Hexamethyldisiloxane and Hexamethyldisilathiane: Reactions with Covalent Metal Halides

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Reactions of $O(SiMe_3)_2$ (1) and $S(SiMe_3)_2$ (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 $[Me_3SiO(Cl)TiO]_n$. Trichloromethylstannane is the major reaction product with $SnCl_4$. With (2), $TiCl_4$ gives monomeric complexes $TiCl_2S{\cdot}2L$ (L = MeCN) and $TiCl_2S{\cdot}3L$ [L = MeCN or tetrahydrofuran (thf)] following solvation of the polymeric $(Cl_2TiS)_n$ formed initially. A six-co-ordinate formulation is proposed based on spectral data. The corresponding $(Cl_2SnS)_n$ formed with $SnCl_4$ does not give similar lattice degradation with strong donors. The lower halides $MCl_3{\cdot}3thf$ (M = Ti, V, or Cl) react with (2) only to give $SiMe_3Cl$ and polymeric complexes $MCl(S){\cdot}n$thf (M = 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 SiOSi 148°,[1] appreciably weakens the O-donor capacity relative to an aliphatic ether. $\pi_{p\text{-}d}$ 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 SiSSi 104° for (2).[2] Interaction of thiosilanes and disilathianes with various metal[3,4] and non-metal[5] 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 $(Cl_2TiNSiMe_3)_2$. 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 $(Cl_2TiO)_n$ and $(Cl_2TiS)_n$ 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 $O(SiMe_3)_2$ 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(trimethylsiloxo)titanium(IV) [equation (i)].

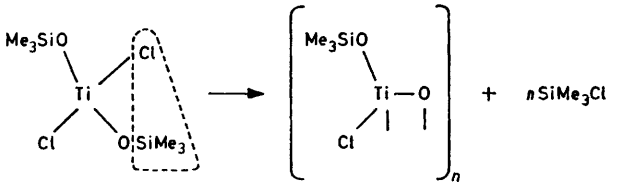
$$O(SiMe_3)_2 + TiCl_4 \longrightarrow [TiCl_3(OSiMe_3)] + SiMe_3Cl \qquad (i)$$

$$O(SiMe_3)_2 + [TiCl_3(OSiMe_3)] \longrightarrow [TiCl_2(OSiMe_3)_2] + SiMe_3Cl \qquad (ii)$$

SCHEME 1

With 1 : 2 molar proportions of $TiCl_4$ and $O(SiMe_3)_2$ 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 $[TiCl_3(OSiMe_3)]$ and one at δ 0.33 due to $[TiCl_2(OSiMe_3)_2]$[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 $O(SiMe_3)_2$ 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.



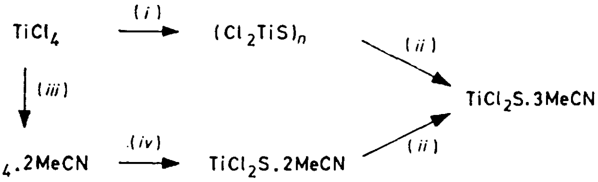
SCHEME 2

The white insoluble solid (A) analyses for $[TiCl(O)(OSiMe_3)]$ and is extremely sensitive to air and moisture. The intense i.r. band at 470 cm^{-1} assigned as ν(TiCl) (terminal) is indicative of a tetrahedral titanium(IV) species[11] so that polymerisation through bridging chlorine seems unlikely. M–O–Si systems exhibit two characteristic i.r. absorptions: an intense band (900—950 cm^{-1}) due to ν(Si–O) and a second somewhat weaker band (500—600 cm^{-1}) due to ν(M–O).[12,13] Two such bands are observed at 985 and 590 cm^{-1}. The band at 755 cm^{-1} $\rho(SiMe_3)$ probably contains a significant contribution from ν(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 reported [15] to yield $SnMeCl_3$, chloro-derivatives of the type $SiR(CH_3)_2Cl$ ($R = CH_3$ 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 Ti > 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 $(Cl_2TiS)_n$ contaminated with a small amount of polymeric titanium sulphide. Treatment with a strong donor solvent, *e.g.* $L = CH_3CN$, pyridine (py), or tetrahydrofuran (thf), effectively breaks down the polymeric lattice of the former to give soluble monomeric adducts $TiCl_2S$·3L. The titanium sulphide impurity is completely insoluble and can be easily removed by filtration. Alternatively, blocking the empty co-ordination sites of titanium(IV) chloride by initial adduct formation, *e.g.* $TiCl_4$·2MeCN, does not appreciably affect the rate of reaction but does allow the 1 : 2 adduct $TiCl_2S$·2MeCN to be isolated. This is easily converted to the 1 : 3 adduct in an excess of donor solvent (Scheme 3).



SCHEME 3 (*i*) $S(SiMe_3)_2$, benzene, 273 K; (*ii*) excess of MeCN; (*iii*) MeCN; (*iv*) $S(SiMe_3)_2$, benzene

The ν(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 ν(CN) stretching mode increases on co-ordination, *e.g.* 2 308 cm^{-1} for $TiCl_2S$·2MeCN, 2 280 cm^{-1} for $TiCl_2S$·3MeCN, as expected,[17,*] and in $TiCl_2S$·3thf 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 $(Me_2SnS)_3$ (Scheme 4).[19]

$$3SnMe_2Cl_2 + 3S(SiMe_3)_2 \longrightarrow (Me_2SnS)_3 + 6SiMe_3Cl$$

SCHEME 4

Reaction of $TiCl_3$·3thf with (2) in tetrahydrofuran solution produced the insoluble (polymeric) grey solid $TiCl(S)$·1.5thf and $SiMe_3Cl$. Infrared bands at 355vs, 325vs, 295s,br, and 270s,br cm^{-1} are assigned to ν(TiCl) stretching modes for octahedral Ti^{III},[16] with some contribution from ν(TiS) in the latter; the two intense bands at 1 035 and 1 005 cm^{-1} [ν_{asym}(COC)] confirm the presence of co-ordinated solvent. Direct treatment with VCl_3·3thf 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 $CrCl_3$·3thf readily reacts with (2) in tetrahydrofuran solution to give $SiMe_3Cl$ and the brown insoluble $CrCl(S)$·1.5thf. Infrared bands at 360vs, 342s, 305br, and 270br cm^{-1} [ν(CrCl)] and 1 035 and 1 015 cm^{-1} [ν(COC)] suggest a six-co-ordinate (polymeric) formulation, *cf.* $Cr(SMe)_3$.[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 $O(SiMe_3)_2$ (1) [23] and $S(SiMe_3)_2$ (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 MCl_3·3thf (M = Ti, 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,

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[*] *cf.* ν(C≡N) of $TiCl_4$·2MeCN at 2 304 cm^{-1} (H. J. Coerver and C. Curran, *J. Amer. Chem. Soc.*, 1958, **80**, 3522).

[†] 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.

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 cm^3, 34.82 mmol) and $SnCl_4$ (1 cm^3, 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 cm^3, 19.10 mmol) and $TiCl_4$ (2 cm^3, 18.2 mmol) were each dissolved in benzene (*ca.* 100 cm^3) and both solutions slowly dripped into benzene (*ca.* 100 cm^3) contained in a round-bottomed flask (500 cm^3) 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 cm^3) with acetonitrile (*ca.* 50 cm^3), 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 cm^3, 18.2 mmol) was dissolved in benzene (*ca.* 100 cm^3) 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 cm^3, 19.1 mmol) in benzene (*ca.* 150 cm^3) 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 $TiCl_2S\cdot3MeCN$ identical with the product obtained in (*a*).

Method (*a*) was used to similarly prepare $TiCl_2S\cdot3thf$ 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 (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 cm^3, 16.52 mmol) was added dropwise to $SnCl_4$ (2 cm^3, 17.35 mmol) dissolved in benzene (*ca.* 150 cm^3). 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 cm^3, 22.71 mmol), each dissolved in benzene (*ca.* 100 cm^3) were slowly added to benzene (*ca.* 100 cm^3) contained in a round-bottomed flask (500 cm^3). 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* $TiCl_3\cdot3thf$. Compound (2) (1.45 cm^3, 5.99 mmol), diluted with tetrahydrofuran (*ca.* 25 cm^3), was slowly dripped into an ampoule (capacity *ca.* 100 cm^3) 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. $TiCl(S)\cdot1.5thf$ requires C, 32.2; H, 5.4; Cl, 16.9%).

(*f*) *With* $VCl_3\cdot3thf$. A mixture of (2) (1.6 cm^3, 6.6 mmol) and $VCl_3\cdot3thf$ (2.50 g, 6.69 mmol) was placed in an ampoule (*ca.* 250 cm^3) and tetrahydrofuran (*ca.* 100 cm^3) 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* $CrCl_3\cdot3thf$. A mixture of $CrCl_3\cdot3thf$ (4.11 g, 10.96 mmol), dissolved in thf (*ca.* 100 cm^3), and (2) (2.60 cm^3, 10.73 mmol) was placed in an ampoule (250 cm^3), 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. $CrCl(S)\cdot1.5thf$ 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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* See footnote † on previous page.

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