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Compounds of elements of Groups 11–13 containing $(Me_3Si)_3C$, $(PhMe_2Si)_3C$ or related ligands[1]

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Contents

Abstract

A survey is given of the preparation and properties of compounds of elements of Groups 11–13 containing the very bulky ligand $(Me_3Si)_3C$ or $(PhMe_2Si)_3C$, or a related ligand of the type $(Me_3Si)_2(XMe_2Si)C$.

Keywords: Group 11; Group 12; Group 13; Bulky ligands

1. Introduction

Much novel chemistry has emerged from studies of compounds in which a bulky ligand $(Me_3Si)_3C$ (R*) (the 'trisyl' ligand) or $(PhMe_2Si)_3C$ (R**) or a related ligand

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[1] Dedicated with affection to the memory of our colleague and friend Joseph Chatt, who played a leading role in the development of inorganic and organometallic chemistry in the second half of the century and whose presence in this School made a major contribution to its success.

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$(\mathrm{Me_3Si})_2(\mathrm{XMe_2Si})\mathrm{C}$ (e.g. $\mathrm{X=CH{=}CH_2}$, OMe or $\mathrm{N_3}$) is attached to a metal or metalloid. Some examples not discussed in the main review below are as follows.

(i) Isolation of salts containing the previously unknown but long sought species $[\mathrm{MR}^*_2]^-$, where M = Li [1,2] or Na [3], the polymeric ionic species $(\mathrm{MR}^*)_n$ with M = K [4] or Rb [5] and $(\mathrm{MR}^{**})_n$ with M = Na [3] or K [4]. (One of the lithate salts, namely $[(\mathrm{pmdeta})\mathrm{Li}(\mu\text{-}\mathrm{Cl})\mathrm{Li}(\mathrm{pmdeta})][\mathrm{LiR}^*_2]$ (pmdeta = $\mathrm{Me_2N(CH_2)_2NMe(CH_2)_2NMe_2}$), provided the first example of a linear chlorine-centred cation [2].)

(ii) Preparation and characterization of the first derivatives of Mg and Mn, i.e. MR^*_2, M = Mg [6,7] or Mn [8], shown to be two-coordinate in the solid state. The Mg compound is remarkably unreactive; for example, it will not react with boiling neat MeCOCl [7].

(iii) Preparation and characterization of (a) the first stable silanetriol $\mathrm{R^*Si(OH)_3}$ [9], (b) the first normal cyanates of silicon, such as $\mathrm{R^*SiMe_2OCN}$ [10], (c) the only normal thiocyanate of silicon $(\mathrm{Me_3Si})_2(\mathrm{MeOMe_2Si})\mathrm{CSiMe_2SCN}$ [11] and (d) the first mono-organolead(II) compounds $[(\mathrm{PbR^{**}Cl})_2]$ [12a] and $[(\mathrm{PbR^*Cl})_3]$ [12b].

(iv) Preparation by Escudié and his colleagues [13a], and independently by Cowley and his colleagues [13b], of the alkyl-substituted diphosphene $\mathrm{R^*P{=}PR^*}$, and by the former group of the first compounds containing an As=As or P=As double bond, namely $\mathrm{R^*As{=}AsR^{**}}$ [13c] and $\mathrm{R^*P{=}AsR^{**}}$ [13d].

(v) Preparation of Arnold and his coworkers of the first stable organotellurium and organoselenium hydrides MR*H [14], by du Mont and his colleagues of the first organotellurium and organoselenium cyanides MR*CN and thiocyanates MR*SCN [15], and by Sladky and coworkers of the first stable compounds $\mathrm{R^*MM'M''R^*}$ containing a Te—Te—Te, Se—Se—Se, Te—Se—Te or Se—Se—Te linkage [16].

(vi) Preparation and characterization of the first organomanganese and organocobalt halides R*MCl as their complexes $[\mathrm{Li(THF)_4}][\mathrm{R^*_3M_3Cl_4(THF)}]$ [17].

(vii) Preparation and characterization of the first solvent-free diorganolanthanides MR^*_2 (M is Yb or Eu) and the first lanthanide metal analogue of a Grignard reagent, namely YbR*I [18].

(vii) Recognition of a range of novel mechanisms of reaction at silicon centres. Particularly noteworthy are those involving (a) formation of transient bridged cations I from the compounds $(\mathrm{Me_3Si})_2\mathrm{C(SiMe_2Z)(SiMe_2X)}$ (such reactions can give products from 1,3-migration of Z (e.g. Z = Ph, OMe, Cl) and formation of the cations is reflected in the large anchimeric assistance by Z to the departure of $\mathrm{X^-}$) [19], (b) generation of silanone ($\mathrm{R_2Si{=}O}$) intermediates [20], (c) generation of silyl radicals by thermolysis of a silicon iodide, e.g. $\{(\mathrm{Me_3Si})_3\mathrm{C}\}\mathrm{Ph_2Si}^{\cdot}$ from $(\mathrm{Me_3Si})_3\mathrm{CSiPh_2I}$, and migration of alkyl or aryl groups within such radicals [21], and (d) rapid Si-to-Si migration of an alkyl or aryl group within a silene intermediate; for example the reversible interconversions between $(\mathrm{Me_3Si})_2\mathrm{C{=}SiPh_2}$, $(\mathrm{Me_3Si})(\mathrm{Ph_2MeSi})\mathrm{C{=}SiMe_2}$, $(\mathrm{Me_3Si})(\mathrm{PhMe_2Si})\mathrm{C{=}SiMePh}$ and $(\mathrm{PhMe_2Si})_2\mathrm{C{=}SiMe_2}$ [22][2]

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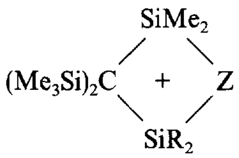
[2] Wiberg and his colleagues have uncovered much novel organosilicon chemistry by making and using a wide range of lithium compounds of the type $(\mathrm{Me_3Si})_2(\mathrm{XMe_2Si})\mathrm{CLi}$ [23].



I

Use of the $(Me_3Si)_3C$ group R* as a ligand in organometallic chemistry began with the demonstration that $(Me_3Si)_3CH$ could be metallated with MeLi in Et_2O—THF to give the reagent R*Li (for the actual composition see below), which was found to react with Me_3MCl (M = Si, Ge or Sn) to give R^*MMe_3 [24]. (The same work [24] also made available for the first time the reagent $LiCH(SiMe_3)_2$, which was obtained analogously by metallation of $(Me_3Si)_2CH_2$ and was used in very fruitful studies by our colleague M.F. Lappert and his coworkers, and later by many others.) However, the remarkable ability of the ligand R* to induce steric hindrance at a metal or metalloid centre was not fully appreciated until the silicon trichloride R^*SiCl_3 was found not to undergo substitution in boiling MeOH containing $AgNO_3$ or NaOMe [25]. A further illustration was then provided by the striking chemical stability of ZnR^*_2 [26]. We have reviewed aspects of the chemistry of compounds in which the R*, R** or related ligand is attached to a metal of Groups 1–3 elsewhere [27], and we concentrate below on corresponding derivatives of the metals of Groups 11–13. A comprehensive review by our former colleague P.D. Lickiss of the preparation of compounds containing R*, R** and related ligands attached to metals or metalloids has appeared recently [28].

It should be noted that when in the subsequent account we use the formula LiR* without qualification we refer to the reagent actually known to be $[Li(THF)_4][LiR^*_2]$ [1,29]. The unsolvated reagent $[\{LiR^*\}_2]$, first made by Uhl and his coworkers [30] by treatment of HgR*Bu with LiBu, is referred to as 'unsolvated LiR*'. The formula LiR** refers to the reagent prepared in Et_2O—THF [31]; this is less reactive than the solvated LiR*, perhaps because it is a neutral species whereas the latter is ionic, and possibly also because the intramolecular coordination of the Ph group to the Li centre that is observed in the solid [32] may persist in solution and shield the Li atom.

$$R^* = C(SiMe_3)_3 \qquad R^{**} = C(SiMe_2Ph)_3$$

2. Group 11

Examples of relevant derivatives of the metals of this group are confined to the following.

(a) The first structurally characterized dialkylcuprate (i.e. a Gilman reagent), namely $[Li(THF)_4][CuR^*_2]$, made by reaction of LiR* with CuI [32]. (However, a compound containing a diarylcuprate ion $[Cu(aryl)_2]^-$ with aryl = 2,4,6-$Me_3C_6H_2$

[33] had been made a little earlier; for other diorganocuprates isolated subsequently see Ref. [34].)

(b) The only known simple diorganoargentate $[Li(THF)_4][AgR^*_2]$, obtained by reaction of LiR* with AgI [35].

(c) The stable crystalline gold complexes AuR*L ($L = PEt_3$, PPh_3, $AsPh_3$), obtained by reaction of LiR* with AuClL [36].

The cuprate and argentate anions are linear, and their geometries are closely similar to those of the corresponding anions containing Li [1] or Na [3]. The main features of the structures are (i) the short $C—SiMe_3$ bond lengths, apparently associated with delocalization of negative charge into the R* group, and (ii) a characteristic disposition of the Me groups, with one Me group of each Me_3Si ligand pointing directly away from the metal and the other two pointing only slightly inwards to leave the metal atom rather exposed (Fig. 1). This arrangement is different from that in the structures of the neutral species MR^*_2 with M = Zn Cd, Hg, Mg, Mn, in which the metal is strongly shielded by Me groups (see below).

3. Group 12

The compounds MR^*_2 (M = Zn [26], Cd [26], Hg [37,38]) are obtained by reaction of LiR* with the appropriate dihalide MCl_2. All three show remarkably high chemical and thermal stability.

Two noteworthy features of the chemistry of HgR^*_2 are (a) its unusual thermal stability (it decomposes, after melting, only at about 300 °C), and (b) the ready

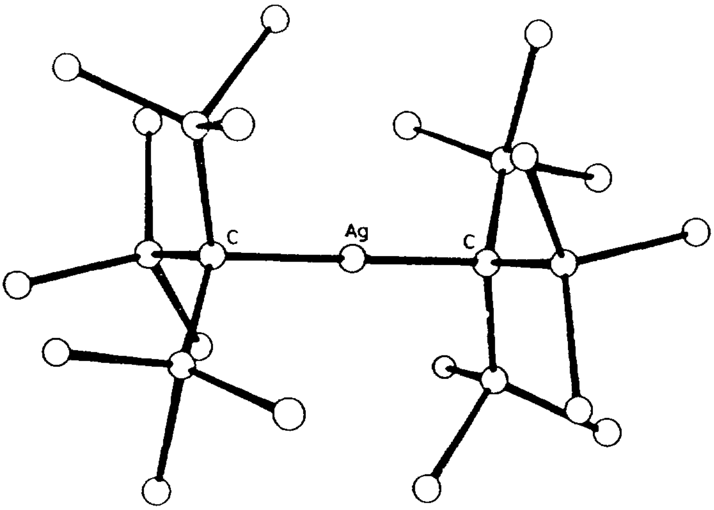


Fig. 1. Structure of the anion $[AgR^*]^-$. One Me from each $SiMe_3$ group points outwards from the metal and two Me groups point slightly in towards it.

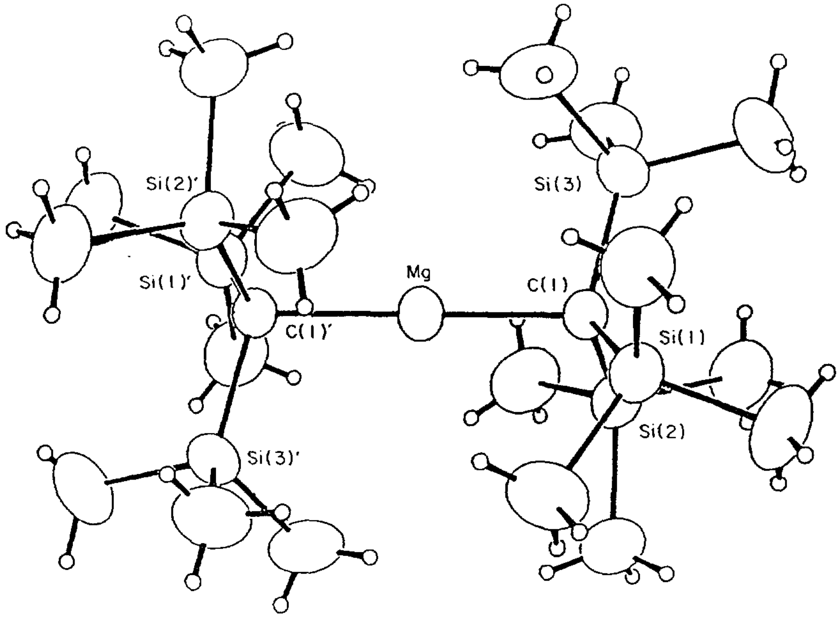


Fig. 2. The (centrosymmetric) structure of the compound MgR^*_2, representative also for those of MR^*_2 (M = Zn, Cd, Hg, Mn). One Me group from each $\mathrm{SiMe_3}$ group points in towards the metal and two point outwards from it. The planes defined by carbon atoms of the inward-pointing Me groups are only 2.97 Å apart, well below the distance of 4.0 Å given by twice the sum of the van der Waals radius of the Me group, but the relevant Me groups mesh together so that no Me···Me distance is below 4.0 Å.

generation from it of the highly persistent radical $\mathrm{R}^{*\cdot}$ by exposure to UV light (possibly the first ESR identification of an organic radical produced in this way) [37].

The strikingly low reactivity of ZnR^*_2 is illustrated by the fact that whereas $\mathrm{ZnMe_2}$, and even $\mathrm{Zn[CH(SiMe_3)_2]_2}$ [39], ignite spontaneously in air and explode in contact with water, ZnR^*_2 can be steam distilled in air [26]. This inertness can be attributed to the very effective shielding of the metal atom by Me groups, three of which from each R* ligand point inwards and interlock with those from the other side (Fig. 2) to hide the metal. Some idea of the degree of protection of the metal atoms in compounds of the type MR^*_2 (except when R = Yb or Eu [18]) can be seen from the photograph of a space-filling scale model of MgR^*_2 shown in Fig. 3.

The remarkable resistance to attack of the Zn—C bond in this type of compound means that a range of derivatives $\mathrm{Zn[C(SiMe_3)_2(SiMe_2X)]_2}$, **1**, can be made, starting from the hydride **1**(X is H) by substitution at the functional silicon centres under conditions in which ordinary organozinc compounds are rapidly destroyed [40]. Some of the reactions are summarized in Eqs. (1)–(5).

$$\mathrm{Zn[C(SiMe_3)_2(SiMe_2X)]_2}\ (\mathbf{1})$$

$$\mathbf{1}(\mathrm{X=H})\xrightarrow[\mathrm{CCl_4}]{\mathrm{Br_2}}\mathbf{1}(\mathrm{X=Br}) \qquad (1)$$

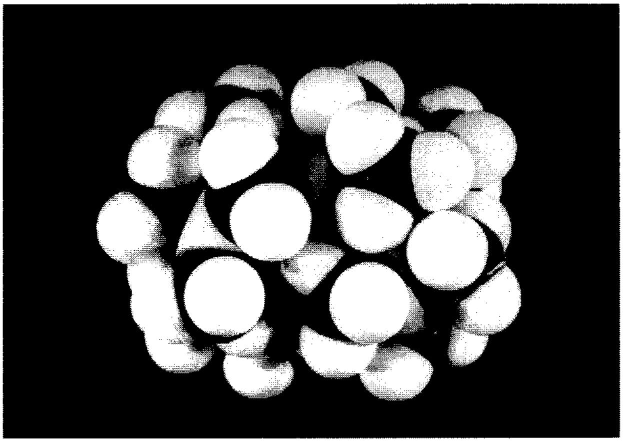


Fig. 3. Space-filling scale model of MgR_2^* showing how Me groups hide the metal. This does not give an exact picture since the $Me_3Si{-}C{-}SiMe_3$ angles open out from the tetrahedral value to a mean of 112.6°, which would bring the interlocking Me groups even closer, but the $Me{-}Si{-}Me$ angles close to a mean of 106.1° to have a counter-effect.

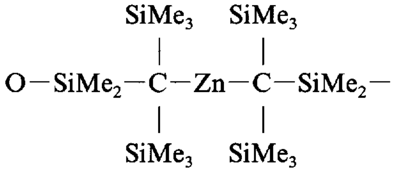
$$\mathbf{1}(X=H)\xrightarrow[CCl_4]{I_2}\mathbf{1}(X=I)\xrightarrow[CF_3CO_2H]{Ag_2O}\mathbf{1}(X\text{ is }O_2CCF_3) \qquad (2)$$

$$\mathbf{1}(X=H)\xrightarrow[CCl_4]{ICl}\mathbf{1}(X=Cl)\xrightarrow{AgBF_4}\mathbf{1}(X=F) \qquad (3)$$

$$\mathbf{1}(X=Cl)\xrightarrow[THF]{H_2O}\mathbf{1}(X=OH)\xrightarrow{MeCOCl}\mathbf{1}(X=OCOMe) \qquad (4)$$

$$\mathbf{1}(X=OH)\xrightarrow{Me_2SiCl_2}\mathbf{1}(X=OSiMe_2Cl) \qquad (5)$$

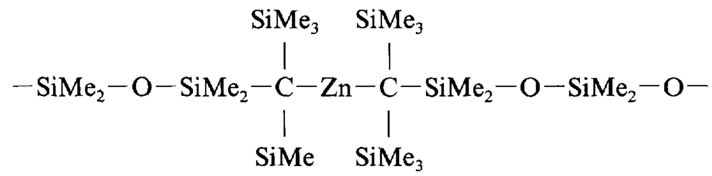
Special interest attaches to the hydroxide **1**(X is OH), because the OH group can be used in principle to introduce the unit **II** into siloxane chains.



$$\begin{array}{c} \quad\quad\quad\quad SiMe_3 \quad\quad SiMe_3 \\ \quad\quad\quad\quad | \quad\quad\quad\quad | \\ O{-}SiMe_2{-}C{-}Zn{-}C{-}SiMe_2{-} \\ \quad\quad\quad\quad | \quad\quad\quad\quad | \\ \quad\quad\quad\quad SiMe_3 \quad\quad SiMe_3 \end{array}$$

II

The Si—OH bond in **1**(X is OH) itself is very resistant towards the attack at oxygen that would be required for direct formation of siloxane linkages. However, although it does not react with Me_3SiCl, **1**(X is OH) does react with Me_2SiCl_2 to give **1**($X=OSiMe_2Cl$), which is readily hydrolysed, presumably to give initially **1**($X=OSiMe_2OSiMe_2OH$), which can be expected to take part readily in siloxane formation to give cyclic or linear polysiloxanes incorporating the unit **III**.



$$-\mathrm{SiMe_2{-}O{-}SiMe_2}-\underset{\mathrm{SiMe}}{\overset{\mathrm{SiMe_3}}{\mathrm{C}}}-\mathrm{Zn}-\underset{\mathrm{SiMe_3}}{\overset{\mathrm{SiMe_3}}{\mathrm{C}}}-\mathrm{SiMe_2{-}O{-}SiMe_2{-}O}-$$

III

There is no reason to doubt that a corresponding range of mercury derivatives $Hg[C(SiMe_3)_2(SiMe_2X)]_2$ could be obtained analogously from $Hg[C(SiMe_3)_2(SiMe_2H)]_2$, but in fact the only one made, i.e. $Hg[C(SiMe_3)_2(SiMe_2OMe)]_2$, was obtained by reaction of $HgCl_2$ with $Li[C(SiMe_3)_2(SiMe_2OMe]$ [41]. In contrast, the Cd—C bonds in $Cd\{CSiMe_3)_2(SiMe_2H)]_2$ were found to be susceptible to attack by halogens, with cleavage occurring upon treatment with Br_2 or ICl in CCl_4 [40]; this was not wholly surprising since CdR^*_2 itself had been observed some years earlier to be cleaved by ICl [26]. The greater ease of attack on the Cd—C than on the Zn—C bonds in these species may arise from the greater length of the former, which leads to a larger exposure of the Cd than of the Zn atom. Thus the M—C distances in a series of compounds **1** fall in the range 1.97–1.98 Å, whereas those in related cadmium compounds are in the range 2.16–2.17 Å, and the planes defined by the three inward-pointing Me groups of each R* ligand (cf. Fig. 2) are about 0.3 Å further apart in the cadmium compounds [40].

The compounds $Cd[(SiMe_3)_2(SiMe_2X)]_2$ with X = H [40], OMe [40] or $CH{=}CH_2$ [42] were obtained by reaction of $CdCl_2$ with the corresponding lithium derivatives $Li[C(SiMe_3)_2(SiMe_2X)]$; it is noteworthy that in the structure of the compound with $X = CH{=}CH_2$ the latter group replaces one of the inward-pointing Me groups.

There is an interesting difference between the crystal structures of the compound $M[C(SiMe_3)_2(SiMe_2OMe)]_2$ with M = Hg on the one hand, and those with M = Zn or Cd on the other [40]. In the latter the OMe groups point inwards towards the metal atom (Fig. 4) in a position that would potentially allow coordination to that atom, although the M···O distance is not significantly different from the sum of the relevant van der Waals radii. In contrast, in the mercury compound the OMe groups point outwards, away from the metal (Fig. 5) [41]. In the case of the zinc compound $Zn\{C(SiMe_3)_2(SiMe_2X)\}_2$ with $X = O_2CCF_3$ the substituents likewise point outwards, there being no room for them to lie pointing in towards the metal [40]. (However, there may be a weak intramolecular interaction between the carbonyl O and the Si atom to which the carbonyl group is attached, as the Si···O distance (3.099(3) Å) is well below the sum (3.60 Å) of the relevant van der Waals radii.)

The most striking of the compounds **1** in terms of structure is that with X = OH, which in the solid is present as dimers with the monomers held together by hydrogen bonds (Fig. 6). There is also hydrogen bonding between the OH groups within each monomer, and the result is that the two attached $SiMe_2$ fragments are drawn together, causing the C—Zn—C linkage to be significantly bent, the relevant angle

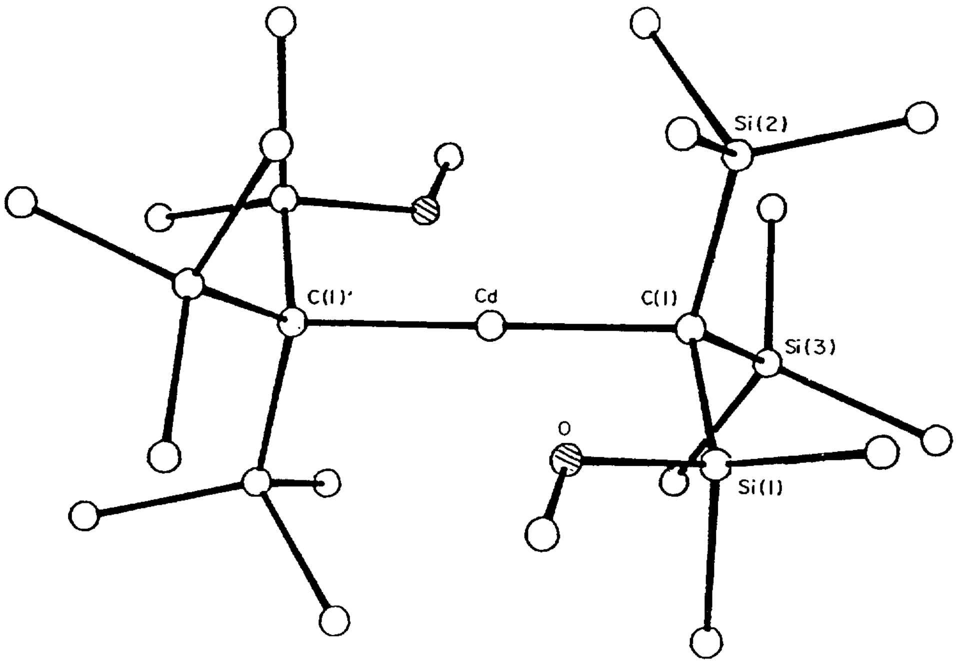


Fig. 4. Structure of Cd{$(SiMe_3)_2(SiMe_2OMe)$}$_2$ (the structure of the corresponding Zn compound is virtually identical) showing the OMe groups pointing in towards the metal.

being 175.9(1)°. Furthermore, because the OH groups in each monomer are inequivalent, with one accepting a hydrogen atom intermolecularly and donating its own hydrogen atom intramolecularly, and the other acting conversely, the two halves of the monomer have distinctly different geometries.

In the crystal structure of compounds containing the R* ligand there is frequently disorder in the silicon sites, and better crystallographic information can often be obtained by using the R** ligand, although this sometimes results in a different type of structure. Treatment of the chlorides MCl_2 (M is Zn, Cd, Hg) with LiR** in Et_2O—THF gives the corresponding metallates $[R^{**}M(\mu\text{-}Cl)_2Li(THF)_2]$, which when heated give the compounds MR**Cl, all of which form dimers in the solid state [43]. For M = Zn or Cd, the metal atoms in the dimers are three-coordinate in a planar environment, with Cl—M—Cl angles of about 136° (Fig. 7), but for M is Hg the geometry is almost that expected for two-coordinate mercury, with a Cl—Hg—Cl angle of 170°, and only a very weak intermolecular Hg···Cl interaction (Fig. 8). Hydrolysis of ZnR*Cl gives the dimeric hydroxide 2 [44]. In the case of Zn it has been shown by Westerhausen and coworkers that reaction of one molar proportion of LiR* with $ZnBr_2$ gives the zincate $Li(THF)_2(Et_2O)[ZnR^*Br_2]$, but $ZnCl_2$ gives the more complex species $Li(THF)_2(Et_2O)[Zn_2R^*_2Cl_3]$ [39]. The latter reacts with a range of simple LiR compounds (e.g. with R = Me, Bu, Ph, or even the

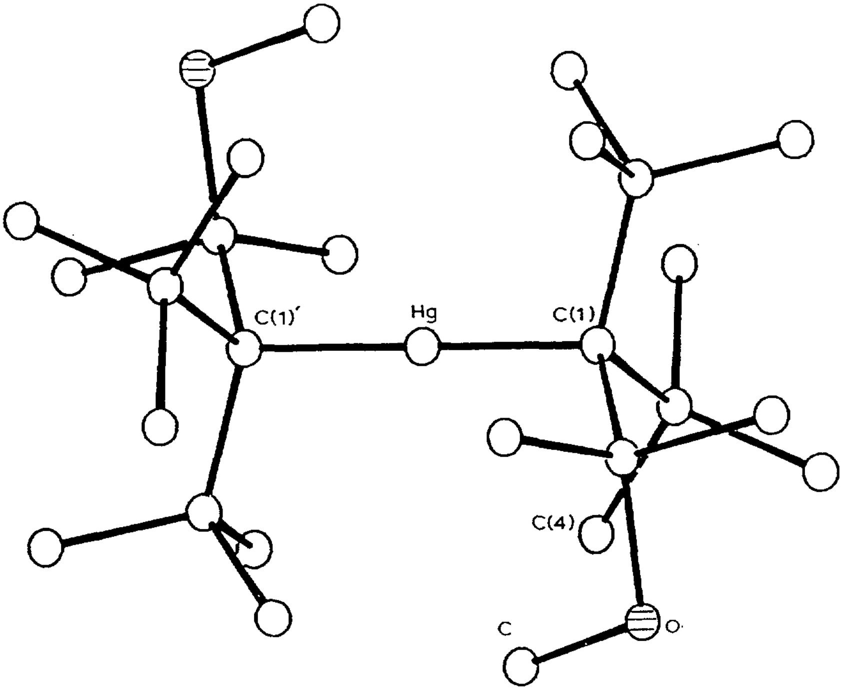
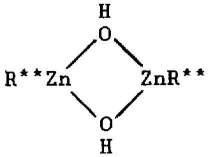


Fig. 5. Structure of $Hg\{(SiMe_3)_2(SiMe_2OMe)\}_2$ showing the OMe groups pointing away from the metal.

bulky $CH(SiMe_3)_2$) to give unsymmetrical compounds ZnR*R. Interestingly, ZnR*Ph reacts with LiPh to give the zincate $[Li(THF)_4][ZnR^*Ph_2]$.



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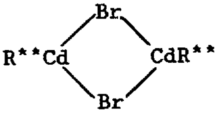

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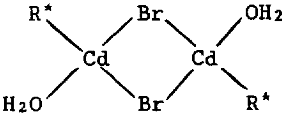

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Reaction of LiR** with $CdBr_2$ gives the cadmate $[Li(THF)_2][CdBr_2R^{**}]$; this on heating gives CdR**Br, which in the crystal has the dimeric structure **3** [45]. On recrystallization from moist tetrahydrofuran (THF), this bromide crystallizes as the hydrate **4**, which in the crystals obtained in the presence of THF has a molecule of the latter hydrogen bonded to each coordinated water molecule.

Treatment of $CdCl_2$ with an equimolar amount of LiR* in Et_2O—THF gives the dicadmate **5**, the anion of which has the structure **6** [46]. When heated, **5** breaks down to give CdR*Cl, which is a tetrameric cubane in the solid state but seems to form dimers in the gas phase [45,46]. A similar reaction of LiR* with $CdBr_2$ gives the tricadmate **7**, the anion of which has the cubic structure **8**. In the

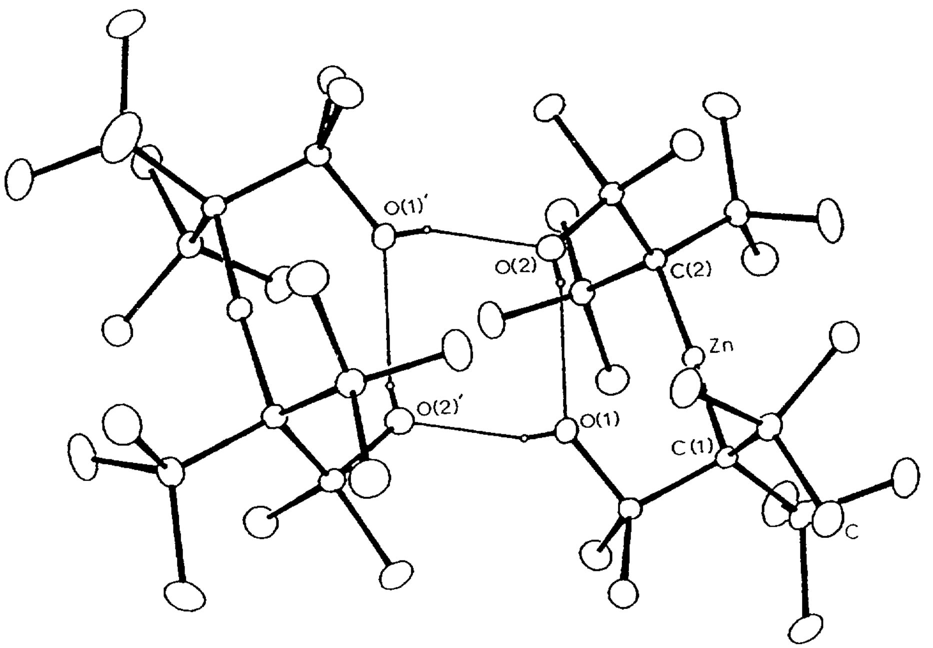
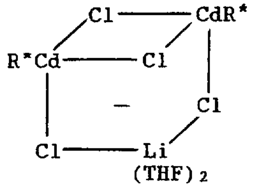


Fig. 6. Structure of the hydrogen-bonded dimer of $Zn\{(SiMe_3)_2(SiMe_2OH)\}_2$. The hydrogen bonding draws together the OH groups within each dimer to give a C—Zn—C angle of 175.9(1)°.

presence of traces of moisture, **7** is converted into the neutral species $[Li(THF)_3(\mu\text{-}Br)_3(\mu_3\text{-}OSiMe_3)(CdR^*)]$ (**9**; for clarity the THF groups on Li are omitted). Both **7** and **9** give CdBrR* on heating; CdBrR* is also formed when either **7** or **9** is treated with aqueous THF, but if alkali is present the hydroxide Cd(OH)R* is obtained.

$[Li(THF)_4][Li(THF)_2(\mu\text{-}Cl)_4(CdR^*)_2]$ **5**

$[Li(THF)_4][(CdR^*)_3(\mu\text{-}Br)_3(\mu_3\text{-}Br)]$ **7**



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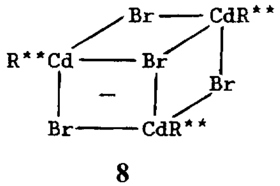

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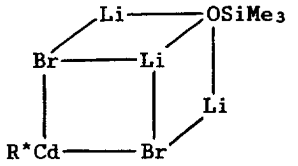

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When $HgCl_2$ is treated with a two-molar or more proportion of LiR** the reaction does not go beyond the monosubstitution stage, and even isolated HgR**Cl does not react further with LiR** [47]. In contrast, reaction of $HgCl_2$ with a half-molar

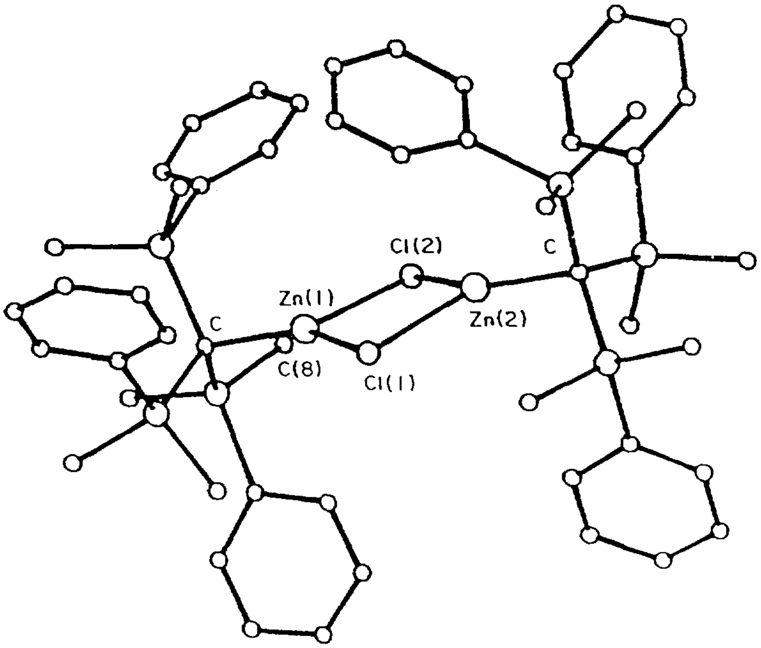


Fig. 7. Structure of $[\{ZnR^*Cl\}_2]$ showing the strong interaction between the molecules in the dimer.

proportion of the more reactive LiR^* gives only HgR^*_2 and unchanged $HgCl_2$. However, $HgR^{**}Cl$ reacts with LiR^* to give the mixed dialkyl derivative HgR^*R^{**}, although only in low yield together with a variety of side-products including R^*H and possibly HgR^*_2. A little surprisingly, reaction of $HgBr_2$ with LiR^* does give the monosubstituted product HgR^*Br [30]; the difference between the behaviour of $HgCl_2$ and $HgBr_2$ may be due to the higher solubility of the bromide in THF, which means that sufficient of it is present in solution to trap the LiR^* before the latter reacts with HgR^*Br.

Some unusual reactions were observed during the preparation of some mixed alkylmercurials HgR^*R and $HgR^{**}R$ where R is a simple alkyl or a Ph group [47]. For example, treatment of HgPhCl with LiR^* in Et_2O—THF did not give the expected $HgPhR^*$ but rather a mixture of HgR^*_2 and $HgPh_2$; it is possible that these reactions involve reversible formation of mercurate ion intermediates (cf. the reaction of ZnR^*Ph with PhLi mentioned earlier):

$$HgPhCl + LiR^* \rightleftharpoons Li[HgPhR^*Cl] \rightleftharpoons HgR^*Cl + LiPh \tag{6a}$$

$$HgR^*Cl + LiR^* \rightleftharpoons Li[HgR^*_2Cl] \rightarrow HgR^*_2 + LiCl \tag{6b}$$

$$HgPhCl + LiPh \rightleftharpoons Li[HgPh_2Cl] \rightarrow HgPh_2 + LiCl \tag{6c}$$

Treatment of HgR^*Br with MeLi also gave mainly HgR^*_2 (though HgR^*Me was obtained by use of MgMeI). Again, it is possible that the intermediate $HgR^*MeBrLi$

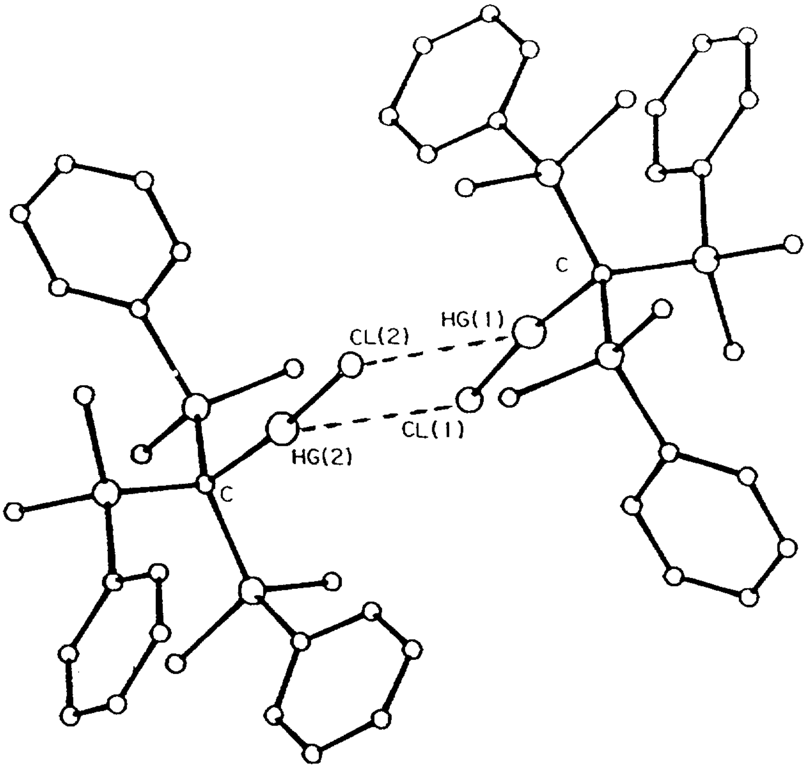


Fig. 8. Structure of [{HgR*Cl}$_2$] showing the weak interaction between the molecules in the dimer.

breaks down to HgMeBr and LiR*, which then reacts with HgR*Br to give HgR$^*_2$. In a mobile system HgR$^*_2$ could well be the favoured product because addition to it of LiCl, LiBr or LiR, to regenerate a mercurate ion, is sterically inhibited.

The availability of a range of compounds HgR*R and HgR**R obtained by the above methods allowed detection of one of the most intriguing effects of the bulky ligands. For these compounds, and for $HgPh_2$ and $Hg(CH_2Ph)_2$, the temperatures of onset of decomposition in sealed melting-point tubes or a differential scan calorimeter were observed, with the results shown in Table 1 [47,48]. (The table also includes a value for the decomposition temperature of $HgBu^t_2$; this is actually the temperature at which rapid decomposition was found to occur in cyclodecane [49], but it has been shown in the case of $Hg(CH_2Ph)_2$ that the decomposition temperature for the melt is similar to that for a solution in toluene [50].) The decomposition temperatures of the HgR*R and HgR**R compounds are much higher than those for the corresponding HgR_2 compounds, and this can clearly be seen from Table 1 by comparison of the values for $HgBu^t_2$ and $Hg(CH_2Ph)_2$ with those for HgR*Bu^t and HgR**(CH$_2$Ph). Furthermore, monitoring by ^{1}H NMR spectroscopy has shown that only at about 245 °C does HgR**CH$_2$Ph decompose in solution at approximately the same rate as $Hg(CH_2Ph)_2$ at 150 °C, implying that the latter is probably

Table 1
Approximate temperatures T of onset of decomposition for some diorganomercury compounds

Compound[a]	T[b] (°C)	Compound[a]	T[b] (°C)
HgR*Me	325	HgR**Ph	280, 280[c]
HgR**Me	307	$HgPh_2$	213, 215[c]
HgR^*Pr^i	233	$HgR^{**}CH_2Ph$	240, 275[c]
HgR*Bu	280, 290[c]	$Hg(CH_2Ph)_2$	155
HgR**Bu	285	HgR^*_2	300, 330[c]
HgR^*Bu^t	220	HgR*R*	322
$HgBu^t_2$	140[d]	HgR**Cl	272
HgR*Ph	268		

[a] R* is $(Me_3Si)_3C$; R** is $(PhMe_2Si)_3C$. [b] To within approximately ±10 °C; in melting-point tube unless otherwise indicated. [c] By differential scan calorimetry. [d] In solution.

at least 4500 times more reactive [48]. These observations are of considerable significance, since they indicate either that the commonly accepted mechanism of the thermal decomposition of diorganomercurials is incorrect or that R* and R** groups can inhibit the unimolecular dissociation of the Hg—R bond by some previously unrecognized effect, as discussed below.

In the usually accepted mechanism of thermal decomposition of a diorganomercurial HgR_2, the rate of the reaction is that of the dissociation of one Hg—R bond into $RHg^{\cdot}$ and $R^{\cdot}$, or of both such bonds simultaneously [51]. Since the bulk of the R* or R** group should have no influence on the ease of homolytic dissociation of the Hg—R bond, the observed stabilization could imply that some other mechanism actually applies [26], such as a chain process involving bimolecular attack on the substrate, which would be sterically inhibited by the presence of the R* or R** group. However, although a chain mechanism does appear to operate in photo-initiated decomposition of $Hg(CH_2Ph)_2$ [52], there is no reason to believe that chains are significantly involved in the thermal decomposition. Furthermore, even in the photo-initiated decomposition the chain length seems to be only about 8 [52], and allowance for participation of a chain of similar length in the thermal process would still leave the rate of decomposition of $Hg(CH_2Ph)_2$ much higher than that of $HgR^{**}CH_2Ph$.

The alternative, and even more interesting, possibility is that the presence of the R* or R** does in fact reduce the ease of dissociation of the $Hg—CH_2Ph$ bond, and we have tentatively suggested that this could be accounted for in terms of the prediction by Marcus [53] that the rate of energy transfer from one ligand to another on the same metal atom should be abnormally low for a heavy metal such as tin. The magnitude of this effect should increase with the mass of the metal, and so should be particularly large for mercury. When a compound of the type HgR*R or HgR**R is in thermal equilibrium at a given temperature in the melt or in solution, a molecule that has acquired an excess of energy at least equal to the energy required for dissociation of the Hg—R bond will usually have most of that excess energy dispersed within the R* or R** ligand, so that it can only rarely be transmitted to the Hg—R bond before the molecule is deactivated by collision. According to this picture it is the molecular complexity of the R* or R** ligand (the R** ligand contains 63 bonds) that matters in this context, and not the bulk and overall shape that are responsible for its steric inhibition of other types of reaction. If this interpretation is correct, then use can be made of the effect in stabilizing other organometallic compounds towards decompositions that occur by a unimolecular mechanism, and not necessarily only those involving generation of radicals.

It is convenient at this point to draw attention to the fact (see below) that reactions of LiR* and LiR** with the di- or trihalides MX_n (M = Mg [6,7], Zn, Cd, Hg, and also (see later) Ga and In) give the stable metallates $Li[MRX_n]$ (R = R* or R**), and even $SnCl_2$ appears to give the stable species $Li[SnR^*Cl_2]$ [54]. Furthermore, these seem to be the initial products, formed by addition of LiR to the metal centre, and not simply the species that separate from a mixture of LiCl and initially formed $MRCl_{n-1}$. (For example, when CdR*Cl is heated with LiCl in THF there is no formation of $LiCdR^*Cl_2$.) It seems likely that reactions of the halides MX_2 and MX_3 with simple LiR species also proceed via the ate complexes $Li[MX_nR]$ rather than by direct displacement of X^- by R^-, but that these are normally only transient species and remain undetectable. What gives rise to the stability of the complexes when R is R* or R**? It is probable that the loss of LiCl from the metallates is a unimolecular process (or at least does not involve attack at the highly sterically hindered metal centre), and if anything the crowding around the metal should act to increase the rate of loss of LiX. Again, our suggestion of dispersal of energy over the complex ligand coupled with slow transfer of energy across the heavy metal atom offers a plausible explanation.

4. Group 13

4.1. Boron

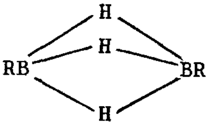
The first attempt to attach the R* group to boron, involving the reaction between LiR* and BF_3 in Et_2O—THF produced a surprise, as the main product was the alkoxy fluoride $BR^*F[O(CH_2)_4R^*]$; upon treatment with LiPh this gave $BR^*Ph[O(CH_2)_4R^*]$, the crystal structure of which was determined [55a]. It seems that in the presence of BF_3 the LiR* cleaves THF to give $R^*(CH_2)_4OLi$, which then reacts at a B—F bond to give a $B—O(CH_2)_4R^*$ bond. (Similar cleavage of THF occurred in the presence of $CdCl_2$ or $AlCl_3$, as described below.) In contrast, the reaction between LiR** and BF_3 in Et_2O—THF gave $BR^{**}F_2$ in 85% yield [55b]; again, the difference in the behaviour of LiR* and LiR** may be associated with the lower reactivity of the latter. The bromide BPh_2Br reacts normally with LiR* to give BR^*Ph_2 [56].

Both Paetzold and his colleagues and Klingebiel and his colleagues have made compounds containing B—R* bonds by reactions of LiR* at B—F bonds. Thus treatment of BBu^tF_2 with LiR* gave BR^*Bu^tF [56]. (In an extension to boron of the method used to generate $(Me_3Si)_2C{=}SiR_2$ species from $(Me_3Si)_3CSiR_2F$ [57]

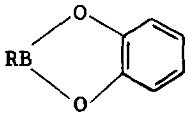
and $(Me_3Si)_2C{=}PR$ species from $(Me_3Si)_3CPRCl$ [13], Paetzold and coworkers thermolysed BR^*Bu^tF to obtain $(Me_3Si)_2C{=}BBu^t$ [56a].) The amino compounds $BF_2[N(SiMe_3)R]$ reacted with LiR^* to give the corresponding compounds $BR^*F[N(SiMe_3)R]$, $R = SiMe_3$, Me, Pr^i or Bu^t [59b], and similar reactions with $BF_2(NPr^i_2)$ gave $BR^*F(NPr^i_2)$ [57]. The compounds $BR^*F[N(SiMe_3)R]$ were found to lose Me_3SiF readily to give the imino derivatives $R^*B{=}NR$ [59]. Hydrolysis of $R^*B{=}NSiMe_3$ gave the diol $R^*B(OH)_2$ [59], which was also made, more conveniently, by hydrolysis of $BR^*(OMe)_2$ (see later).

The boron fluoride $BF_2[C(SiMe_3)(SiMe_2Bu^t_2)(SiMe_2F)]$, which contains a ligand related to R^* and R^{**} in that it has three substituted silyl groups attached to the same carbon atom, was unexpectedly obtained by Wiberg and his colleagues on treatment of BF_3 with $Li[C(SiMe_3)_2(SiBu^t_2F)]$, a fluorine atom and an Me group having exchanged positions [60]. The fluoride $BF_2\{C(SiMe_3)(SiMeBu^t_2)(SiMe_2F)\}$ was also obtained more straightforwardly by addition of BF_3 to the double bond of the silene $(Me_3Si)(MeBu^t_2Si)C{=}SiMe_2$.

Reaction of $BR^*F[O(CH_2)_4R^*]$ [61] or $BR^*F(OMe)$ [62] with $LiAlH_4$ gave the alkyltrihydroborate **10a**, and similar reduction of $BR^{**}F_2$ gave the related trihydrodoborate **10b**, the crystal structure of which was determined [55b]. This was the first structural characterization of an organotrihydroborate.



10a R = R*, **10b** R = R**



11a R = R*, **11b** R = R**

The hydrogen-bridged structure depicted for **10a** and **10b** was shown to be retained in solution. First the presence of the BH_3 fragment was confirmed by the ^{11}B and ^{1}H NMR spectra. Subsequently (in a study that also incidentally demonstrated the advantage that can sometimes arise from use of the ^{6}Li rather than the ^{7}Li nucleus) the nuclear Overhauser effect (nOe) revealed by gated decoupling experiments showed that the hydrogen atoms attached to boron atoms also lay near the lithium atom [63]. Indeed, it was possible to determine the $Li\cdots H$ distance, which was 2.2 Å, a value between the sum of the covalent radii (1.71 Å) and the sum of the van der Waals radii (3.0 Å).

The trihydroborate **10a** was found to react with catechol (1,2-dihydroxybenzene) to give the cyclic product **11a**, which in turn reacted with water to give $BR^*(OH)_2$ [61].

The trihydro species **10b** was also made by reduction with $LiAlH_4$ of $BR^{**}F(OMe)$, itself obtained by methanolysis of $BR^{**}F_2$ [55b]. Reaction of **10b** with catechol gave the chelate **11b**.

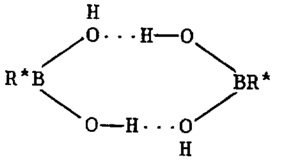
Reaction of LiR^* with $B(OMe)_3$ provided an entry to a substantial range of compounds with R^* attached to boron [64]. The initial product was shown to be the alkyltrimethoxyborate $LiBR^*(OMe)_3$ which, however, reacts with the remaining $B(OMe)_3$ in a slow step by transfer of an OMe group, with relief of steric strain as the coordination at the boron atom bearing R* changes from four to three:

$$LiR^* + B(OMe)_3 \rightarrow LiBr^*(OMe)_3 \xrightarrow[\text{slow}]{B(OMe)_3} BR^*(OMe)_2 + LiB(OMe)_4 \qquad (7)$$

It is noteworthy that when $LiB(OMe)_4$ was recrystallized from MeOH the product, which was characterized by an X-ray diffraction study, was the methanol solvate $[(MeOH)_2Li(\mu\text{-}OMe)_2B(OMe)_2]$ which appears to have been first isolated in 1914 [65].

Paetzold and coworkers reduced $BR^*(OMe)_2$ with $LiAlH_4$ in ether to give the lithium trihydroborate $(Et_2O)_2Li(\mu\text{-}H)_3BR^*$, which on treatment (a) with I_2 or Me_3NHCl gave $(BR^*H_2)_2$ (which with PMe_3 gave $BR^*H_2 \cdot PMe_3$), (b) with alcohols ROH gave the alkoxy hydrides $BR^*H(OR)$ ($R = Me$, Et, Pr^i), and (c) with $ZrCl_4$ gave the remarkable zirconium tris(trihydroborate) $ClZr\{(\mu\text{-}H)_3BR^*\}_3$ which was structurally characterized as an ether solvate [66].

Hydrolysis of $BR^*(OMe)_2$ gave the dihydroxy compound $BR^*(OH)_2$, which was shown to be present in the solid as the dimer **12** formed by hydrogen bonding [61]. (The hydrogen atoms in the bonds were not located.) Oxidation of this diol with aqueous hydrogen peroxide containing NaO_2CMe was shown by Lickiss [67] to give the alcohol R*OH.



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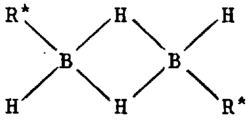

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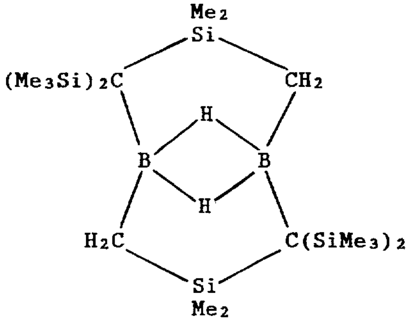


14

Treatment of $BR^*(OH)_2$ with PCl_5 gave BR^*Cl_2, which was used to produce a range of derivatives [64]:

$$BR^{*}Cl_2 \xrightarrow[THF]{LiAlH_4} R^{*}B(\mu\text{-}H)_3Li(THF)_3 \xrightarrow{H_2O} BR(OH)_2 \tag{8}$$

$$\xrightarrow{SbF_3} BR^{*}F_2 \xrightarrow{H_2O} BR^{*}(OH)F \tag{9}$$

$$\xrightarrow{LiPh} BR^{*}Ph_2 \tag{10}$$

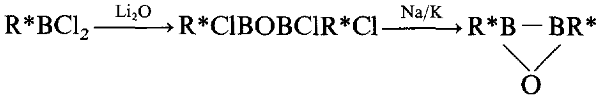
$$\xrightarrow[Et_2O]{LiMe} [Li(OEt_2)_2\{BR^{*}Me_3\}] \xrightarrow{Me_3SiCl} R^{*}BMe_2 \tag{11}$$

The dichloride $BR^{*}Cl_2$ was also shown to be reduced by $LiBH_4$ (or with lower yield by $NaBH_4$) to give the alkyldiborane *trans*-$R^{*}HB(\mu\text{-}H_2)BHR^{*}$ (**13**), the first 1,2-substituted borane to be structurally characterized in the solid state [64,66]. It is noteworthy that the distance between the central carbon atoms in the two R* ligands (4.58 Å) is not much larger than those (4.10–4.36 Å) in the species MR^{*}_2 (M = Mg, Mn, Hg) or $[MR^{*}_2]^-$ (M = Li, Na, Cu, Ag).

The diborane **13** was found to react with NH_3 to give the diaminoborane $BR^{*}(NH_2)_2$, which on warming gave the bis(aminoboryl)amine $\{R^{*}(H_2N)B\}_2NH$ [64]. Both of these products are unusual. The only other bis(amino)borane without substituents on nitrogen appears to be $BH(NH_2)_2$ (which slowly loses NH_3 in the liquid state but is stable in the vapour phase or in solution in liquid ammonia [68]), and $\{R^{*}(H_2N)B\}_2NH$ is the first stable crystalline bis(aminoboryl)amine without substituents on nitrogen.

In an attempt to obtain the diborene $R^{*}B{=}BR^{*}$ by reaction of $BR^{*}Cl_2$ with NaK alloy, Paetzold and his colleagues instead obtained the remarkable product **14**, possibly formed by intramolecular addition of C—H bonds across the B=B bond [69a]. The B···B distance in **14** (1.856(3) Å) is slightly longer than that in $R^{*}HB(\mu\text{-}H)_2BHR^{*}$ (1.839(1) Å) [64], and is much longer than that in B_2H_6 (1.763 Å) [70].

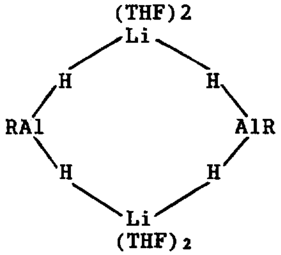
A striking example of the use of the stabilizing effect of the ligand R* was provided by the first preparation of an oxadiborane, again by Paetzold and his colleagues, by the route [69b]



$$R^{*}BCl_2 \xrightarrow{Li_2O} R^{*}ClBOBClR^{*}Cl \xrightarrow{Na/K} R^{*}B{-}BR^{*}\ (\text{bridged by } O)$$

4.2. Aluminium, gallium, indium and thallium

The first attempt to attach the R* group to aluminium met with only limited success [57]. It involved treatment of $AlCl_3$ with LiR^{*} in $Et_2O{-}THF$ and, as described for the reaction with BF_3, resulted mainly in cleavage of the THF to give in this case, after work-up, the alcohol $R^{*}(CH_2)_4OH$, probably via initially formed $R^{*}Al(Cl)O(CH_2)_4R^{*}$. However, the expected dichloride $AlR^{*}Cl_2$ was isolated in 15% yield; it was shown to be monomeric in solution, and probably also in the gas phase as indicated by the mass spectrum. The dimethyl compound AlR^*Me_2 was subsequently obtained by treatment of $AlMe_3$ with LiR^*, and its crystal structure determined [71b].



15a R = R*, **15b** R = R**

More recently, a useful entry into the chemistry of compounds with the R* or R** ligand attached to Al was revealed by the demonstration that both LiR* and LiR** react with $LiAlH_4$ in THF to give the corresponding lithium organotrihydroaluminates **15a** and **15b** [72]. The solid state structure of the latter was determined. Molar mass measurements for solutions in benzene indicate that the dimeric structure found for **15b** in the solid state is retained in solution, and nOe measurements confirmed that in both THF and toluene there are hydrogen bridges between Al and Li. The short Al—H and long Li—H bond lengths (1.61(4) Å and 1.93(4) Å respectively) in solid **15b** show that each dimer consists essentially of two $[Li(THF)_2][AlR^{**}H_3]$ ion pairs. Organotrihydroaluminates with smaller organic ligands have not been isolated, presumably because the anions readily undergo disproportionation

$$2[AlRH_3]^- \rightarrow [AlH_4]^- + [AlR_2H]^- \qquad (12)$$

and this is inhibited by large R groups. Another compound containing an $[AlRH_3]^-$ anion, in which R is the bulky group $2,6\text{-}Pr^i_2C_6H_4$, was subsequently isolated by Wehmschulte and Power [73].

The crystalline solids **15a** and **15b** have proved to be valuable starting materials for the synthesis of a range of other organoaluminium compounds [71a,72]

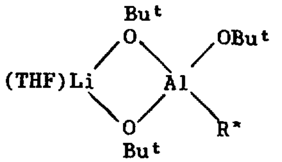
$$\mathbf{15a} \xrightarrow{X_2} AlR^*BX_2\cdot THF \qquad (X = Br \text{ or } I) \qquad (13)$$

$$\xrightarrow{HX} AlR^*X_2\cdot THF \qquad (X = Cl \text{ or } Br) \qquad (14)$$

$$\xrightarrow{HF/C_5H_5N} \{[Li(THF)][AlR^*F_3]\}_4\ (\mathbf{16}) \qquad (15)$$

The structure of the fluorocompound **16** was confirmed by an X-ray diffraction study, providing the first structural characterization of an organotrifluoroaluminate [72]. The structure consists of units made up of four ion pairs with six almost planar eight-membered rings forming a cubane-like Li_4Al_4 core (Fig. 9). Apparently, the greater bridging ability of fluoride than of hydride brings together two eight-membered rings of the kind found in **15a** and **15b**, with displacement of one THF ligand from each Li centre to give the tetrameric structure shown.

The reactions of **15a** with alcohols have given a novel series of alkoxy or aryloxy aluminates $(THF)LiAl(OR)_3$ (e.g. $R = Pr^i, Bu^t, Ph$); an X-ray diffraction study has shown that the t-butoxy compound has the structure **17** [71a]. Reactions with thiols RSH have likewise given the thiolates $(THF)LiAl(SR)_3$ ($R = Pr^i, Bu^t$), and reactions with the disulphides RSSH have given the corresponding compound with R = Me, Et or Ph. In the first structural characterization of an organotri(alkanethiolato) aluminium derivative, the compound with R = Me (**18**) has been shown to be present in the solid as $(\mu\text{-SMe})_2$-bridged dimers with terminal SMe ligands [71]; $(\mu\text{-SR})_2$-bridging is well known for the diorganoaluminium derivatives $[R_2Al(\mu\text{-SR})_2AlR_2]$ [74].



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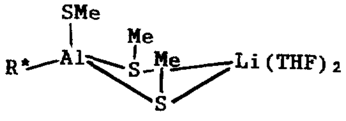


18

Reaction of $GaCl_3$ with an excess of LiR*, which evidently contained some of the MeLi used in its preparation, unexpectedly led to isolation of the hydroxide GaR*(OH)Me, probably formed by hydrolysis of GaR*ClMe during work-up [62]. However, reaction of a one-molar proportion of LiR* or LiR** in THF with the trihalides MCl_3 (M = Ga, In, Tl) gave metallates of the form $Li(THF)_nMCl_3R$,

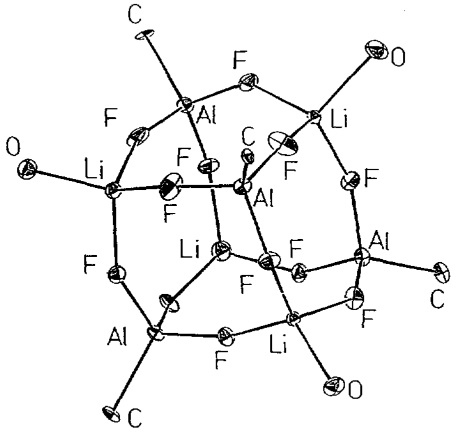
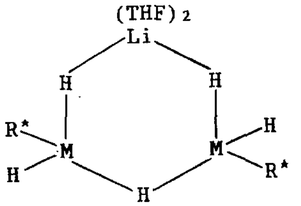


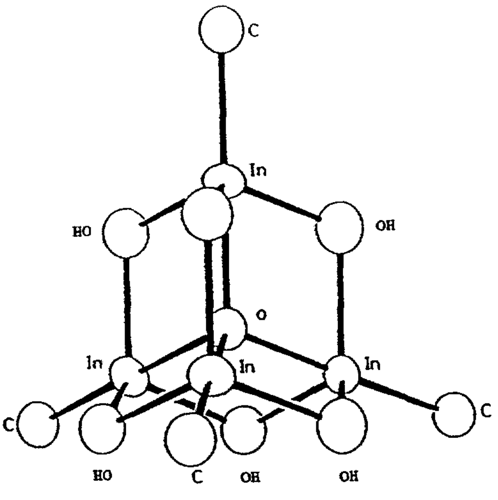
Fig. 9. Structure of the cage of the anion in $\{(Li(THF)_4][(AlR^*F_3]\}_4$ (**16**). The $SiMe_3$ groups and carbon atoms of the THF ligands are omitted for clarity.

namely $Li(THF)_2(\mu\text{-}Cl)_2GaClR^{**}$, $Li(THF)_3(\mu\text{-}Cl)InCl_2R^*$ and $Li(THF)TlCl_3R^*$ [75]. It is noteworthy that there is only one bridging chloride in the compound containing In and R* but two in that containing Ga and R**; whether the change of metal or that of the ligand is responsible for this difference is not known. The structure of the thallium compound has not yet been determined.

The alkyltrichlorometallates of Ga, In and Tl containing the R* ligand were reduced by $LiAlH_4$ to give the corresponding dimetallates **19a–19c** [75]. The solid state structure of the indium compound was determined, and nOe experiments indicated that μ—H bridges were present in **19a** and **19b** in toluene or THF solutions [63].



19a M = Ga, **19b** M = In, **19c** M = Tl

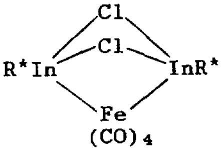


20

Reaction of **19b** with $MeOH—H_2O$ gave the oxide hydroxide $[O(InR^*)_4(OH)_6]$ in which the In—O framework has the structure **20** [44]. It was not surprising that an oxide hydroxide should be formed since InO(OH) has been known for a long time. Although indium is normally four- or six-coordinate, five-coordination is occasionally observed.

Compound **19b** was found to serve as a reducing agent towards the trichlorometalate $[Li(THF)_3(\mu\text{-}Cl)InCl_2R^*]$; the initial product was probably InClHR*, but this could not be obtained pure and was exposed to air to give InCl(OH)R* [75]. Reaction of **19b** with 1-phenylethylamine ($MePhCHNH_2$) gave an amido derivative of indium that was shown to reduce the ketone $PhCH_2COMe$ to give (after work-up) the alcohol $PhCH_2C(Me)HOH$, generating the oxide hydroxide mentioned above [75].

Although formation of the 'free' dichloro compounds MCl_2R from heated samples of the metallates $Li(THF)_nMCl_3R$ ($R = R^*$, R^{**}; M = Ga, In, Tl) was detected by mass spectrometry, such thermolysis could not be used to give the MCl_3R^* compounds on a preparative scale because the high temperatures required lead to side-reactions [75]. (When the thallium derivative Li(THF)$TlCl_3R^*$ was heated at 120–130 °C under vacuum the compound R*Cl sublimed out.) That LiCl can be removed from [$Li(THF)_3(\mu\text{-}Cl)InCl_2R^*$] was demonstrated by treating the latter with $Na_2[Fe(CO)_4]$, which gave the unusual compound **21**.



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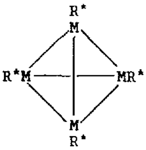

22a M is Ga, **22b** M is In

The In···In distance in **21**, i.e. 3.048(1) Å, is surprisingly short and is only a little longer than twice the sum of the covalent radius (1.42 Å). The shortest In—In distances in metallic indium range from 3.25–3.48 Å, and those in the four-membered ring of In_2Cl_2 are longer than 4.00 Å. If there is assumed to be no interaction between the indium atoms, then the 'one-angle' radius [76] for In (In···In) must be close to 1·54 Å. An alternative view is that of a cluster with 18 valence electrons; in accord with Wade's rules [77], the five cluster atoms form a dodecahedron with three missing corners.

An interesting transfer of the R* ligand was observed when a suspension of the thallate Li(THF)$TlCl_3R^*$ was treated with $LiAlH_4$ in THF, the product isolated being the trihydroaluminate $Li(THF)_3AlH_3R^*$ (**15a**) [75].

Uhl and his colleagues found that reaction of $Ga_2Br_4\cdot$2dioxane with LiR* bearing coordinated Et_2O or THF gave only R*H, but when unsolvated LiR* was used the product was the tetragallium tetrahedrane **21a** [78a]. The indium analogue of the latter (**22b**) was obtained similarly from $In_2Br_4\cdot(tmeda)_2$, and subsequently from InBr and LiR* by Cowley and coworkers [79] and from InCl and LiR* by Uhl and coworkers [78b], and structurally characterized [78b,79].

5. Concluding remarks

Many novel types of compound have been generated using the bulky ligands considered in this review and elsewhere [27], but it is clear that there is much more to be done. There are still many metals and metalloids to which such ligands have not been attached, and many ligands of the types $(Me_3Si)_2(XMe_2Si)C$, $(Me_3Si)(XMe_2Si)_2C$ and $(XMe_2Si)_3C$ yet to be used. The recent preparation of unsolvated LiR* [30] and of the highly reactive MR* (M = Na, K) [4] should allow synthesis of some compounds not previously available from the $LiR^*(Et_2O)_2$ mainly used up to now. Even further widening of the scope is made possible by the availability of the potentially chelating dicarbanionic 'siamyl' ligand, as noted below. Furthermore, the studies so far have concentrated on the synthesis of novel species, and in most cases systematic investigations of their properties have yet to be undertaken. The prospects are unlimited!

While this review has concentrated on syntheses that make use of the steric effect of bulky trisyl and related ligands in the stabilization of new species, particularly those with metals in a low coordination state, it should be appreciated that the ligands have other important applications, in particular (i) exploitation of the comparative ease of thermal elimination of Me_3SiX from compounds containing $(Me_3Si)_3C\cdots M\cdots X$ linkages to give $(Me_3Si)_2C{=}M$ bonds (e.g. M = Si [57], P [13,58], and B [57]) and (ii) use of the ligands to block bimolecular reaction at a metal or metalloid centre, thus allowing observation of previously unobservable mechanisms of reaction at such centres (so far applied only to silicon [19–22]). The remarkable thermal stability of HgR*R and HgR**R compounds, discussed in Section 3, further illustrates a way in which the ligands can be used to give mechanistic information, since it shows either that the long-accepted mechanism involving initial unimolecular dissociation is incorrect or (which would be even more significant) that the ligands can inhibit unimolecular reactions in some previously unrecognized way. If the existence of such inhibition (which we suggest would be related to the complexity of the ligands rather than their steric effects [48]) is confirmed, it could have important application in organometallic chemistry.

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Appendix

Relevant developments since the above review was submitted include the following.

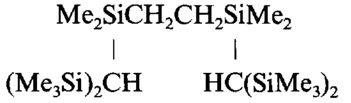
(i) The generation as an intermediate of the compound $R^*B{=}O$ (which the authors prefer to write as $R^*B{\equiv}O$) by thermolysis of, for example, $R^*B(OSiMe_3)Cl$ or $R^*B(OH)Cl$ [80]. When this is generated at lower temperatures it condenses to the trimeric $(R^*BO)_3$, but when generated at higher temperatures it gives more complex products.

(ii) The preparation and structural characterization of $Zr(H_3BR^*)_4$ [81].

(iii) The observation that treatment of BF_3, BCl_3, BBr_3 or $AlCl_3$ with LiR* in Et_2O gives R*OEt, not a trisylboron or trisylaluminium compound [82].

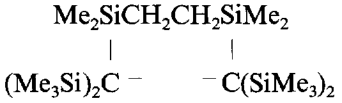
(iv) The preparation of the reagent $LiC(SiMe_2NMe_2)_3$ and hence the mercury compound $Hg\{C(SiMe_2NMe_2)_3\}_2$, a potentially hexadentate ligand [83]. The lithium reagent can be expected to give derivatives of other metals in which, in addition to the central carbon, one or more of the Me_2N groups is coordinated to the metal.

(v) The synthesis of compound **23** as a precursor of the potentially chelating dicarbanionic ligand **24**, metallation of **23** with MeLi to give the lithate anion **25** as its [Li(tmeda)$_2$] salt, and use of the latter to give the chelated mercury derivative **26** [84]. In the ligand **24** both ligating carbon centres are as crowded as in the trisyl ligand itself. We call it the siamyl ligand, because it is a Siamese twin pair of trisyl ligands, and at the same time the two initial letters indicate that it is a silicon-containing species.



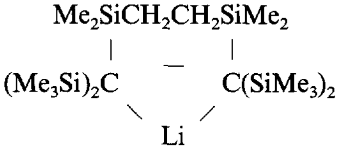
$$\begin{array}{cc} \multicolumn{2}{c}{\mathrm{Me_2SiCH_2CH_2SiMe_2}} \\ | & | \\ \mathrm{(Me_3Si)_2CH} & \mathrm{HC(SiMe_3)_2} \end{array}$$

23

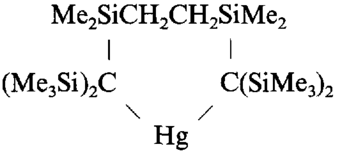


$$\begin{array}{cc} \multicolumn{2}{c}{\mathrm{Me_2SiCH_2CH_2SiMe_2}} \\ | & | \\ \mathrm{(Me_3Si)_2C^-} & \mathrm{^-C(SiMe_3)_2} \end{array}$$

24



25



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