DALTON
PERSPECTIVE

Organometallic compounds containing tris(trimethylsilyl)methyl or related ligands †

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This review is concerned with compounds containing tris(trimethylsilyl)methyl or closely related ligands in which three organosilyl substituents are attached to the central carbon atom. We refer to the prototype ligand derived from $(Me_3Si)_3CH$[1] as 'trisyl' (denoted by Tsi) and the broader class as 'trisyl-type'. Such ligands have been attached to elements of all groups of the Periodic Table except 18. Numerous derivatives have been made of the s, p and some f block elements and there are over 300 relevant references in the literature, but few compounds of the transition metals are known as yet. Many organometallic compounds bearing two silicon substituents at the central carbon, *i.e.* containing ligands such as $(Me_3Si)_2CH$[2] or $(Me_3Si)_2C(C_5H_4N\text{-}2)$[3], have been described, but their chemistry is often quite different from that of the tris(triorganosilyl)methyl derivatives. The much greater steric protection at an adjacent metal atom when the third organosilyl group is present significantly affects the structures and reactivity of organometallic derivatives. The emphasis is on the 'inorganic' aspects of trisyl chemistry and on the implications of this new work in organometallic chemistry generally.[4–6] We discuss mainly our own research but give extensive references to chemistry that has been developed by others.

Compounds of the alkali metals

The main interest here lies in the remarkable range of novel structural types that have been discovered, and in the use of alkali metal compounds as ligand transfer reagents for attachment of groups $C(SiMe_3)_n(SiMe_2Y)_{3-n}$ to other elements. The synthesis of the parent compound $(Me_3Si)_3CH$ was reported in 1963[7] but little attention was paid to it until it was shown that it could be metallated by LiMe in tetrahydrofuran (thf) to give the unusually stable $LiC(SiMe_3)_3$.[1,8] The kinetic acidity of $(Me_3Si)_3CH$, shown to be greater than that of triphenylmethane,[9] was attributed to the delocalisation of the lone pair of the carbanion by interaction with the d- or σ^*-orbitals of silicon.[10–12]

The lithium dialkyllithate $[Li(thf)_4][LiTsi_2]$ **1** was obtained when LiTsi was crystallised from thf.[13] Such species had been postulated by Wittig over 30 years earlier[14] but not previously isolated and structurally characterised. Multinuclear NMR measurements show that in toluene or thf solutions a variety of other species, depending on the temperature and the concentration, are present.[15,16] These probably include the electron-deficient dimer $(LiTsi)_2$ **2** and monomeric LiTsi·thf. The solvent-free compound **2** was first obtained from an organomercury precursor,[17] but it is most conveniently made by reaction of TsiCl with Li in toluene.[18] It reacts with dioxygen to give the strawberry red 1 : 1 adduct $LiTsi{\cdot}OC(SiMe_3)_2$.[19]

The $[LiTsi_2]^-$ anion has been identified in several other species,[15,20] including *e.g.* LiTsi·1.5thf, obtained in low yield by sublimation of **1** at 180 °C/10^{-4} Pa,[19] and $[(pmdien)LiClLi(pmdien)][LiTsi_2]$ (pmdien) = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine), in which the Li_2Cl-skeleton of the novel cation is linear.[21]

Derivatives of the heavier alkali metals are readily obtained by the metallation of TsiH by the methylmetals, made by

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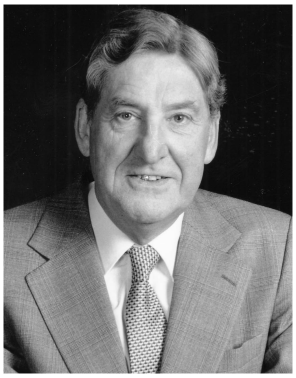
† Electronic supplementary information (ESI) available: a complete list of our publications, with titles, on compounds containing trisyl-type groups. See http://www.rsc.org/suppdata/dt/b1/b100741f/

After studying at the (now) University of Wales, Bangor (PhD with E. D. Hughes, 1947; Honorary Fellow 2000) Colin Eaborn was at the University of Leicester until 1962, when he moved to the University of Sussex as the founding Professor of Chemistry (Pro-Vice-Chancellor 1964–1973; Professor Emeritus 1988, Honorary DSc 1988). He was Honorary Secretary of the Chemical Society from 1968–1973. Honours include FRS (1970), Kipping Award for Organosilicon Chemistry of the American Chemical Society (1964), the Ingold Medal, Organometallic Award, and Main Group Award of the RSC.



Colin Eaborn

David Smith obtained his PhD degree from Cambridge in 1958. After short periods in Cornell and Leicester, he moved in January 1963 to Sussex, where he has been lecturer and, from 1974, reader. He was Dean of the School of Chemistry and Molecular Sciences from 1992–1996. His research has been on a variety of topics in inorganic chemistry, including aluminium–nitrogen compounds and, since 1980, organometallic compounds containing tris(triorganosilyl)methyl groups.

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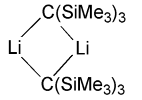
Table 1 Structure types for the alkali metal derivatives MR R = $C(SiMe_3)_n(SiMe_2Y)_{3-n}$

A	Dimer $(MR)_2$ *e.g.* **2**	**E**	Ate complex $[ML_n][MR_2]$. L_n = 4thf, 2tmen, C_6H_6, *e.g.* **1**
B	Monomer MRL L = thf, Et_2O, $(C_6H_6)_3$	**F**	Cage dimer *e.g.* **7**
C	Chain M^+R^- M^+R^- M^+R^-, *e.g.* **4**	**G**	Cage monomer, *e.g.* **8**
D	Lattice M^+R^-		

M	Y	*n*	Structure type, ref.	M	Y	*n*	Structure type, ref.
Li	Me	3	**A**[17]**E**[13]	Na	Me	3	**E**[22]
Li	Ph	2	**B**[25]**E**[35]	Na	Ph	2	**B**[25]
Li	Ph	0	**B**[37]	Na	Ph	1	**B**[25]
Li	C_5H_4Me-4	0	**D**[26]	Na	Ph	0	**C**[22]
Li	OMe	2	**B**[27]	Na	PPh_2	2	**C**[33]
Li	OMe	1	**F**[28]	K	Me	3	**C**[23]
Li	OMe	0	**F**[29]	K	Ph	2	**E**[36]
Li	NMe_2	2	**B**[30]	K	Ph	0	**C**[23]
Li	NMe_2	0	**C**[31]	K	NMe_2	2	**C**[28]
Li	C_6H_4N-2	2	**B**[32]	K	NMe_2	0	**C**[28]
Li	CH_2PPh_2	0	**G**[33]	K	C_5H_4N-2	2	**C**[32]
Li	PPh_2	0	**D**[34]	Rb	Me	3	**C**[24]
				Rb	Ph	0	**C**[25]
				Cs	Me	3	**B**[24]
				Cs	Ph	0	**C**[25]

$[Li(thf)_4]$ $[(Me_3Si)_3CLiC(SiMe_3)_3]$

1



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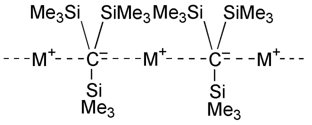
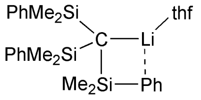


3a M = K, **3b** M = Rb



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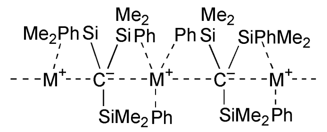
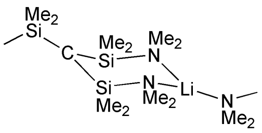


5 M = K, Rb or Cs



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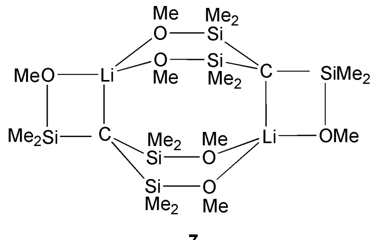
treatment of LiMe with NaOBu^t, KOBu^t, or the 2-ethylhexoxy-derivatives of Rb or Cs.[22–24] The sodium compound $[Na(tmen)_2(OEt_2)][NaTsi_2]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) is, as far as we are aware, the only structurally characterised diorganosodate.[22] The structures of the potassium and rubidium compounds **3** comprise linear chains of metal cations and planar carbanions but recrystallisation of the caesium compound from benzene gives the molecular species $Cs(C_6H_6)_3C(SiMe_3)_3$.[24]

More structural types (see Table 1) are observed when methyl groups of the Tsi ligand are replaced by groups Y such as Ph or $CH{=}CH_2$ capable of donating electrons from π-systems.[25–36] In the lithium derivative **4**,[37] the lithium is essentially two-coordinate but there are weak intramolecular interactions with the *ipso*- and *ortho*-carbon atoms of one of the phenyl groups ($Li{-}C_{ipso}$ = 2.4 Å). There are similar interactions in the derivatives of the heavier alkali metals, but the M–C distances around the ring are more even so that the coordination is best described as η^4 or η^6. It is noteworthy that the interionic interactions that bring methyl or phenyl groups close to the metal are usually sufficiently strong to exclude donor solvent molecules from the metal coordination sphere. Thus KTsi **3a**, RbTsi **3b**, $\{LiCH(SiMe_2Ph)_2\}_2$, and $MC(SiMe_2Ph)_3$ **5** crystallise from solutions containing thf, or in some cases tmen, without incorporation of donor solvent.[25] The tenacity of potassium–phenyl interactions is also shown in the remarkable structure of $[K(C_6H_6)][K\{C(SiMe_3)_2(SiMe_2Ph)\}_2]$, the only diorganopotassate to have been structurally characterised.[4,36] One potassium atom is coordinated by benzene and by phenyl groups from two anions and the other is at the centre of the diorganopotassate anion.

The methyl groups of TsiH can also be replaced by groups, such as OMe or NMe_2, bearing lone pairs, which facilitate metallation by bases to give lithium derivatives.[31] Many of these have been used without isolation for the synthesis of organometallic compounds of other elements,[38–43] or as precursors for the generation of silenes, [*e.g.* $(Me_3Si)_2C{=}SiMe_2$][44–50] but in a few cases the crystal structures of the lithium derivatives themselves have been determined (Table 1). Some, *e.g.* **6**,[31] form chain structures with intermolecular coordination from the donor atom to the metal, but there are also some remarkable polycyclic compounds such as $[LiC(SiMe_2OMe)_3]_2$ **7**[29] and $LiC(SiMe_2CH_2PPh_2)_3$ **8**.[33] In **6** there is no bond between lithium and the planar carbanionic centre; in **7** the bond is weak [Li–C 2.401(9) Å, Si–C–Si 117.1(2)°], but in **8** somewhat stronger [Li–C 2.222(13) Å, Si–C–Si 114.4(3)°]. In a few cases, *e.g.* $[Li(tmen)_2][C(SiMe_2C_6H_4Me\text{-}4)_3]$[26] and $[Li(tmen)_2][C(SiMe_2PPh_2)_3]$,[34] the cations and planar anions are wholly discrete.



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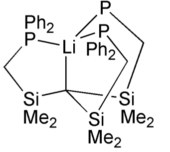

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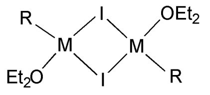


9a M = Mg, **9b** M = Yb
R = $C(SiMe_3)_3$

Compounds in which two methyl groups of the Tsi ligand have been replaced by donor groups are accessible by the reaction sequence in Scheme 1.

$$\mathrm{HCBr_3} \xrightarrow{\text{(i)}} \mathrm{HCBr(SiMe_2Ph)_2} \xrightarrow{\text{(ii)}} \mathrm{HC(SiMe_3)(SiMe_2Ph)_2} \xrightarrow{\text{(iii)}}$$

$$\mathrm{HC(SiMe_3)(SiMe_3Br)_2} \xrightarrow{\text{(iv)}} \mathrm{HC(SiMe_3)(SiMe_2X)_2}$$

$$\mathrm{X = NMe_2 \text{ or } OMe}$$

Scheme 1 (i) 2LiBu/2Me$_2$PhSiCl, (ii) LiBu/Me$_3$SiCl, (iii) Br$_2$/Al, (iv) NMe$_2$H (X = NMe$_2$) or MeOH/Et$_3$N (X = OMe).

So far the structure of only one compound of this type, *viz* {LiC(SiMe$_3$)(SiMe$_2$OMe)$_2$}$_2$ has been determined.[28] The molecule consists of a cage, somewhat similar to that of **7**.

The lithium derivatives containing ethers or amines have been used in donor solvents but toluene has been employed for syntheses involving the ether-free LiTsi.[18,51,52] The potassium compound KTsi has been used as a ligand transfer reagent in benzene to obtain dialkyls, *e.g.* those of Groups 2 or 3, that react with ethers (see below).[53–55]

Some reactions of Li(thf)$_2$C(SiMe$_2$H)$_3$, obtained by deprotonation of (HMe$_2$Si)$_3$CH with LiNPr$^i_2$, have been studied.[38,56] The compounds LiC(SiMe$_2$R)$_3$ (R = Et, Pr^i, Bu or cyclo-C$_6$H$_{11}$), LiC(SiEt$_2$Me)$_3$[57–59] and LiC(SiMe$_3$)$_2$(SiMe$_2$R′) (R′ = H, CH=CH$_2$ or C$_6$H$_4$X; X = H, *p*-OMe, Me, Cl or *m*-CF$_3$) have also been made and used as ligand transfer reagents.[60–63]

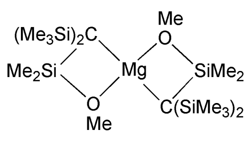
It is sometimes difficult to obtain good X-ray data from Tsi compounds because the high symmetry of the ligand results in extensive crystallographic disorder, and better data are usually obtained from compounds containing the less symmetrical C(SiMe$_2$Ph)$_3$ ligand, which are readily made by reactions of the lithium compound **4** with metal halides. The structures of Tsi and the corresponding C(SiMe$_2$Ph)$_3$ derivatives are often very similar but both ligands adopt a range of conformations so that their effective size varies from compound to compound.[64–67] For Tsi derivatives cone angles of 190–216° have been calculated.[67] Steric effects within Tsi groups are discussed elsewhere.[68,69]

Compounds of Groups 2 and 3

The dialkylmagnesium MgTsi$_2$ is, as far as we are aware, the only example of a compound containing two-co-ordinate Mg in the solid state. The C–Mg–C skeleton is linear and the SiMe$_3$ groups from the two sides interlock to protect the metal centre.[4,70] This protection is reflected in the remarkably low reactivity; for example, MgTsi$_2$ does not react with Me$_3$SiCl or even neat boiling MeCOCl. It does react with water but the intermediate TsiMgOH cannot be detected, showing that the Mg–C bond is very reactive once the protection of one of the Tsi groups is removed.[71] It does not decompose below 350 °C. The Grignard reagents TsiMgI·OEt$_2$ **9a**[35,72] and (Me$_3$Si)$_2$(PhMe$_2$Si)CMgI·OEt$_2$[35] have the usual dimeric structures found for this class of compound.

The methoxy derivative (Me$_3$Si)$_2$(MeOMe$_2$Si)CMgI·OEt$_2$ was prepared by the reaction of magnesium metal with (Me$_3$Si)$_2$(MeOMe$_2$Si)CI. It could not be completely characterised crystallographically, but in Et$_2$O it was converted by a Schlenk reaction into MgI$_2$(OEt$_2$)$_2$ and the dialkyl **10**, which has distorted tetrahedral coordination at Mg with large C–Mg–C (144°) and narrow O–Mg–O (94.5°) angles.[73] We consider that reactions of these bulky alkyl iodides with activated metals, especially when facilitated by the presence of donor groups in the organosilyl substituents, have considerable potential for further development. The reaction of Mg with the iodide (Me$_2$NMe$_2$Si)$_3$CI gives MgI{C(SiMe$_2$NMe$_2$)$_3$} **11**, which crystallises with a remarkable tricyclic structure having planar coordination at carbon. Compound **11** is the only Grignard reagent without a Mg–C bond.[74]

A number of alkylmagnesates, *e.g.* Li(thf)$_2$(μ-Br)$_2$MgTsi(OEt$_2$) **12**, have also been reported.[35,68,75] Indeed we consider that the formation of an intermediate halide-bridged ate complex may be a general feature of the reactions between TsiLi and halides MX$_2$ and MX$_3$.[5] Some of these, like **12**, have molecular structures, in which one cation is linked with a specific anion; others crystallise in lattices with only long-range attractions between cations and anions.[64,68,76,77]



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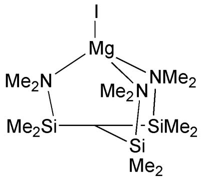

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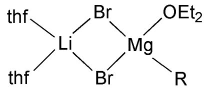


12 R = C(SiMe$_3$)$_3$

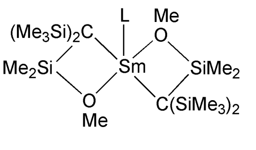
Organometallic compounds of the heavier alkaline earth elements have been less studied than those of magnesium, so it was an obvious challenge to attempt to make trisyl-type derivatives in the hope that they would be sufficiently stable for isolation and structural characterisation. Our results with lanthanide compounds (see next section) suggested that we should avoid ether solvents by using KTsi rather than LiTsi as the source of the Tsi group. The potassium compound reacted with CaI$_2$ in benzene to give the extremely reactive white crystalline CaTsi$_2$, the first solvent-free σ-bonded diorganocalcium to be structurally characterised.[52] (It was insufficiently stable at 200 °C for an electron diffraction study.) The C–Ca–C angle is 150°, in contrast to the 180° predicted by simple electron repulsion rules. The non-linear C–Ca–C skeleton brings methyl groups of the peripheral SiMe$_3$ fragments close to the metal, but it is not clear whether this is a consequence of metal–methyl ‘agostic’ interactions or, as seems more likely, that the methyl groups are forced to be near to the metal because the valence electrons of the metal are best accommodated in a non-linear C–M–C skeleton. There is no relevant experimental evidence on this point, but it is noteworthy that bent X–Ca–X skeletons are found in gaseous CaI$_2$ and cyclopentadienyl derivatives. However the presence of short Li···Me distances in solvent-free LiTsi **2**[17] and the generation of methyl-bridged cations in reactions of organosilicon iodides TsiSiR$_2$I (see below) give support to the notion that methyl–metal interactions may be significant. The compound CaTsi$_2$ reacts rapidly with diethyl ether to give Ca(OEt)$_2$. With one equivalent of the ether only half of the dialkyl is consumed, indicating that the intermediate TsiCaOEt reacts more rapidly with ether than does the dialkyl.

An initial attempt to make YbTsi$_2$ from LiTsi and YbI$_2$ in diethyl ether gave YbTsi(OEt)(OEt$_2$), TsiH and C$_2$H$_4$.[78,79] The syntheses of YbTsi$_2$ and EuTsi$_2$, were subsequently accomplished by the use of KTsi in benzene, and the products, the first σ-bonded diorganolanthanides to be isolated, were characterised by X-ray studies.[54,55] The C–Ln–C angle (Ln = Yb or Eu) is *ca.* 140° (see discussion of CaTsi$_2$ above).

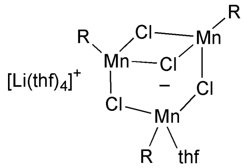
The dialkyl YbTsi$_2$ (but not EuTsi$_2$) reacts with ethers EtOR but the reaction is inhibited in compounds Yb{C(SiMe$_3$)$_2$(SiMe$_2$X)}$_2$ (X = CH=CH$_2$ or OMe) which are presumably stabilised by internal coordination of X to the metal.[55] The reaction between YbTsi$_2$ and MeI gives the Grignard analogue YbTsiI (recrystallised from Et$_2$O as the etherate **9b**) and a variety of other products, *e.g.* TsiI, TsiMe and TsiH, that indicate a radical pathway; in contrast bis(cyclopentadienyl) derivatives are oxidised by halocarbons to Ln^{III} compounds LnCp$_2$X. The conversion of YbTsi$_2$ into TsiYbI is more cleanly achieved by treatment with ICH$_2$CH$_2$I. The conversion of TsiYbI into YbTsi$_2$ is effected by heating a solution in toluene, from which YbI$_2$ separates. The iodide TsiYbI can also be made directly by reaction between Yb metal and the iodide TsiI.[54] The compounds

$[Yb\{C(SiMe_3)_2(SiMe_2X)\}I(OEt_2)]_2$ ($X = CH{=}CH_2$ or OMe) adopt similar structures, but with five-coordinate Yb. Even the rather weak coordination of $CH{=}CH_2$ drastically slows down the reaction of $Yb\{C(SiMe_3)_2(SiMe_2CH{=}CH_2)\}_2$ with Et_2O; ethylene was detected only after 3–4 months at room temperature.[55]

The only trisyl-type organolanthanide(III) compound at present characterised, **13b**, was obtained by the reaction of the organosamarium(II) compound **13a** [easily made from $K\{C(SiMe_3)_2(SiMe_2OMe)\}$ and $SmI_2{\cdot}2thf$] with benzophenone. The deep purple **13b** has a structure almost identical with that of **13a** but with Ph_2CO in place of thf, and comparison of the bond lengths and angles in **13a** and **13b** shows that **13b** is a Sm^{III} complex of a ketyl radical ion.[80]



13a L = thf, **13b** L = OCPh2



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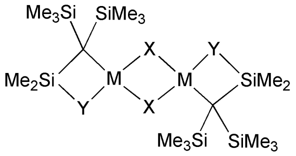
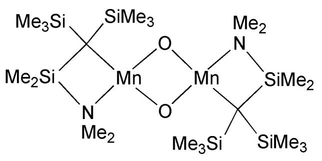


15a M = Mn, X = Cl, Y = NMe2 or OMe
15b M = Co, X = Br, Y = NMe2

Compounds of Groups 6 to 10

Organometallic compounds of transition elements are widely used as reagents, or postulated as intermediates, in organic syntheses. For example, manganese compounds have been employed for more than 60 years, especially for the preparation of a range of ketones, but they are generated from Grignard reagents and Mn^{II} halides and used without isolation. We obtained the mononuclear d^5 compound $MnTsi_2$ from the reaction between **1** and $MnCl_2$ and showed it to be isostructural with the d^0 Mg^{II} and d^{10} Zn^{II} analogues.[81] We also obtained a lithium manganate **14**, which was shown to contain a cage anion, and an incompletely characterised cobalt analogue.[82] Reactions of **1** with other transition metals halides led to black precipitates and intractable mixtures. (A compound $ZrCp_2Tsi_2$, unstable above −20 °C, has been reported.[83]) We thus turned to ligands of the type $R = C(SiMe_3)_2(SiMe_2Y)$ in the expectation that coordination of the group Y would stabilise the products. The validity of this approach was confirmed by isolation of the Grignard reagent analogues RMX ($M = Mn$, $X = Cl$, $Y = NMe_2$ **15a** or OMe; $M = Co$, $X = Br$ and $Y = NMe_2$ **15b**), which have dimeric halide-bridged structures like those of the Grignard reagents themselves. The exceedingly air-sensitive dialkyl $Mn[C(SiMe_3)_2(SiMe_2NMe_2)]_2$ is oxidised by traces of oxygen to give the alkylmanganese(III) derivative $[MnO\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ **16**. The Mn^{II} and Co^{II} centres in **15a** and **15b** have tetrahedral environments, but the coordination at the Mn^{III} atom in **16** is square planar, as expected for a d^4 configuration.[84]

A particularly extensive series of compounds containing the ligand $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$, R, has been obtained, including derivatives of Cr^{II}, Mn^{II}, Co^{II}, Ni^{I} and Pd^{II}.[32] The square planar d^4 compound CrR_2 and the d^9 Ni^{I} derivative $NiRPPh_3$ are especially noteworthy. The compound $[PdRCl]_2$ **17** was obtained straightforwardly from the reaction of $[PdCl_2(PPh_3)_2]$ with two equivalents of LiR but the corresponding



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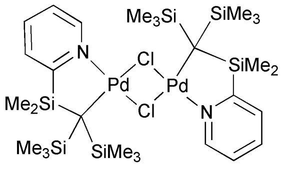

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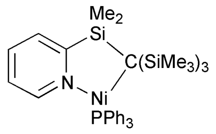

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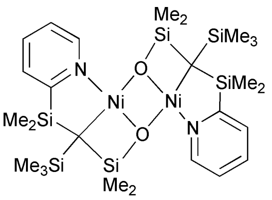
reaction of $[NiCl_2(PPh_3)_2]$ resulted in reduction. However, the coordination of the bulky ligand prevented aggregation to give metallic nickel and the Ni^{I} species **18** was obtained.[85] Compound **18** is the first structurally characterised compound to contain a Ni^{I}–C σ-bond and the first structurally characterised σ-bonded d^9 organometallic compound. From a 1 : 1 mixture of LiR and $[NiCl_2(PPh_3)_2]$ a small amount of the silanolato compound **19** was obtained, apparently by intramolecular elimination of CH_4 from traces of an Ni–OH species.

Very recently $FeTsi_2$ has been made in good yield from the reaction of $FeCl_3$ with three equivalents of LiTsi in toluene; one equivalent acts as a reducing agent.[52] This suggests that the formation of trisyl derivatives of the transition metals may not require the presence of stabilising ligands provided that unwanted side reactions can be avoided in their synthesis. Indeed, it is likely that trisyl-type ligands will eventually be attached to all the transition metals.



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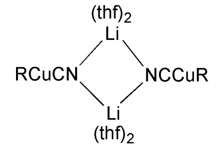
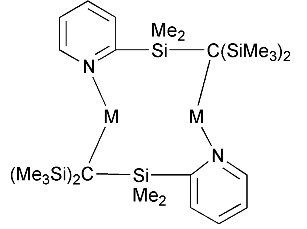




20 **21a** M = Cu **21b** M = Au

Compounds of Groups 11 and 12

Only a few compounds of the Group 11 elements, all with the metal in oxidation state +1, have been reported. The unprecedented diorganometallate complexes $[Li(thf)_4][MTsi_2]$ $M = Cu$[86] or Ag[87] are isostructural with the lithium compound **1**. More recently, a series of cyanocuprates have been characterised. The compounds $Li(thf)_2NCCuR$ [$R = Tsi$, $(PhMe_2Si)_3C$ or $(Me_2NMe_2Si)(Me_3Si)_2C$] have the dimeric structure **20**, but a monomeric compound $Li(thf)_3NCCuC(SiMe_2Ph)_3$ has also been characterised. The compound with $R = (MeOMe_2Si)(Me_3Si)_2C$ adopts a different dimeric structure in which $Li(thf)NCCuR$ units are linked by MeO–Li coordination, and the potassium compound corresponding to **20** [$R = (PhMe_2Si)_3C$] has a tetrameric structure stabilised, like $KC(SiMe_2Ph)_3$, by K–Ph interactions.[88]

The Cu^I and Au^I derivatives **21** have similar structures and the gold compound **21b** shows significant transannular metal–metal interactions [Au–Au 3.0749(16) Å].[89] The complexes TsiAuL ($L = Et_3P$, Ph_3P or Ph_3As) have also been isolated as white crystalline solids stable in water but decomposing slowly in solution at room temperature and rapidly in daylight.[90]

The dialkyls $MTsi_2$ (M = Zn, Cd or Hg) are obtained from reactions between the dichlorides and the lithium reagent **1**.[91] The zinc[92] and mercury[93] compounds [and $Cd\{C(SiMe_3)_2(SiMe_2CH{=}CH_2)\}_2$][39] are linear like $MgTsi_2$, with interlocking Me_3Si groups that protect the central metal–carbon bonds. This is probably an important factor in accounting for the extraordinary chemical stability of these compounds. For example, $ZnTsi_2$ is stable in air up to 300 °C, and can be distilled in steam. In contrast, even the related compound $Zn\{CH(SiMe_3)_2\}_2$ is pyrophoric, like $ZnMe_2$.[92] Compounds of the type TsiZnX or TsiZnR have been studied in considerable detail by Westerhausen.[94–98]

The chemistry of the organozinc compounds $Zn\{C(SiMe_3)_2(SiMe_2Y)\}_2$ shows a number of interesting, unusual and potentially important features.[40,41,99] A series of substitutions at the Si–Y bond, involving quite strong electrophilic reagents, *e.g.* CF_3CO_2H, H_2O or hydrogen halides, can be made without breaking the Zn–C bond (*e.g.* Scheme 2).

$$\mathrm{Zn\{C(SiMe_3)_2(SiMe_2H)\}_2 \xrightarrow{(i)} Zn\{C(SiMe_3)_2(SiMe_2I)\}_2 \xrightarrow{(ii)} Zn\{(SiMe_3)_2(SiMe_2OCOCF_3)\}_2}$$

Scheme 2 (i) I_2/CCl_4; (ii)Ag_2O, CF_2CO_2H.

The mercury compounds undergo similar reactions,[39] but the potential for exploiting this kind of chemistry for cadmium seems to be lower than that for zinc because the Cd–C bonds are more susceptible to attack by electrophilic reagents.[40]

The structures of a number of alkylzinc and alkylcadmium halides and some related compounds[40,64,65,68,100] have been discussed in our previous review.[5]

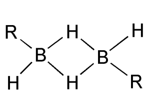
The mercury compound $HgTsi_2$ shows remarkable thermal stability for an organomercury compound and decomposes only above 300 °C. This stability is seen also in *cis*-$Fe(CO)_4(HgTsi)_2$[101] and in the compounds HgTsiR (R = Me, Pr^i, Bu, Bu^t or Ph) and $Hg\{C(SiMe_2Ph)_3\}R$. All the dialkyls bearing the bulky groups decompose at temperatures about 100 °C higher than the corresponding dialkyls HgR_2. For example, $Hg\{C(SiMe_2Ph)_3\}CH_2Ph$ decomposes in solution at 245 °C at about the same rate as $Hg(CH_2Ph)_2$ at 150 °C.[102,103] These observations are of considerable significance since diorganomercury compounds are generally assumed to decompose by unimolecular homolytic breaking of Hg–C bonds, and, if this is so, there seems to be no reason why the Hg–R bonds in $Hg\{C(SiMe_2Ph)_3\}R$ should break less easily than those in HgR_2. It is possible that the accepted mechanism is incorrect and that decomposition actually occurs by a chain mechanism involving bimolecular attack at mercury, which would be inhibited by bulky groups. An even more interesting possibility is that the presence of bulky groups does indeed reduce the ease of fission of adjacent $Hg–CH_2Ph$ bonds. We have suggested that this could be accounted for in terms of the proposal by Marcus[104] that the rate of energy transfer from one ligand to another on the same metal atom is abnormally low for a heavy metal. A molecule in thermal equilibrium at a given temperature that has acquired sufficient energy for dissociation will have most of this dispersed within the large group so that it can only rarely be transmitted to the $Hg–CH_2Ph$ bond. [In this context, it is the molecular complexity, not the bulk, of the $C(SiMe_2Ph)_3$ group that matters.] If this is true, use can be made of the effect in stabilising organometallic compounds towards unimolecular decomposition, and not only in cases involving homolytic bond-breaking. Photolysis of $HgTsi_2$ was found to give the remarkably persistent $Tsi^\bullet$ radical, the first example of a radical produced in this way from a mercurial to be detected by ESR spectroscopy.[105]

In the compounds $Hg\{C(SiMe_2NMe_2)_3\}_2$ **22** and $Hg\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2$ the NMe_2 groups are not coordinated to the mercury and the molecular parameters and conformation are almost the same as those in $HgTsi_2$. An intriguing possibility is that compound **22** could be used as a hexadentate ligand bridging two or more metal atoms. There is weak internal coordination from pyridine to mercury in the monomeric structure of $Hg\{C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}Cl$; in contrast, the zinc and cadmium analogues $Zn\{(CSiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}Br$ and $Cd\{(CSiMe_3)_2(SiMe_2C_5H_4N\text{-}2)\}Cl$ are dimeric, with halide bridges and four-coordinate metals.[89]

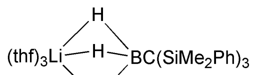
Compounds of Group 13

Initial attempts to prepare trisyl-boron derivatives from LiTsi and $BF_3{\cdot}OEt_2$ in thf led to cleavage of the C–O bond of the solvent and migration of the Tsi group to oxygen to give $TsiB(F)O(CH_2)_4OTsi$.[106] The corresponding reactions with $LiC(SiMe_2Ph)_3$ were more straightforward. The compound RBF_2 [$R = C(SiMe_2Ph)_3$] was readily obtained and converted into RB(F)OH and RB(F)OMe.[107] The reaction between LiTsi (obtained from TsiBr and Li) and $BF_3{\cdot}OEt_2$ in hexane also results in attack on the ether to give TsiOEt as the principal product.[108] It was however found that the reaction of LiTsi with $B(OMe)_3$ gave good yields of $TsiB(OMe)_2$, from which a wide range of compounds $BTsiX_2$ (X = OH, Cl, F, NH_2, H, Me, *etc.*) could be obtained,[109–115] and that $BTsiPh_2$ could be made from LiTsi and Ph_2BBr.[113]

Most of these new boron compounds are monomeric but the alkylborane $BTsiH_2$ **23**, the first 1,2-substituted diorganodiborane to be structurally characterised in the solid state, adopts an electron-deficient dimeric structure.[112,114] Reduction of $BTsiFO(CH_2)_4OTsi$[107] or $BTsi(OMe)_2$[114] with $LiAlH_4$ gave the organotrihydroborate $Li(thf)_3(BTsiH_3)$. The structure of the solid could not be determined by X-ray diffraction because of disorder but the corresponding $C(SiMe_2Ph)_3$ derivative **24** was found to comprise lithium cations and $[B\{C(SiMe_2Ph)_3\}H_3]^-$ anions linked by $(\mu\text{-H})_3$ bridges. In order to establish whether the species $[Li(thf)_3(BTsiH_3)]$ were preserved in solution, we recorded the $^6Li\{^1H\}$ spectra and found that there was a strong nuclear Overhauser effect on the Li signals upon irradiation at the precise frequencies of the four BH_3 resonances in the proton spectrum, providing strong evidence that the Li^+ ions remain attached to the $[BTsiH_3]^-$ ions.[116] We have employed this technique to show the presence of similar hydride bridges between lithium and hydrometallates of Al, Ga and In.[117,118]



23 $R = C(SiMe_3)_3$



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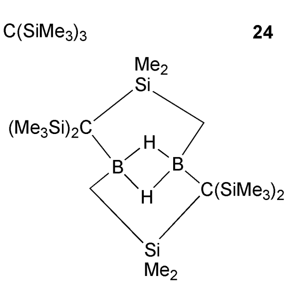
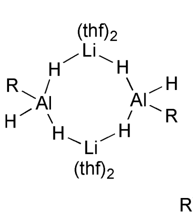


25

The chemistry of Tsi-boron compounds has been considerably extended by Paetzold,[20,119–124] and Klingebiel,[125,126] with particular emphasis on the search for compounds containing B=C, B=O and B=N bonds stabilised by the presence of the bulky group. The reactions of the diborane **23** have been explored and eliminations of Me_3SiX (X = F, Cl or OMe) from trisylboron precursors to give the allene analogue $Pr^i_2N{=}B{=}C(SiMe_3)_2$,[20,120] $(Me_3Si)_2C{=}BR$,[121] and $(BTsiO)_3$. This last compound could be sublimed as a crystalline solid.[122] Further reactions, involving BTsiO as intermediate and migration of methyl groups, are observed at 600–700 °C.[122] The borane **25**[124] has been obtained from $TsiBCl_2$, and the imino derivatives TsiB=NR have been reported.[125,126]

Ether solvents were also cleaved during reactions of TsiLi with aluminium halides but good yields of trisylaluminium derivatives can now be obtained by other routes, as follows. (1) Ether-free LiTsi was used by Weidlein[18] to prepare the donor-free monomeric compounds $MTsiMe_2$ (M = Al, Ga and In), as well as some unusual ate complexes, *e.g.* [Li(toluene)][$TsiMeClAl(\mu\text{-}Cl)AlCl_2Tsi$]. In reactions with the triiodides, LiTsi behaves as a methylating agent to give $TsiMeGa(\mu\text{-}I)_2GaMeTsi$ or $InTsi_2Me$ and $[Me_2SiC(SiMe_3)_2]_2$. The monomeric $InTsi_2Me$ is the first example of a three-coordinate atom bearing two Tsi groups.[52] (2) The reaction between LiTsi and $LiAlH_4$ in thf gave the compound $[Li(thf)_2\{AlTsiH_3\}]_2$ **26**,[127] which proved to be a valuable starting material for the synthesis of thf adducts of organoaluminium dihalides $AlTsiX_2$.[117] (The reactions occur cleanly without attack at the hindered Tsi–Al bonds.) Attempts to make organotrihydroaluminates containing ions with smaller organic groups are usually frustrated by the reaction $2[AlRH_3]^- \longrightarrow [AlR_2H_2]^- + [AlH_4]^-$ but this is inhibited when the group R is large and the $[AlTsiH_3]^-$ ion has been characterised in the crystal structure of the $[Li(tmen)_2]^+$ salt.[117] (3) The compounds MMe_2Cl (M = Al or Ga), in contrast to $AlCl_3$, were found to react smoothly with LiTsi to give $TsiMMe_2$ in good yields.[128] Reactions at the very reactive Al–Me bonds have been used by Roesky to give numerous trisylaluminium compounds, especially halides- and oxygen-containing derivatives.[129,130]



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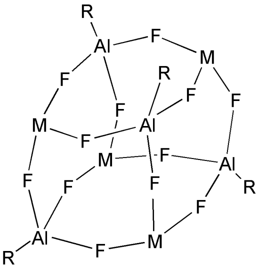
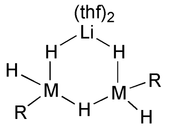


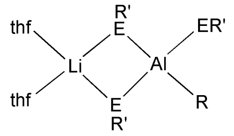
27a M = Li(thf), **27b** M = Na



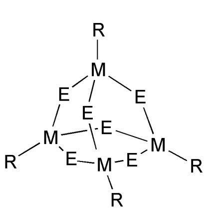
28a M = Al, **28b** M = In

R = C(SiMe₃)₃

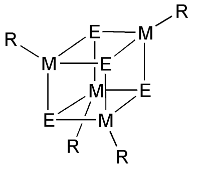
Reaction of **26** with HF in pyridine gave $\{Li(thf)AlTsiF_3\}_4$ **27a**, which has an interesting cage structure in which Li(thf) and $AlTsiF_3$ fragments occupy alternate corners of a distorted cube. Multinuclear NMR data show that the cage structure is preserved in solution but the $AlTsiF_3$ fragments rapidly rotate on the NMR timescale so that each fluorine jumps from one bridge position to another.[132] The sodium compound $(NaAlTsiF_3)_4$ **27b** has a similar structure.[131] The alkylalane $AlTsiH_2{\cdot}thf$ and the hydroaluminate $Li(AlTsi)_2H_5$ **28a** can be obtained by reaction of **26** with the appropriate quantity of $SiMe_3Cl$.[118] Reactions with alcohols, amines or thiols give a range of di- and tri-alkoxoaluminates containing the species $[AlTsiH(OR)_2]^-$ or $[AlTsi(OR)_3]^-$ [132,133] and thiolato- and amido-aluminates containing the ions $[AlTsi(SR)_3]^-$ [134] and $[AlTsi(NHR)_3]^-$.[117] The same products are obtained from alcohols as from aldehydes or ketones and from thiols as from disulfides. Organoaluminates of these types have hitherto been little studied even though they are related to the intermediates in the reduction of carbonyl compounds and disulfides by $LiAlH_4$. For several classes of aluminate the trisyl derivatives are the first to be structurally characterised. In most cases, lithium and aluminium are bridged by two oxygen, sulfur or nitrogen atoms to give four-membered rings as in **29**, but $[Li(thf)_4][AlTsi(NHPh)_3]$ crystallises in a lattice with discrete cations and anions.[117]



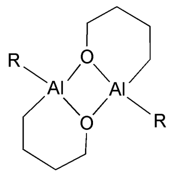
29 E = O or S, R′ = alkyl



30 M = Al, E₆ = O₂(OH)₄
M = Sn, E = S, Se or Te
R = C(SiMe₃)₃



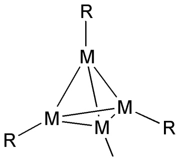
31 M = Ga or In
E = S, Se or Te



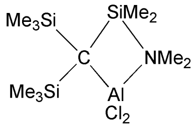
32

The compounds $MTsiMe_2$ are hydrolysed to give the dialkylmetal hydroxides $(AlTsiMeOH{\cdot}thf)_2$ and $(GaTsiMeOH)_3$, which can be converted into $[(MTsi)_4(\mu\text{-}O)_2(\mu\text{-}OH)_4]$, with adamantine-like cage structures **30**, in which the protons are statistically distributed over the six oxygen atoms.[128] Reaction of $AlTsiMe_2$ with Bu_4NF gives $[Bu_4N][AlTsiMeF_2]$ [135] and that with $SnMe_3F$ gives the fluoride-bridged $(AlTsiF_2)_3$, the first alkylaluminium difluoride to be characterised. The compound is an excellent fluoride acceptor.[136,137]

Reaction of $AlTsiMe_2$ with H_2S gives $\{AlTsi(thf)S\}_2$, which on heating gives the cubane $(AlTsiS)_4$ **31**, M = Al, E = S. The gallium compound $(GaTsiS)_4$ can be made similarly.[138] When the chloride $AlTsiCl_2{\cdot}thf$ is reduced by Na–K in thf the solvent is incorporated into the product **32**; $AlTsiI_2$ is, however, converted cleanly into the cluster **33a**, which is stable up to 282 °C.[139]



M = Al **33a**, Ga **33b**,
In **33c**, Tl **33d**
R = C(SiMe₃)₃



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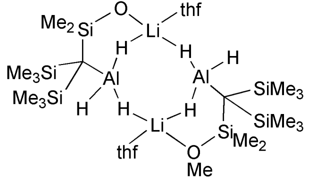


35

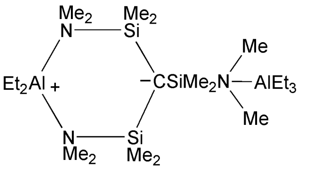
The ability of trisyl-type groups to stabilise metals in low oxidation states has been particularly well exploited by Uhl for the preparation of compounds of the heavier Group 13 elements. The compound $(GaTsi)_4$ **33b**[140] is made in good yield[57] by reduction of $Li[GaCl_3Tsi]{\cdot}3thf$[76] with Mg, the violet indium derivative **33c** from InBr and LiTsi,[141,142] and the thallium compound **33d** from TlCp and LiTsi.[143] All four compounds $(MTsi)_4$ **33** have a tetrahedral M_4 core. It has been shown by an electron diffraction study that TsiGa is monomeric in the gas phase;[144] the less thermally stable InTsi can be detected by trapping to give cycloaddition products, *e.g.* with benzil derivatives.[145] A detailed theoretical and experimental study of the compounds $\{InC[SiMeRR']_3\}_4$ R = Me or Et, R′ = Me, Et, Bu, Pr^i or Ph, shows that the tetramer–monomer equilibrium can be displaced towards monomer by increasing the size of the groups R and R′.[58,146]

The compounds $(MTsi)_4$ **33b** and **33c** are readily oxidised by sulfur, selenium or tellurium to give the cubanes $(MTsiE)_4$ **31** M = Ga,[147] or In;[148] (E = S, Se or Te) and the analogous InO-cubane is obtained by oxidation of **33c** with *o*-nitrosotoluene.[149] The MTsi monomers have two empty p orbitals perpendicular to the M–C axis as well as a lone pair on the Group 13 element M, so that they are isolobal with CO. When $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) is treated with $(GaTsi)_4$ or $(InTsi)_4$ the cod is displaced and the compounds $Ni(GaTsi)_4$[150] or $Ni(InTsi)_4$,[151] analogous to $Ni(CO)_4$, are obtained. The platinum derivative $[Pt(InTsi)_4]$ has also been made,[152] and a range of compounds of Mn, Fe and Co having InTsi or GaTsi fragments in place of one or more CO groups in the parent carbonyl compounds.[153–157] The MTsi groups have also been incorporated into Main Group clusters.[158–160]

The reduction of the ate complex $[Li(thf)_3(\mu\text{-}Cl)InCl_2Tsi]$ with $LiAlH_4$ gives a hydride-bridged compound $Li(thf)_2(InTsi)_2H_5$ **28b**,[161] which is converted by methanol–water into $[(InTsi)_4(\mu_4\text{-}O)(OH)_6]$.[100] The hydroxide $(InTsiPrOH)_3$ has also been reported.[162]

The chemistry of Group 13 compounds containing trisyl-type ligands with donor substituents has yet to be thoroughly explored. The compounds $[MX_2\{C(SiMe_3)_2(SiMe_2NMe_2)\}]$ (M = Al, X = Cl **34** or Ph; M = Ga, X = Cl)[30] and $AlCl_2\{C(SiMe_2NMe_2)(SiMe_2NMe_2)_2\}$,[163] made in the presence of thf, adopt internally coordinated structures having four-membered MCSiN rings, but $AlCl_2\{C(SiMe_3)_2(SiMe_2OMe)\}$ is obtained as a thf complex with uncoordinated OMe.[27] In the dimeric hydroaluminate $[Li(thf)(\mu\text{-}H)AlH_2\{C(SiMe_3)_2(SiMe_2O\text{-}Me)\}]_2$ **35** the association is through Li···H–Al bridges.

The reaction of $LiC(SiMe_2NMe_2)_3$[31] with $AlEt_2Cl$ gives $Et_2Al(\mu\text{-}NMe_2SiMe_2)_2CSiMe_2NMe_2{\cdot}AlEt_3$ **36**,[163] a zwitterionic species containing a cationic Al^{III} centre and a planar carbanionic centre separated by 3.65 Å (the structure bears some resemblance to that of **11** but the M···C distance is much longer). The compounds MCl_2R [M = Al or In, R = $C(SiMe_3)_2(SiMe_2C_5H_4N\text{-}2)$] can be made without difficulty from LiR and the Group 13 halides. The aluminium compound is monomeric with internal coordination from the pyridine substituent and four-coordinate aluminium; the dimeric indium compound also shows internal coordination but five-coordinate indium centres are linked by chloride bridges.[89] Another internally stabilised compound, $AlTsiClC_6H_4CH_2NMe_2\text{-}2$, has been described briefly.[164]



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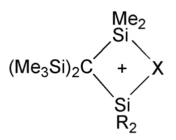

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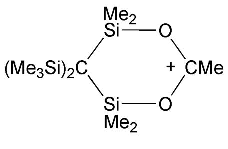


38

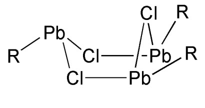
Compounds of Group 14

The chemistry of compounds in which the Tsi or related ligand is attached to silicon is much too extensive for inclusion in this review but some aspects of it will be outlined in a future Dalton Perspective. It is appropriate to mention here, however, that reactions of iodides of the type $(Me_3Si)_2(XMe_2Si)CSiR_2I$ (including simple trisyl compounds with X = Me) with some electrophiles, including silver or mercury salts and trifluoroethanol, proceed *via* anchimerically-assisted formation of bridged cations **37**. It will be apparent that there is an analogy between the bridging by the X groups to a positively charged silicon centre and that of the intramolecular coordination of the groups X to electron deficient metal centres in compounds containing $(Me_3Si)_2(XMe_2Si)C$–metal bonds. The strength of the bridge in the cations **37**, as indicated by the degree of anchimeric assistance, falls in the approximate order (X =) OCOMe > OMe > $OCOCF_3$ > MeS > PhS, PhO > N_3, Cl > NCS > Ph > $CH{=}CH_2$ > Me. (The assistance by the acetoxy group probably involves bridging *via* the carbonyl group in a six-membered ring **38**.) Cations **37** with R = Me and X = Me or Ph have been structurally characterised.[165]

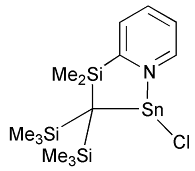
The attachment of Tsi or related groups to polysiloxanes or polystyrenes leads to polymers with greatly increased glass transition temperatures and thermal stability and it is likely that these can be developed in a range of new high-value applications.[166]

Many compounds of Ge,[167–172] Sn,[1,167,173–185] and Pb[186–189] have been isolated. Substitution reactions at the metal centre are less hindered than those at Si so the reactions of trisyl-germanium and -tin compounds are generally like those of compounds bearing smaller alkyl groups, but slower. The SnTsi fragment can be incorporated into inorganic cages. For example, $SnTsiBr_3$ reacts with Na_3E (E = S, Se or Te) in liquid ammonia to give the adamantanes $(SnTsi)_4E_6$ **30**.[190]

As with the compounds of Group 13, the use of the trisyl-type organic groups as ligands makes possible the isolation of a range of compounds in which a Group 14 metal is in the lower oxidation state. For example, reduction of $TsiGeBr_3$ with Mg in the presence of alkenes or alkynes gives a series of products arising from trapping of the bromogermylene TsiGeBr.[191,192] The diorganogermylenes $TsiGeC_5Me_5$[193] and $TsiGeCH(SiMe_3)_2$[194] are monomeric; in contrast, the less sterically hindered $Ge\{CH(SiMe_3)_2\}_2$ is dimeric in the solid state.[195] The reaction of $GeTsiH_3$ with sulfur or selenium gives a mixture of oxidation products $(TsiGe)_2E_n$. Reduction of the compounds with E = Se and $n = 4$ gives the novel compound $TsiGe(\mu\text{-}Se)_3GeTsi$.[196–198]



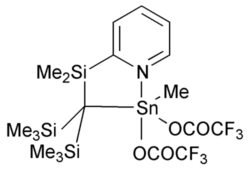
39 R = $C(SiMe_3)_3$



40

Reactions between lithium reagents $LiC(SiMe_3)_2(SiMe_2Y)$ (Y = Me, OMe or $C_5H_4N\text{-}2$) and $SnCl_2$ or $PbCl_2$ gave the first organometallic compounds of the general types RSnCl or RPbCl in which the Group 14 element is in oxidation state +2.[66,199] The product from TsiLi and $PbCl_2$ was shown to be the trimer $(TsiPbCl)_3$ **39** in which the narrow Cl–Pb–Cl angles (88–92°) reflect the presence of the lone pairs. The related compound $[Pb\{C(SiMe_2Ph)_3\}Cl]_2$ was also fully characterised, but both compounds are extremely reactive towards air, moisture, and light, and difficult to work with. The stability is improved by the introduction of groups which can form additional bonds from the ligand to the metal and the isolation of the compounds $[M\{C(SiMe_3)_2(SiMe_2Y)\}Cl]_2$ (Y = OMe, M = Sn or Pb;[66] Y = C_5H_4N, M = Ge, Sn **40**, or Pb[200]) should now make it possible to explore the chemistry of the M^{II} organometallic compounds in more detail. Compound **40** reacts with MeI to give the oxidative addition product

$\overline{\mathrm{SnMeClI\{C(SiMe_3)_2(SiMe_2C_5H_4N}}\mathrm{\text{-}2)}$, and this with Ag-$OCOCF_3$ gives the bis(trifluoroacetate) **41**. In the solid state the tin in **41** is five-co-ordinate in spite of the presence of the bulky trisyl-type ligand, and NMR spectra show that the five-coordinate species are present in solution also. There is evidence that LiTsi reacts with $SnCl_2$ to give the ate complex Li[Sn-$TsiCl_2$],[201] and the compounds [Li(μ-SBu)$_2$MTsi] (M = Ge or Sn) **42**, isolated from reactions between TsiLi and $M(SBu)_2$, have been structurally characterised.[202]



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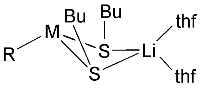
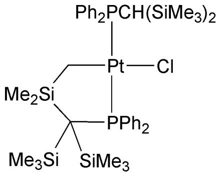


42 M = Ge or Sn
R = $C(SiMe_3)_3$



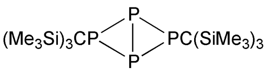
43

Compounds of Group 15

The compounds $MTsiCl_2$ or MTsiRCl (M = P,[203,204] As,[205] or Sb[206]) can be readily made from LiTsi and MCl_3 or $PRCl_2$. The dihalides may be recrystallised from ethanol indicating that the bulky Tsi group is effectively protecting the P (or As)–Cl bonds from attack. The antimony derivative $SbTsiCl_2$, however, is light-sensitive. The compound $PTsiCl_2$ is reduced by $LiAlH_4$ to the phosphine $PTsiH_2$, which, unlike most primary phosphines, is air-stable.[207,208] Its structure has been determined by gas phase electron diffraction[209] and that of $P\{C(SiMe_2Ph)_3\}Cl_2$ by X-ray crystallography.[210] Interestingly, the tertiary phosphine $PTsiPh_2$ is unstable in hydroxylic solvents such as methanol. The ready protonation at phosphorus facilitates attack by OMe^- at an Me_3Si–C bond of the Tsi group and degradation *via* $(Me_3Si)_2CHPPh_2$ and $Me_3SiCH_2PPh_2$ leads to $MePPh_2$.[211] Similar degradation of trisyl groups has been observed in tin oxinate derivatives.[176] An attempt to make a platinum complex $[PtCl_2(PTsiPh_2)_2]$ resulted in the loss of a trimethylsilyl group from one phosphine ligand and activation of a C–H bond in another to give the complex **43**.[212] On heating, $TsiPCl_2$ and TsiPRCl readily lose $SiMe_3Cl$ to give the phosphaalkenes $(Me_3Si)_2C{=}PCl$ (and eventually $Me_3SiC{\equiv}P$) and $(Me_3Si)_2C{=}PR$ (R = Bu^t or Ph).[207,213,214]

The greatest emphasis in the study of the trisyl chemistry of phosphorus and arsenic has been on the stabilisation of compounds in which the P or As has a low coordination number.[215] The diphosphene TsiP=PTsi,[210,216–221] diarsene TsiAs=AsTsi,[205,222–224] phosphaarsene TsiP=AsTsi,[225] made from $TsiMCl_2$ and 2 equivalents of LiTsi or sodium naphthalenide, as well as the compounds $(Cl_3Si)(Me_3Si)_2P{=}P(SiMe_3)_2(SiCl_3)$[226] and $TsiP{=}P(C_6H_2Bu^t{}_3\text{-}2,4,6)$,[227] have been characterised spectroscopically, and the structures of the first two found by X-ray studies. The bulky groups are *trans* and all the evidence suggests that these compounds contain genuine double bonds between Group 15 elements. The reactions of TsiP=PTsi and TsiAs= AsTsi have been studied extensively.[228–232]

Attempts to make diphosphenes with smaller substituents yield polyphosphanes but diphosphenes with bulky substituents are usually stable. However, the diphosphene TsiP=$PSiPh_3$[233] and the diarsene TsiAs=AsTsi[224] oligomerise slowly at room temperature. In contrast, TsiP=$PSiMe_3$ is unstable and decomposes to give **44**, in which two Tsi groups are joined by a P_4 tetrahedron.[233]



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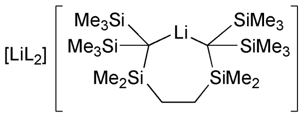

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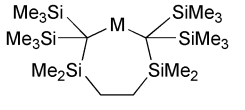


46 M = Sn **46a**
M = Pb **46b**, Zn, Hg or Yb

Compounds of the elements of Group 16 and 17

The silanol TsiOH can be made by oxidation of $TsiB(OH)_2$ with aqueous hydrogen peroxide, in the presence of sodium acetate to control the pH,[115] but its chemistry has not been studied extensively. The thiol TsiSH is obtained by the reaction between LiTsi and elemental sulfur.[234,235] On treatment with LiMe then Br_2, $SiMe_3Br$ is eliminated to give the thioketone $(Me_3Si)_2C{=}S$ as a red-violet oil. The lithium thiolate $[Li_2(thf)_{3.5}(STsi)_2]$ has been shown by an X-ray study to contain Li_2S_2 rings.[236]

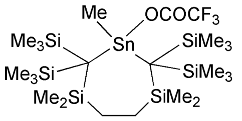
Similar reactions between LiTsi and Se or Te gave the lithium selenolates and tellurolates $[(thf)_2Li(ETsi)]$, which could be hydrolysed to TsiSeH and TsiTeH.[237] The bulky Tsi group stabilises a number of polychalcogenides of the heavier Group 16 elements.[238–240]

The halides TsiF,[241] TsiCl,[1,242–244] TsiBr,[72,245,246] TsiI,[90] $(PhMe_2Si)_3CX$ (X = Cl[247] or Br[210]) are valuable starting materials for the synthesis of organic or organometallic compounds and many examples of their use are given in the papers cited in this review. Trisyl-type halides RX (X = halogen) containing the ligands $C(SiMe_3)_n(SiMe_2Y)_{3-n}$ not previously reported in the literature can usually be made from RH by treatment with LiR then XCH_2CH_2X.[35,74]

A remarkable property of TsiI is that exposure to daylight of its solution in MeOH containing NaOMe or a soluble silver salt results in its rapid conversion into TsiH, *via* an initial dissociation into $Tsi^{\bullet}$ radicals and $I^{\bullet}$ atoms followed by a radical chain process in which hydrogen is abstracted from the CH_3 group of MeOH; the function of the base or silver ion is to remove I_2 which would otherwise trap the $Tsi^{\bullet}$ radicals. The hydrogen abstraction shows a remarkably large deuterium kinetic isotope effect of *ca.* 20.[248]

Compounds containing the bidentate ‘trisiamyl’ $C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$ and related ligands

The development of unusual chemistry associated with trisyl compounds led us to consider whether it was possible to make derivatives containing two trisyl groups attached to a single four-coordinate metal centre. Syntheses of such compounds from four-coordinate starting materials are likely to be difficult since they require five-coordinate transition states involving two trisyl groups and these are inevitably very crowded. Considerable insight is gained by the use of the bulky bidentate ‘trisiamyl’ ligand $C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$, in which two trisyl groups are effectively joined like Siamese twins.[249] The lithium compound **45** crystallises from thf or thf–tmen, with an ionic structure like that of **1**, containing a remarkable cyclic diorganolithiate anion with C–Li–C 171°. We attempted to make analogous compounds of the heavier alkali metals but obtained instead compounds containing open-chain dianions and benzene- or thf-solvated cations.[6] The alkali metal compounds reacted with four-coordinate halides, *e.g.* $SnCl_4$ or $SnMe_2Cl_2$, to give open-chain bis-metallated species irrespective of the alkali metal/tin mole ratio. This was not surprising since the formation of a metallacycle containing four-coordinate tin would require reaction through a five-coordinate transition state between the sterically hindered organoalkali metal centre and the sterically hindered tin centre in the same molecule. In contrast with two-coordinate halides MCl_2 (M = Zn, Hg, Sn, Pb, or Yb) metallacycles **46** are obtained.[6,249–251] The plumbylene **46b** was the first σ-bonded diorganolead(II) compound to be characterised.[250] It is remarkable that the C–M–C angle can vary from 166–170° in the zinc and mercury derivatives to as low as 117–118° in the tin and lead compounds. The stannylene **46a** reacts with MeI to give the oxidative addition product, which has been characterised by its conversion into the trifluoroacetate **47**, and a number of other derivatives containing four-coordinate tin.[251] These results suggest that it should be possible to make four-coordinate bis(trisyl)tin compounds. Substitutions at the highly crowded Sn^{IV} centre are of considerable interest and are currently being studied further. There is considerable scope for the development of the trisiamyl chemistry of the transition metals. So far only one compound, an ate complex **48** containing a three-coordinate Mn^{II} centre, has been reported.[252]



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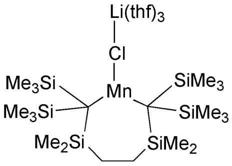

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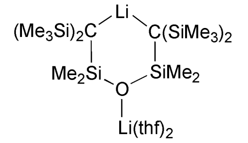

49

We have shown that the cyclic lithiate **49** can be obtained by metallation of the disiloxane $O\{SiMe_2CH(SiMe_3)_2\}_2$. In **49**, in contrast to **45**, the lithium cation is bound to the anion through the oxygen of the siloxane linkage. As far as we are aware, this is the first structurally characterised disiloxane–metal complex in which the metal is attached only through oxygen. The strength of the siloxane–lithium bond is shown by the similar Li–O(thf) and Li–O(siloxane) bond lengths and the delocalisation of carbanionic charge towards oxygen by the exceptionally short $C–SiMe_2O$ [1.806(6) Å] and long Si–O bonds [1.704(5) Å].[253] The use of **49** as a ligand transfer reagent is illustrated by the synthesis of the mercury derivative $Hg\{C(SiMe_3)_2SiMe_2\}_2O$.[35]

Further bidentate dicarbanionic ligands can be envisaged with spacers other than $–CH_2CH_2–$ or –O–, *e.g.*, $–(CH_2)_n–$, $–(OSiMe_2)_n–$, $–CH_2SiMe_2CH_2–$. Multidentate ligands with donor groups or carbanionic centres in well-defined spacial arrays should give a wide range of new coordination and organometallic chemistry, *e.g.* plausible syntheses can be devised for $R'N\{SiMe_2CLi(SiMe_3)_2\}_2$ or $R'Si\{OSiMe_2CLi(SiMe_3)_2\}_3$.

Ligand configuration

Since much of the interesting chemistry of trisyl-type compounds can be attributed to steric effects at the adjacent metal centre, it is pertinent to enquire what general points can be made about the configuration of the ligands themselves. There is considerable variation in the mean length of the bond from the central carbon to silicon. When an electronegative atom is adjacent to the carbon, electrons are withdrawn from Si–C bonds, which become weaker and longer [*e.g.* for TsiCl, Si–C = 1.939(6) Å]; when the adjacent atom has low electronegativity electrons are delocalised into the Si–C bonds, which become shorter and stronger {*e.g.* Si–C = 1.818(10) Å in $Cs(C_6H_6)_3Tsi$ and 1.800(8) Å in the anion $[C\{SiMe_2C_6H_4\text{-}Me\text{-}o\}_3]^-$}.[4,26,254] However, steric effects are superimposed on these electronic effects, *e.g.* the inner Si–C bond lengths are 1.886(6) Å in $(Me_3Si)_3CH$ and 1.928(3) Å in $(Me_3Si)_3CSiMe_3$, even though the electronegativities of H and Si are not very different.[69] In general as the Si–C bonds become shorter, the Si–C–Si angles become wider and reach 120° in the free carbanion. The delocalisation of charge has little effect on the Si–Me bond lengths at the periphery of the molecule; these are always close (±0.01 Å) to 1.875 Å, the value in $SiMe_4$.

In all compounds intraligand strain is reduced by twisting of $SiMe_3$ groups about Si–C bonds to give M–C–Si–C torsion angles of 40, −80 and 160° (±2°), instead of 60, −60 and 180° for fully staggered conformations.[68] Within a particular Tsi group all the Me_3Si are twisted in the same direction so that they interlock, making the group as a whole chiral. The barrier to interconversion of the enantiomers through the eclipsed position is usually low enough to ensure that there is fast exchange on the NMR timescale in solution.[255,256]

Some of the features of trisyl chemistry described in this review are shown in the chemistry of organometallic compounds containing other bulky ligands, most notably aryl groups $C_6H_2R'_3$ (R′ = Ph, Pr^i, Bu^t, or another bulky aryl),[257] $Si(SiMe_3)_3$,[258] $SiBu^t_3$,[259] or cyclopentadienyl groups bearing bulky substituents.

Acknowledgements

We thank the many people who have worked with us on trisyl chemistry over the years; several made key contributions to the research. Their names appear in the full list of our publications in this area that is included in the supplementary electronic material.† We acknowledge in particular the help given by Dr D. A. R. Happer in the preparation of this review, and the contributions from joint projects with him, Professor W. A. Stańczyk, Professor A. I. Almansour, and Dr Paul Lickiss. We are grateful for the important contribution of Dr P. B. Hitchcock, who determined the great majority of the crystal structures reported, and thank also Dr A. G. Avent for valuable help in recording and interpreting NMR spectra, and Dr A. Abdul-Sada for help with mass spectrometry. The programme was consistently supported by the EPSRC (currently by Grant GR/L83585).

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