

Some highly sterically hindered organosilicon compounds

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Abstract - The chemistry of organometallic compounds with bulky ligands such as $(\text{Me}_3\text{Si})_3\text{C}(\text{Tsi})$ or $(\text{Me}_2\text{PhSi})_3\text{C}(\text{Tpsi})$ attached to a variety of metal centres is reviewed. The compounds Tsi_2M ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$) and the rare two co-ordinate Tsi_2Mn show exceptional thermal and hydrolytic stability. The corresponding alkylmetal halides form ring or cage structures. In a range of new boron compounds the structures of $\text{TpsiBF}(\text{OH})$ and $\text{TpsiB}(\mu\text{-H})_3\text{Li}(\text{thf})_3$ are especially interesting. Each of the three metal-carbon bonds in the $\text{Me-SiMe}_2\text{-C}(\text{SiMe}_3)_2\text{-M}$ systems may participate in reactions at the metal centre.

INTRODUCTION

New insight into organometallic chemistry has been gained from the isolation of compounds with large alkyl groups. This paper deals with tris(trimethylsilyl)methyl $(\text{Me}_3\text{Si})_3\text{C}$ (denoted by Tsi), or tris(dimethylphenylsilyl)methyl $(\text{Me}_2\text{PhSi})_3\text{C}$ (Tpsi), derivatives of a variety of elements. Derivatives of silicon, i.e. those with the TsiSi or TpsiSi systems, have been reviewed elsewhere (ref. 1 and 2).

The starting material for the preparation of tris(trimethylsilylmethyl)metal derivatives is TsiH, made in 50-70% yield from lithium metal, Me_3SiCl and chloroform. The methine hydrogen, which has a kinetic acidity about five times that of the methine hydrogen in triphenylmethane, may be removed by the strong base methyl-lithium in ether-tetrahydrofuran (thf) to give 90% yields of the reagent TsiLi which reacts with a wide range of metal halides. TpsiH may be made in lower (35%) yield from CCl_4 , magnesium and Me_2PhSiCl and converted to TpsiLi by reaction with methyl-lithium (ref. 3). The size of the Tsi or Tpsi groups restricts the number which may be accommodated round one metal centre, and no compounds with more than two Tsi groups bound to one atom have been made.

BIS[TRIS(TRIMETHYLSILYL)METHYL]METAL DERIVATIVES

The anhydrous halides MCl_2 ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ or Mn) react with an excess of TsiLi in ether/thf to give good yields of the dialkyl compounds Tsi_2M . The white derivatives of the Group 12 elements (ref. 4 and 5) and the pale yellow manganese compound (ref. 6) show remarkable thermal stability: all melt sharply, without decomposition, at ca. 300°C , though TsiH is formed slowly above ca. 320°C . The zinc compound is unusually stable hydrolytically: whereas dimethylzinc reacts explosively with water, Tsi_2Zn may be distilled unchanged in steam. Tsi_2Mn is slowly hydrolysed by wet thf to TsiH, and rapidly attacked by molecular oxygen to give unidentified products. The magnetic moment ($\mu_B = 5.1$), which does not vary significantly between 213 and 343 K, indicates a high spin d^5 species.

The centrosymmetrical molecule (Figure 1) is the first example of two-coordinate manganese, though bis(neopentyl)manganese has since been shown to be monomeric in the gas phase (ref. 7).

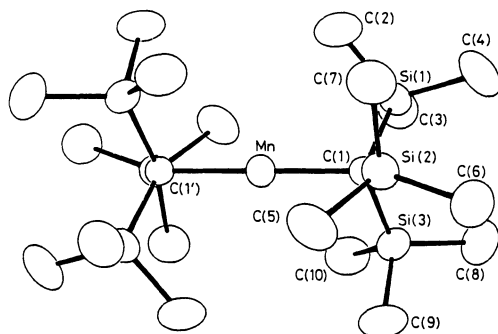


Fig. 1 The molecular structure of $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{Mn}$. Mn-C(1) 210.2(4)
C(1)-Si 188.1(8) Si-Me 188.3(9) pm
SiC(1)Si 112.3(2) C(1)SiMe 113.1(16),
MeSiMe 105.6(17) $^\circ$.

Steric hindrance is shown by the opening of the SiC(1)Si angles from the tetrahedral value, by the contraction of the MeSiMe angles, and by the fact that the distance (300 pm) between the planes defined by C(2), C(5) and C(10) and by C(2)', C(5)' and C(10)' is considerably less than the sum of the Van der Waals radii of the methyl groups. This accounts for the low coordination number of the manganese and the slow hydrolysis. The crystal packing is dominated by the methyl groups on the periphery of the molecule, and this explains the closely similar melting points of the Zn, Cd, Hg and Mn derivatives. The high thermal stability of these compounds suggests that the rate-determining step in decomposition is not simply homolytic fission of metal-carbon bonds, since that would be assisted rather than inhibited by intramolecular steric hindrance. Most probably the decomposition can proceed only if the radical Tsi· is able to become sufficiently free to abstract a hydrogen atom by bimolecular attack on another species.

The only other bis[tris(trimethylsilyl)methyl]metal species are in the ate complexes $[\text{LiL}_n][\text{Tsi}_2\text{M}]$ $\text{L}_n = (\text{thf})_4$ or $(\text{tmeda})_2$ tmeda = tetramethylethylenediamine. $\text{M} = \text{Li}$ (ref. 8), Cu (ref. 9), or Ag (ref. 10). The dialkyl-cuprate and -argentate anions are isoelectronic and isostructural with the neutral zinc and cadmium compounds. Solutions of TsiLi in thf, and the solid, contain ionic species $[\text{Li}(\text{thf})_4]^+[\text{Tsi}_2\text{Li}]^-$. Whereas the Si-Me bonds are similar to or slightly shorter than the C(1)-Si bonds in the neutral species Tsi_2M , the Si-Me bonds in the anionic species are significantly longer than the C(1)-Si bonds (e.g. 190(4) vs 183(3) pm in Tsi_2Ag^-). This provides structural evidence for delocalisation of negative charge through contributions of structures such as $(\text{Me}_3\text{Si})_2\text{C}=\text{SiMe}_3$. Since the ate complexes $[\text{Li}(\text{thf})_4]^+[\text{Tsi}_2\text{M}]^-$ are isostructural, it should be possible to obtain a direct comparison between the sizes of the atoms M from the metal-carbon bond lengths: Li-C 218, Cu-C 205, Ag-C 218 pm. It may be, however, that all the M-C bond lengths in the anions Tsi_2M^- are long because of intramolecular repulsion between methyl groups (Cu-C in CuMe_2^- : 193.5(8) pm, ref. 11) so that the relative sizes deduced from the X-ray structures are not necessarily those which would be shown in less congested conditions.

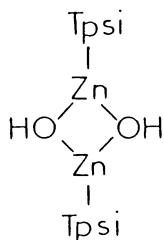
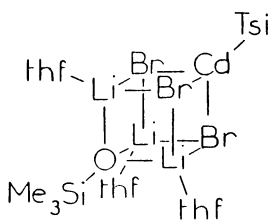
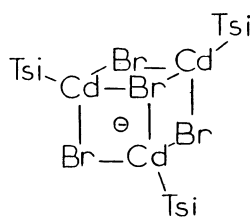
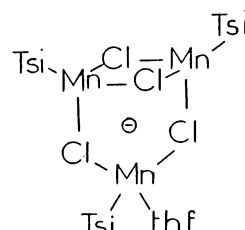
So far no species Tpsi_2M have been characterised probably because the reagent TpsiLi , which has a molecular rather than an ionic structure (ref. 3), is insufficiently reactive towards the intermediates TpsiMX ($\text{X} = \text{halogen}$). A series of unsymmetrical compounds TpsiHgR ($\text{R} = \text{Me}$, Bu , Ph , $\text{C}_6\text{H}_4\text{Me-4}$, or Tsi) can be obtained and the properties of these compounds are being studied (ref. 12).

MONO[TRIS(TRIMETHYLSILYL)METHYL]- AND MONO[TRIS(DIMETHYLPHENYLSILYL)METHYL]-METAL DERIVATIVES

The replacement of the hydrogen atoms in methylmetal compounds by more bulky silyl groups may inhibit condensation or substitution reactions at the metal centre. Hence $(\text{Me}_3\text{Si})_3\text{C}$ or $(\text{Me}_3\text{PhSi})_3\text{C}$ derivatives may sometimes be made whereas the corresponding H_3C compounds may be detected or postulated only as reaction intermediates. The Tsi or Tpsi groups do not, however, always remain unchanged in a reaction sequence involving the adjacent metal. They themselves contain metal-carbon bonds which may participate in a range of rearrangements and eliminations. These points are illustrated in the remainder of this paper.

Compounds of zinc, cadmium and manganese

The reaction between zinc(II) chloride and one equivalent of TpsiLi gives a crystalline compound which is probably $\text{TpsiZnCl}_2\text{Li}(\text{thf})_2$. On heating this gives TpsiZnCl , which is hydrolysed by sodium hydroxide in aqueous thf to TpsiZnOH . This is the first alkylzinc hydroxide to be characterised: the dimeric structure 1 has been confirmed by X-ray diffraction, and the packing diagram shows that further interaction between dimers, e.g. by hydrogen bonding, is prevented by the large alkyl groups (ref. 12). The reaction between cadmium bromide and TsiLi also gives an ate complex which has been shown by an X-ray study (ref. 13) to be $[\text{Li}(\text{thf})_4][\text{Tsi}_3\text{Cd}_3\text{Br}_4]$ 5. A second compound $\text{TsiCdBr}_3\text{Li}_3(\text{thf})_3\text{OSiMe}_3$ 2, obtained when traces of moisture are accidentally admitted, is thought to be formed by the

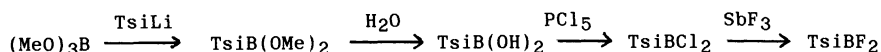
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cadmium bromide-catalysed attack of TsiLi on the thf solvent. The resulting $\text{Tsi}(\text{CH}_2)_4\text{OLi}$ may be hydrolysed to the alcohol $\text{Tsi}(\text{CH}_2)_4\text{OH}$, which has been shown to rearrange in the presence of base to $(\text{Me}_3\text{Si})_2\text{CH}(\text{CH}_2)_4\text{OSiMe}_3$ (ref. 14). The OSiMe_3 fragment may then be incorporated in the cage compound 2.

The anion of the ate complex $[\text{Li}(\text{thf})_4][\text{Tsi}_3\text{Mn}_3\text{Cl}_4\text{thf}]$ 6, made by the reaction between manganese(II) chloride and TsiLi (1 equiv.) has the slightly different structure 4. Solutions of 'alkylmanganese chlorides' were first considered about 50 years ago as reagents in organic synthesis, but all attempts to determine the structures of the species in solution were unsuccessful. The salt 6, which has the stoichiometry $\text{LiCl} \cdot 3\text{TsiMnCl}$, is the first compound isolated from an 'alkylmanganese chloride' solution to be structurally characterised. The cages 2-4 have cubane structures but in the anions 3 and 4 one corner is missing. The Lewis base strength of thf seems to be sufficient to prevent the formation of a Mn-Cl cage like 3: instead one of the Mn-Cl bonds is broken to give 4. It seems likely that it will be possible to isolate compounds with a series of related molecular cages, the species formed in any one case being dependent on a fine balance between the energies of the bonds within the cage and those between metal and solvent.

Boron and silicon derivatives

Boron(III) fluoride-ether reacts with TpsiLi to give TpsiBF_2 , which is hydrolysed in moist air to $\text{TpsiBF}(\text{OH})$ and by sodium hydroxide in thf-water to the boronic acid $\text{TpsiB}(\text{OH})_2$. The reaction between $\text{BF}_3 \cdot \text{OEt}_2$ and TsiLi is complicated by attack on the thf solvent, but a series of tris(trimethylsilyl)methylboron compounds may be obtained from trimethyl borate as starting material (ref. 16).



The hydroxide-fluoride $\text{TpsiBF}(\text{OH})$ is the first example of this type of organometallic compound to be characterised by X-ray crystallography (ref. 17). The large Tpsi-groups prevent the molecular association by hydrogen bonds as in the isoelectronic carboxylic acids $\text{RCO}(\text{OH})$ or in the unusual silane di- or tri-ols $\text{R}_2\text{Si}(\text{OH})_n$ $n = 2$ or 3 (ref. 18-21). Compounds $\text{RBF}(\text{OH})$ with small alkyl groups probably react with intramolecular elimination of HF to form condensed BOB systems so that they cannot be purified; with the bulky silicon-substituted alkyl groups such reactions are prevented. Similar considerations apply to the isolation of $\text{TsiSiPhI}(\text{OH})$ (ref. 21); normally HI is eliminated from organosilicon iodide hydroxides $\text{R}_2\text{SiI}(\text{OH})$ with formation of siloxanes.

The difluoride TpsiBF_2 is reduced by lithium aluminium hydride in thf to the alkyl bridge trihydroborate $\text{TpsiB}(\mu\text{-H})_3\text{Li}(\text{thf})_3$, which crystallises as white needles. The $(\mu\text{-H})_3$ -bridge between boron and lithium has been confirmed by an X-ray study (ref. 22). Although alkyltrihydroborates are used as selective reducing agents in organic synthesis, the structures of the active species have not been determined. It is of interest therefore to establish whether the hydrogen bridged tight ion pairs found in the crystal of $\text{TpsiB}(\mu\text{-H})_3\text{Li}(\text{thf})_3$ are preserved in toluene or thf.

We have recently shown (ref. 23) that $^6\text{Li}\{^1\text{H}\}$ nuclear Overhauser effects may be used for this purpose. The quadrupole moment of ^6Li ($I = 1$) is so small that it behaves in many respects like a spin- $\frac{1}{2}$ nucleus: relaxation is dominated by dipolar interactions with the closest protons. The ^1H nmr spectrum of $\text{TsiB}(\mu\text{-H})_3\text{Li}(\text{thf})_3$ is shown in Fig. 2(a). Figure 2(b) shows the $^6\text{Li}\{^1\text{H}\}$ spectrum from gated decoupling experiments with selective irradiation at various

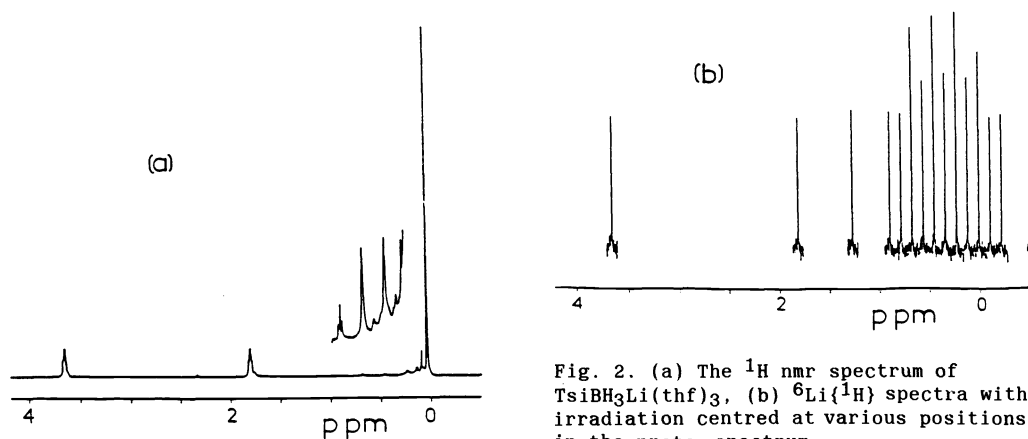


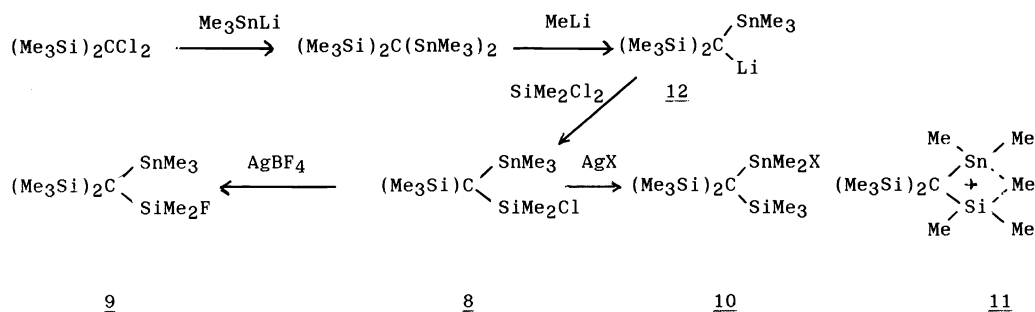
Fig. 2. (a) The ^1H nmr spectrum of $\text{TsiBH}_3\text{Li}(\text{thf})_3$, (b) $^6\text{Li}\{^1\text{H}\}$ spectra with irradiation centred at various positions in the proton spectrum.

positions in the ^1H spectra. The ^6Li signal is enhanced only when the irradiation is at the frequencies of the four equal peaks attributed to the three protons bound to boron ($I = 3/2$). This shows that the protons closest to the lithium are those of the BH_3 -group and that the compound probably retains its hydrogen-bridged structure in solution.

Many unusual organosilicon compounds have been stabilised by the bulky Tsi-group (ref. 2). For example $\text{TsiSiMe}_2\text{OCN}$, obtained from the reaction between $\text{TsiSiMe}_2\text{I}$ and silver cyanate, was the first silicon cyanate to be isolated; it slowly rearranges by a bimolecular process to the isocyanate $\text{TsiSiMe}_2\text{NCO}$.

Migration of methyl groups from tin to silicon

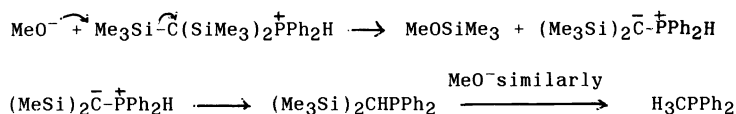
The compound $\text{TsiSnMe}_2\text{Cl}$ 7 is readily obtained from the reaction between TsiLi and SnMe_2Cl_2 : it reacts with a range of silver or alkali metal salts to give compounds $\text{TsiSnMe}_2\text{X}$ (e.g. $\text{X} = \text{F}, \text{Br}, \text{I}, \text{SCN}, \text{OCOMe}, \text{OCOCF}_3, \text{OSO}_2\text{CF}_3$). An isomer 8 of 7 may be made by the following reaction sequence (ref. 24).



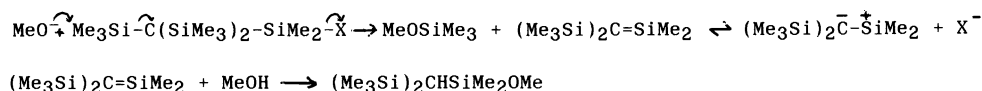
The chloride in 8 may be replaced by other anions in reactions with silver or alkali metal salts, but the structure of the product now depends on the replacing nucleophile X. When $\text{X} = \text{F}$ the product is 9, but for all other cases so far investigated ($\text{X} = \text{OCOMe}, \text{OCOCF}_3, \text{OSO}_2\text{CF}_3$) the product is the rearranged compound $(\text{Me}_3\text{Si})_3\text{CSnMe}_2\text{X}$ 10. It seems likely that the rearrangement involves cationic intermediates 11 which incoming nucleophiles attack at the less sterically hindered tin rather than at silicon. When the attacking nucleophile is fluoride, formation of strong Si-F bonds must be important in the transition state, since no methyl migration is observed. Similar migrations via cationic intermediates have been observed from Ge to Si and from Si to Si but the reactions are often less clean than the migrations from tin, so that mixtures of products are obtained (ref. 2,25). The structure of the lithium compound 12 is clearly of interest and this is being studied.

Eliminations of methoxytrimethylsilanes

In a second series of reactions the migrating group is trimethylsilyl rather than methyl. The reaction between phosphorus(III) chloride and TsiLi yields TsiPCl_2 which reacts so slowly with boiling methanol that it may be conveniently recrystallised from this solvent (Ref. 26). The compound TsiPPh_2 (easily made from TsiLi and Ph_2PCl) is, however, rapidly decomposed: trimethylsilyl groups are successively stripped off the carbon adjacent to the phosphorus and the final product is simply methylidiphenylphosphine (ref. 27). A careful study of this reaction shows that the crucial step is protonation of the phosphine. The positive charge on phosphorus then makes the silicon-carbon bonds of the Tsi-group extremely susceptible to nucleophilic attack by methoxide and the resulting ylide rapidly rearranges by exchanging protons with solvent.

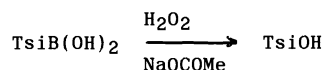


The reaction between $\text{TsiSiMe}_2\text{I}$ and methanolic sodium methoxide was earlier shown to proceed by a similar reaction sequence (ref. 1).



Migrations of tris(trimethylsilyl)methyl groups

There has so far been little work on reactions involving the transfer of Tsi or Tpsi groups from one element to another, apart from those used in preparations of compounds from TsiLi or TpsiLi. Such reactions are, however, of interest because they may provide preparative routes to a wider range of organometallic compounds. The possibilities are illustrated by the synthesis of TsiOH, an alcohol which has proved to be difficult to make. The preparative route to alcohols by the oxidation of boranes with alkaline hydrogen peroxide is well known. In order to avoid breakdown of the Tsi group by base as described above, the boronic acid was treated with hydrogen peroxide/sodium acetate to give a good yield of TsiOH mp. 35°C, (ref. 28).



Further work on tris(trimethylsilyl)methyl- and tris(dimethylphenylsilyl)methyl-metal compounds is expected to yield derivatives of a wider range of elements and further unusual organometallic compounds, as well as new migration and elimination reactions involving the silicon and the metal centres.

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