuran solution resulted in release of SiMe_3Cl and the surprising formation of a black insoluble vanadium sulphide VClS_4 .^{20,21} There is no co-ordinated solvent present. The compound $\text{CrCl}_3\cdot 3\text{thf}$ readily reacts with (2) in tetrahydrofuran solution to give SiMe_3Cl and the brown insoluble $\text{CrCl}(\text{S})\cdot 1.5\text{thf}$. Infrared bands at 360vs, 342s, 305br, and 270br cm^{-1} [$\nu(\text{CrCl})$] and 1 035 and 1 015 cm^{-1} [$\nu(\text{COC})$] suggest a six-co-ordinate (polymeric) formulation, *cf.* $\text{Cr}(\text{SMe})_3$.²²

EXPERIMENTAL

Extreme care was taken to exclude air and moisture from reaction systems and products. Solvents were distilled over CaH_2 or P_2O_5 under a nitrogen atmosphere; tetrahydrofuran was distilled over Na and benzoquinone under vacuum.

The compounds $\text{O}(\text{SiMe}_3)_2$ (1)²³ and $\text{S}(\text{SiMe}_3)_2$ (2)²⁴ were prepared by literature methods: (1) was rapidly (to prevent phosphate formation) distilled from P_2O_5 to ensure complete removal of water; (2) was distilled under a nitrogen atmosphere (b.p. 162 °C) and stored in a flask fitted with a Subaseal cap to allow ready withdrawal of required quantities by syringe. (NB. Extreme caution is needed in handling (2) since even minute traces in the atmosphere give the most unpleasant sulphur odour. We thank our laboratory colleagues for their forbearance during this work.) The anhydrous metal halides were used as supplied commercially. The 1 : 3 adducts $\text{MCl}_3\cdot 3\text{thf}$ ($\text{M} = \text{Ti}, \text{V}$, or Cr) were prepared by repeated extraction of the appropriate halide with boiling solution using a Soxhlet apparatus under a nitrogen atmosphere.

Infrared spectra were obtained using Perkin-Elmer 621 (200—4 000 cm^{-1}) and Fourier FS720 (50—200 cm^{-1}) instruments with samples as Nujol and hexachlorobutadiene mulls. Proton n.m.r. spectra were recorded on a Brüker WH90 spectrometer (90 MHz) with SiMe_4 as internal reference.

Reactions of (1).† (a) *With TiCl_4 .* Compound (1) (15 cm^3 , 70.57 mmol) and TiCl_4 (3.90 cm^3 , 35.48 mmol) were syringed into an ampoule (capacity *ca.* 100 cm^3) which was evacuated and sealed at -96 K. Slow precipitation of a white solid commenced after *ca.* 10 d. After 1 month the white solid was collected, washed thoroughly with hexane,

† In each experiment the formation (or otherwise) of chlorotrimethylsilane was confirmed by careful fractionation of the resulting filtrate: SiMe_3Cl , b.p. 332 K; ^1H n.m.r., δ 0.38.

* *cf.* $\nu(\text{C}\equiv\text{N})$ of $\text{TiCl}_4\cdot 2\text{MeCN}$ at 2 304 cm^{-1} (H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522).

and pumped dry to give a felt-like mass of minute white needles, which showed complete insolubility in all common organic solvents (5.87 g, 88%; m.p. >523 K) (Found: C, 20.1; H, 4.7; Cl, 18.2. $C_3H_9ClO_2SiTi$ requires C, 19.1; H, 4.8; Cl, 18.8%).

(b) *With $SnCl_4$.* Compound (1) (7.40 cm³, 34.82 mmol) and $SnCl_4$ (1 cm³, 8.68 mmol) were placed in an ampoule as above. Slow precipitation of a white solid occurred at 323 K. Vacuum sublimation gave $SnMeCl_3$ (0.21 g, 10%) as confirmed by its i.r. and ¹H n.m.r. spectra.

*Reactions of (2).** *With $TiCl_4$. Method (a).* Compound (2) (4 cm³, 19.10 mmol) and $TiCl_4$ (2 cm³, 18.2 mmol) were each dissolved in benzene (ca. 100 cm³) and both solutions slowly dripped into benzene (ca. 100 cm³) contained in a round-bottomed flask (500 cm³) with continuous stirring at 273 K. Immediate reaction occurred to precipitate a dark brown solid, which was filtered off, thoroughly washed with benzene, and pumped dry (2.67 g, 97%). Infrared spectrum (cm⁻¹): 1 255m, 1 080mbr, 1 040m, 995m, 830s, 675m, and 350s.

The dark brown solid (1.25 g) was placed in an ampoule (ca. 100 cm³) with acetonitrile (ca. 50 cm³), evacuated and sealed at 96 K. On warming to room temperature an orange-red solution developed. A trace of an insoluble black residue was filtered off, washed with acetonitrile, and pumped dry (Found: S, 25.3. Ti_2S requires S, 25.1%). The solvent was removed from the filtrate to give a red solid (1.83 g, 81%) which was insoluble in non-co-ordinating solvents but soluble with reaction in co-ordinating ones [Found: C, 26.8; H, 3.6; Cl, 25.6; N, 15.0%; *M*, 291 (osmometry in acetonitrile). $C_6H_9Cl_2N_3STi$ requires C, 26.3; H, 3.3; Cl, 25.8; N, 15.3%; *M*, 274]. Infrared, data (cm⁻¹): 2 945w, 2 918m, 2 840w, 2 305m, 2 280m, 2 242w (sh), 1 734m, 1 670m, 1 630m, 1 570m, 1 400m, 1 360m, 1 295m, 1 257m, 1 210m, 1 190w (sh), 1 150vw, 1 085s, 932m (sh), 880s,br, 840s,br, 800s,br, 750s,br, 720m (sh), 615m, 545vs, 485w, 400m (sh), 363s, 325vs, 270w, and 195m. Hydrogen-1 n.m.r. data in $S(CD_3)_2O$: δ 2.08 (s).

Method (b). Titanium(IV) chloride (2 cm³, 18.2 mmol) was dissolved in benzene (ca. 100 cm³) and acetonitrile (1.50 g, 36.54 mmol) added to give the bis(acetonitrile) adduct as a slurry in benzene. A solution of (2) (4 cm³, 19.1 mmol) in benzene (ca. 150 cm³) was added dropwise into this slurry at room temperature to give an orange-brown precipitate. The solid product was filtered off, washed with benzene, and pumped dry (4.1 g, 96%) (Found: C, 20.0; H, 2.5; Cl, 30.1; N, 12.0. $C_4H_6Cl_2N_2STi$ requires C, 20.6; H, 2.6; Cl, 30.4; N, 12.0%). Infrared data (cm⁻¹): 2 980vw, 2 950vw, 2 920s, 2 850w, 2 308s, 2 280s, 1 585w,br, 1 400w, 1 355m, 1 250vw, 1 020m, 943m, 840w, 800vw,br, 680 vw, 550w, 400s (sh), 376s, and 320m (sh). Hydrogen-1 n.m.r. in $S(CD_3)_2O$: δ 1.98 (s).

Treatment of the orange-brown solid with an excess of acetonitrile yielded a red solution which on removal of solvent gave the orange-red solid $TiCl_2S \cdot 3MeCN$ identical with the product obtained in (a).

Method (a) was used to similarly prepare $TiCl_2S \cdot 3thf$ as an orange-red solid (Found: C, 39.1; H, 6.7; Cl, 19.1. $C_{12}H_{24}Cl_2O_3STi$ requires C, 39.2; H, 6.6; Cl, 19.3%). This product was insoluble in non-polar media but soluble with reaction in co-ordinating solvents. Infrared data (cm⁻¹): 2 950s, 2 860s, 2 800w (sh), 1 640w, 1 580vw, 1 445s, 1 410w, 1 362m, 1 342m, 1 300m, 1 255vs, 1 170w, 1 090vs

* See footnote † on previous page.

(sh), 1 072vs, 1 038vs, 1 015vs, 915m, 840s, 800vs, 720vs, 665m, 540m, 496w (sh), 365vs,br, 325vs,br, 272w, and 198m. Hydrogen-1 n.m.r. data in $S(CD_3)_2O$: δ 1.49 (1), 1.74 (2), 3.35 (1) and 3.58 (2) (all slightly broadened singlets).

(c) *With $SnCl_4$.* Compound (2) (4 cm³, 16.52 mmol) was added dropwise to $SnCl_4$ (2 cm³, 17.35 mmol) dissolved in benzene (ca. 150 cm³). Immediate reaction occurred to precipitate a yellow solid which on stirring overnight darkened to a mustard colour. The product was filtered off, washed thoroughly with benzene and hexane, and pumped dry (3.16 g, 82%) (Found: Cl, 31.7; S, 15.1. $SnCl_2S$ requires Cl, 32.0; S, 14.5%). The mustard solid was insoluble in all common organic solvents and showed no reaction with thf, acetonitrile, dimethylformamide, or dimethyl sulphoxide after prolonged contact at 323 K. Infrared data (cm⁻¹): 1 270m, 1 090m,br, 1 040s,br, 805s, 730vw, 550vw, 325s (sh), and 260vs.

(d) *With $SnMe_2Cl_2$.* The compound $SnMe_2Cl_2$ (5.01 g, 22.81 mmol) and (2) (5.50 cm³, 22.71 mmol), each dissolved in benzene (ca. 100 cm³) were slowly added to benzene (ca. 100 cm³) contained in a round-bottomed flask (500 cm³). After stirring overnight, a white precipitate started to form. The white product formed after ca. 10 d was filtered off, washed thoroughly with benzene, and carefully purified by vacuum sublimation. Infrared and ¹H n.m.r. data confirm the product as $(Me_2SnS)_3$.¹⁹

(e) *With $TiCl_3 \cdot 3thf$.* Compound (2) (1.45 cm³, 5.99 mmol), diluted with tetrahydrofuran (ca. 25 cm³), was slowly dripped into an ampoule (capacity ca. 100 cm³) containing a tetrahydrofuran solution of $TiCl_3$ (0.92 g, 5.96 mmol). The ampoule was evacuated and sealed at 96 K. On warming to 323 K a grey precipitate and slate-grey solution developed. The grey solid was washed with hexane and pumped dry. The product (0.83 g) showed a slight solubility in polar solvents but was insoluble in non-polar ones (Found: C, 32.5; H, 5.5; Cl, 18.0. $TiCl(S) \cdot 1.5thf$ requires C, 32.2; H, 5.4; Cl, 16.9%).

(f) *With $VCl_3 \cdot 3thf$.* A mixture of (2) (1.6 cm³, 6.6 mmol) and $VCl_3 \cdot 3thf$ (2.50 g, 6.69 mmol) was placed in an ampoule (ca. 250 cm³) and tetrahydrofuran (ca. 100 cm³) was added. The ampoule was evacuated and sealed at 96 K. On warming to room temperature the solution slowly precipitated a black solid which was filtered off and washed with thf to remove unchanged reactants. The black product was insoluble in all common organic solvents (0.25 g, 17.7%) (Found: S, 57.9; V, 24.2. $VClS_4$ requires S, 59.8; V, 23.7%). Chloride estimates proved unreliable.

(g) *With $CrCl_3 \cdot 3thf$.* A mixture of $CrCl_3 \cdot 3thf$ (4.11 g, 10.96 mmol), dissolved in thf (ca. 100 cm³), and (2) (2.60 cm³, 10.73 mmol) was placed in an ampoule (250 cm³), which was then evacuated and sealed at 96 K. On warming to 323 K a dark brown solid slowly separated. This was filtered off, washed with thf and hexane, and pumped dry *in vacuo* at room temperature (Found: C, 28.3; H, 4.5; Cl, 15.5; S, 13.6. $CrCl(S) \cdot 1.5thf$ requires C, 31.5; H, 5.3; Cl, 15.5; S, 14.0%). Again there is complete insolubility in the common solvents.

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