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The preparation and crystal structures of the compounds $(\text{Ph}_2\text{MeSi})_3\text{CMCl}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{or Hg}$) *

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Abstract

The compounds $(\text{PhMe}_2\text{Si})_3\text{CMCl}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{or Hg}$) have been prepared by reaction of $(\text{PhMe}_2\text{Si})_3\text{CLi}$ with the chlorides MCl_2 ; for $\text{M} = \text{Zn}$ or Cd they were obtained *via* (isolated) Li-containing intermediates thought to $[(\text{PhMe}_2\text{Si})_3\text{CM}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$. The crystal structures of all three compounds $(\text{PhMe}_2\text{Si})_3\text{CMCl}$ have been determined. The zinc and cadmium chlorides are present in the crystal as the dimers $[(\text{PhMe}_2\text{Si})_3\text{CM}(\mu\text{-Cl})_2\text{MC}(\text{SiMe}_2\text{Ph})_3]$, with the metals three-coordinate in a planar environment (for $\text{M} = \text{Zn}$, the C-M-Cl angles average 136° , and the Cl-M-Cl angles 88° ; for $\text{M} = \text{Cd}$ the corresponding values are 137° and 86°) and the chloride bridges slightly unsymmetrical. The cadmium compound is also dimeric in solution in benzene. The compounds appear to be the first structurally characterized organo-zinc or -cadmium halides in which the metal is three-coordinate. The mercury compound also forms dimers in the solid, but the geometry is almost that expected for two-coordinate mercury (the C-Hg-Cl angles at the two metal centres are $171.0(3)$ and $171.3(3)^\circ$, with a very weak intermolecular $\text{Hg} \cdots \text{Cl}$ interaction (mean distance $3.29 \text{ \AA}$). The conformations of the $(\text{PhMe}_2\text{Si})_3\text{C}$ groups in all three compounds are discussed.

1. Introduction

Interesting information can often be gained by examination of the crystal structures of a set of organometallic compounds differing only in the identity of the central metal. (An especially relevant example in the context of the present paper is provided by the study by Lappert and his colleagues of the compounds $[(\text{Me}_3\text{Si})_2\text{C}(\text{C}_5\text{H}_4\text{N})]_2\text{M}$ with $\text{M} = \text{Zn}, \text{Cd}, \text{or Hg}$ [1]). Having for other purposes made the compounds $(\text{Me}_2\text{PhSi})_3\text{CMCl}$ with $\text{M} = \text{Zn}, \text{Cd}, \text{or Hg}$, we thus determined their crystal structures, with the results described below. For convenience the ligand $(\text{PhMe}_2\text{Si})_3\text{C}$ is frequently denoted by Tpsi [2].

2. Results and discussion

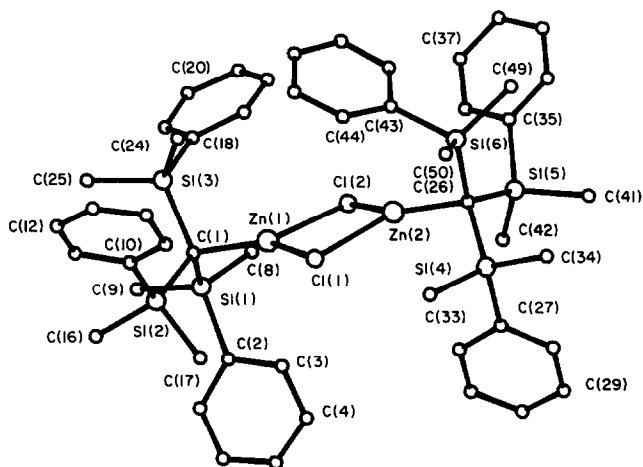
2.1. Syntheses

The $(\text{PhMe}_2\text{Si})_3\text{CH}$ used for the preparation of TpsiLi was made by a much better method than that previously employed [2]. Yields were in the region of 70%, compared with the earlier 20%.

The mercury compound TpsiHgCl was made by reaction of HgCl_2 with TpsiLi [2] in tetrahydrofuran (THF). The corresponding reactions with ZnCl_2 and CdCl_2 were found to give lithium-containing complexes, which were isolated as white crystals. From elemental analysis and NMR spectroscopic data these are thought to be $[\text{TpsiM}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2]$ ($\text{M} = \text{Zn}$ or Cd), but more complex structures, such as that found for $[\text{Li}(\text{THF})_4][\text{Li}(\text{THF})_2(\mu\text{-Cl})_4(\text{Cd}(\text{C}(\text{SiMe}_3)_3)_2)]$ [3], cannot be ruled out; crystals suitable for an X-ray diffraction study could not be obtained. The lithium complexes were found to break down when heated under reduced pressure, or in the case of the cadmium compound simply upon recrystallization from boiling toluene, to give the simple derivatives TpsiMCl with

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* Dedicated to Professor Michael Lappert on the occasion of his 65th birthday, in recognition of his outstanding achievements in organometallic chemistry and his very important contribution to the success of chemistry in the University of Sussex from its early years.

Fig. 1. Molecular structure of $[(\text{TpsiZnCl})_2]$.

$M = \text{Zn}$ or Cd . Determination of the molecular weight of TpsiCdCl by the freezing point method in benzene indicated that in solution under such conditions it was present as the dimer, as in the solid (see below).

2.2. Structures

The structure of TpsiZnCl is shown in Fig. 1, and the bond lengths and angles are listed in Table 1. For ease of comparison, the more relevant parameters are also listed in Table 2, along with the corresponding data for the cadmium and mercury compounds.

It will be seen that the compound is present in dimeric form. The geometries in the two components of the dimer are not identical, the main difference being in the conformation of the Tpsi ligands (see later) but both zinc atoms are three-coordinate in a planar environment (the sums of the three angles at $\text{Zn}(1)$ and $\text{Zn}(2)$ are 360° and 359° , respectively). As far as we are aware there are no crystal structure data available for any other organozinc halide in which the metal is three-coordinate. The iodide EtZnI forms a polymer, with the zinc four-coordinate [4], and EtZnCl and EtZnBr are tetrameric in benzene, with the metal presumably again four-coordinate [5].

The lengths of the two $\text{Zn}-\text{Cl}$ bonds at each zinc centre differ slightly but significantly ($\text{Zn}(1)-\text{Cl}(1)$, 2.303(3); $\text{Zn}(1)-\text{Cl}(2)$ 2.335(3). $\text{Zn}(2)-\text{Cl}(2)$ 2.304(3); $\text{Zn}(2)-\text{Cl}(1)$ 2.365(3) Å), and those of the shorter bonds are similar to the mean $\text{Zn}-\text{Cl}$ bond length in ZnCl_2 (2.273(4)) [6], in which the zinc is four-coordinate. They are possibly slightly longer than those in the other four-coordinate zinc species $(\text{MeNH}_3)_2\text{ZnCl}_4$ (2.267(2) Å) [7], Cs_2ZnCl_4 (2.253(3) Å) [8], and $\text{ZnCl}_2(\text{py})_2$ (2.221(2) Å) [9]. The bonds in monomeric ZnCl_2 , containing two-coordinate zinc, in the gas phase are distinctly shorter, at 2.072(4) Å [10].

The $\text{Zn}-\text{C}$ bond lengths (1.970(8) and 1.984(7) Å) are similar to those in the compounds $[(\text{XMe}_2\text{Si})_3\text{C}]_2\text{Zn}$ with $\text{X} = \text{Me}, \text{OMe}, \text{OH}$, or O_2CCF_3 , which range from 1.968(2) to 1.982(2) Å [11,12], the compounds $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2]_2\text{Zn}$ (1.984(5) Å), and gas-phase $(\text{Me}_2\text{SCH}_2\text{CH}_2\text{CH}_2)_2\text{Zn}$ (1.984(5) Å, in which there is

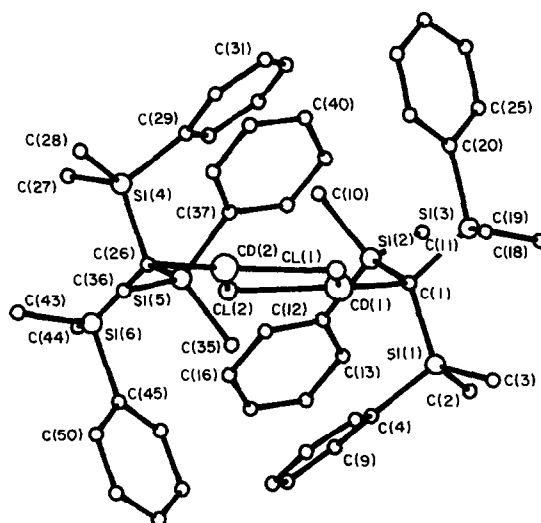
TABLE 1. Intramolecular distances (Å) and angles ($^\circ$) in $[(\text{TpsiZnCl})_2]$, with estimated standard deviations in parentheses

(a) Bonds			
$\text{Zn}(1)-\text{Cl}(1)$	2.303(3)	$\text{Zn}(1)-\text{Cl}(2)$	2.335(3)
$\text{Zn}(1)-\text{C}(1)$	1.970(8)	$\text{Zn}(2)-\text{Cl}(1)$	2.365(3)
$\text{Zn}(2)-\text{Cl}(2)$	2.304(3)	$\text{Zn}(2)-\text{C}(26)$	1.984(7)
$\text{Si}(1)-\text{C}(1)$	1.883(8)	$\text{Si}(1)-\text{C}(2)2$	1.884(9)
$\text{Si}(1)-\text{C}(8)$	1.860(10)	$\text{Si}(1)-\text{C}(9)$	1.852(10)
$\text{Si}(2)-\text{C}(1)$	1.910(8)	$\text{Si}(2)-\text{C}(10)$	1.909(9)
$\text{Si}(2)-\text{C}(16)$	1.863(10)	$\text{Si}(2)-\text{C}(17)$	1.885(10)
$\text{Si}(3)-\text{C}(1)$	1.897(8)	$\text{Si}(3)-\text{C}(18)$	1.886(10)
$\text{Si}(3)-\text{C}(24)$	1.857(11)	$\text{Si}(3)-\text{C}(25)$	1.872(10)
$\text{Si}(4)-\text{C}(26)$	1.893(8)	$\text{Si}(4)-\text{C}(27)$	1.882(8)
$\text{Si}(4)-\text{C}(33)$	1.880(10)	$\text{Si}(4)-\text{C}(34)$	1.873(9)
$\text{Si}(5)-\text{C}(26)$	1.901(8)	$\text{Si}(5)-\text{C}(42)$	1.879(9)
$\text{Si}(6)-\text{C}(26)$	1.893(8)	$\text{Si}(6)-\text{C}(43)$	1.884(9)
$\text{Si}(6)-\text{C}(49)$	1.855(11)	$\text{Si}(6)-\text{C}(50)$	1.876(11)
$\text{C}(2)-\text{C}(3)$	1.394(12)	$\text{C}(2)-\text{C}(7)$	1.388(13)
$\text{C}(3)-\text{C}(4)$	1.403(14)	$\text{C}(4)-\text{C}(5)$	1.359(15)
$\text{C}(5)-\text{C}(6)$	1.36(2)	$\text{C}(6)-\text{C}(7)$	1.368(14)
$\text{C}(10)-\text{C}(11)$	1.387(12)	$\text{C}(10)-\text{C}(15)$	1.401(13)
$\text{C}(11)-\text{C}(12)$	1.397(14)	$\text{C}(12)-\text{C}(13)$	1.37(2)
$\text{C}(13)-\text{C}(14)$	1.344(14)	$\text{C}(14)-\text{C}(15)$	1.395(15)
$\text{C}(18)-\text{C}(19)$	1.407(13)	$\text{C}(18)-\text{C}(23)$	1.408(14)
$\text{C}(19)-\text{C}(20)$	1.396(15)	$\text{C}(20)-\text{C}(21)$	1.37(2)
$\text{C}(21)-\text{C}(22)$	1.36(2)	$\text{C}(22)-\text{C}(23)$	1.407(14)
$\text{C}(27)-\text{C}(28)$	1.400(11)	$\text{C}(27)-\text{C}(32)$	1.395(12)
$\text{C}(28)-\text{C}(29)$	1.399(13)	$\text{C}(29)-\text{C}(30)$	1.368(13)
$\text{C}(30)-\text{C}(31)$	1.364(13)	$\text{C}(31)-\text{C}(32)$	1.397(13)
$\text{C}(35)-\text{C}(36)$	1.404(12)	$\text{C}(35)-\text{C}(40)$	1.380(13)
$\text{C}(36)-\text{C}(37)$	1.406(14)	$\text{C}(37)-\text{C}(38)$	1.370(15)
$\text{C}(38)-\text{C}(39)$	1.37(2)	$\text{C}(39)-\text{C}(40)$	1.378(14)
$\text{C}(43)-\text{C}(44)$	1.367(14)	$\text{C}(43)-\text{C}(48)$	1.418(14)
$\text{C}(44)-\text{C}(45)$	1.380(15)	$\text{C}(45)-\text{C}(46)$	1.35(2)
$\text{C}(46)-\text{C}(47)$	1.39(2)	$\text{C}(47)-\text{C}(48)$	1.390(15)

(b) Angles			
$\text{Cl}(1)-\text{Zn}(1)-\text{Cl}(2)$	88.2(1)	$\text{Cl}(1)-\text{Zn}(1)-\text{C}(1)$	137.9(2)
$\text{Cl}(2)-\text{Zn}(1)-\text{C}(1)$	133.9(2)	$\text{Cl}(1)-\text{Zn}(2)-\text{Cl}(2)$	87.5(1)
$\text{Cl}(1)-\text{Zn}(2)-\text{C}(26)$	133.0(2)	$\text{Cl}(2)-\text{Zn}(2)-\text{C}(26)$	138.6(2)
$\text{Zn}(1)-\text{Cl}(1)-\text{Zn}(2)$	91.5(1)	$\text{Zn}(1)-\text{Cl}(2)-\text{Zn}(2)$	92.3(1)
$\text{C}(1)-\text{Si}(1)-\text{C}(2)$	109.7(4)	$\text{C}(1)-\text{Si}(1)-\text{C}(8)$	114.9(4)
$\text{C}(1)-\text{Si}(1)-\text{C}(9)$	113.2(4)	$\text{C}(2)-\text{Si}(1)-\text{C}(8)$	103.7(4)
$\text{C}(2)-\text{Si}(1)-\text{C}(9)$	109.1(5)	$\text{C}(8)-\text{Si}(1)-\text{C}(9)$	105.7(5)
$\text{C}(1)-\text{Si}(2)-\text{C}(10)$	112.9(4)	$\text{C}(1)-\text{Si}(2)-\text{C}(16)$	112.8(4)
$\text{C}(1)-\text{Si}(2)-\text{C}(17)$	113.2(4)	$\text{C}(10)-\text{Si}(2)-\text{C}(16)$	106.4(4)
$\text{C}(10)-\text{Si}(2)-\text{C}(17)$	104.8(4)	$\text{C}(16)-\text{Si}(2)-\text{C}(17)$	106.0(4)
$\text{C}(1)-\text{Si}(3)-\text{C}(18)$	112.1(4)	$\text{C}(1)-\text{Si}(3)-\text{C}(24)$	112.7(4)
$\text{C}(1)-\text{Si}(3)-\text{C}(25)$	113.9(4)	$\text{C}(18)-\text{Si}(3)-\text{C}(24)$	103.2(5)
$\text{C}(18)-\text{Si}(3)-\text{C}(25)$	106.7(4)	$\text{C}(24)-\text{Si}(3)-\text{C}(25)$	107.5(5)
$\text{C}(26)-\text{Si}(4)-\text{C}(27)$	110.2(4)	$\text{C}(26)-\text{Si}(4)-\text{C}(33)$	114.2(4)
$\text{C}(26)-\text{Si}(4)-\text{C}(34)$	112.6(4)	$\text{C}(27)-\text{Si}(4)-\text{C}(33)$	104.0(4)
$\text{C}(27)-\text{Si}(4)-\text{C}(34)$	108.9(4)	$\text{C}(33)-\text{Si}(4)-\text{C}(34)$	106.4(4)
$\text{C}(26)-\text{Si}(5)-\text{C}(35)$	114.5(4)	$\text{C}(26)-\text{Si}(5)-\text{C}(41)$	112.7(4)

TABLE 1 (continued)

(b) Angles			
C(26)–Si(5)–C(42)	113.6(4)	C(35)–Si(5)–C(41)	104.6(4)
C(35)–Si(5)–C(42)	104.1(4)	C(41)–Si(5)–C(42)	106.4(4)
C(26)–Si(6)–C(43)	108.1(4)	C(26)–Si(6)–C(49)	115.7(4)
C(26)–Si(6)–C(50)	115.7(4)	C(43)–Si(6)–C(49)	108.6(4)
C(43)–Si(6)–C(50)	104.0(4)	C(49)–Si(6)–C(50)	104.0(5)
Zn(1)–C(1)–Si(1)	106.4(4)	Zn(1)–C(1)–Si(2)	107.1(4)
Zn(1)–C(1)–Si(3)	105.2(4)	Si(1)–C(1)–Si(2)	111.9(4)
Si(1)–C(1)–Si(3)	113.2(4)	Si(2)–C(1)–Si(3)	112.4(4)
Si(1)–C(2)–C(3)	119.2(7)	Si(1)–C(2)–C(7)	126.3(7)
C(3)–C(2)–C(7)	114.4(8)	C(2)–C(3)–C(4)	123.7(9)
C(3)–C(4)–C(5)	117.1(9)	C(4)–C(5)–C(6)	122(1)
C(5)–C(6)–C(7)	119(1)	C(2)–C(7)–C(6)	123.5(9)
Si(2)–C(10)–C(11)	121.4(7)	Si(2)–C(10)–C(15)	121.4(7)
C(11)–C(10)–C(15)	117.2(8)	C(10)–C(11)–C(12)	120.2(9)
C(11)–C(12)–C(13)	121.1(9)	C(12)–C(13)–C(14)	120(1)
C(13)–C(14)–C(15)	120(1)	C(10)–C(15)–C(14)	121.1(9)
Si(3)–C(18)–C(19)	123.1(7)	Si(3)–C(18)–C(23)	120.8(7)
C(19)–C(18)–C(23)	116.0(9)	C(18)–C(19)–C(20)	120.8(9)
C(19)–C(20)–C(21)	121(1)	C(20)–C(21)–C(22)	121(1)
C(21)–C(22)–C(23)	119(1)	C(18)–C(23)–C(22)	123(1)
Zn(2)–C(26)–Si(4)	107.8(4)	Zn(2)–C(26)–Si(5)	107.2(4)
Zn(2)–C(26)–Si(6)	99.4(3)	Si(4)–C(26)–Si(5)	112.0(4)
Si(4)–C(26)–Si(6)	113.2(4)	Si(5)–C(26)–Si(6)	115.9(4)
Si(4)–C(27)–C(28)	122.3(6)	Si(4)–C(27)–C(32)	121.2(6)
C(28)–C(27)–C(32)	116.5(8)	C(27)–C(28)–C(29)	121.9(8)
C(28)–C(29)–C(30)	119.6(8)	C(29)–C(30)–C(31)	120.2(9)
C(30)–C(31)–C(32)	120.5(9)	C(27)–C(32)–C(31)	121.3(8)
Si(5)–C(35)–C(36)	119.1(6)	Si(5)–C(35)–C(40)	124.5(7)
C(36)–C(35)–C(40)	116.2(8)	C(35)–C(36)–C(37)	121.1(9)
C(36)–C(37)–C(38)	120(1)	C(37)–C(38)–C(39)	119(1)
C(38)–C(39)–C(40)	120(1)	C(35)–C(40)–C(39)	112.7(9)
Si(6)–C(43)–C(44)	122.0(7)	Si(6)–C(43)–C(48)	121.7(7)
C(44)–C(43)–C(48)	116.2(8)	C(43)–C(44)–C(45)	123(1)
C(44)–C(45)–C(46)	120(1)	C(45)–C(46)–C(47)	122(1)
C(46)–C(47)–C(48)	118(1)	C(43)–C(48)–C(47)	122(1)

Fig. 2. Molecular structure of $[(TpsiCdCl)_2]$.

listed in Table 3. The crystals were found to be isomorphous with those in the corresponding bromide, $TpsiCdBr$ [3], which simplified the structure analysis. Like its zinc analogue, the chloride is present in dimeric form with each metal atom in a three-coordinate, planar environment (the sums of the angles at the Cd centres are both 359°). In contrast to the situation for the zinc analogue, there is little difference between the two halves of the dimer, which is almost centrosymmetric.

As in the zinc compound, each metal atom in the dimer has one longer and one shorter bond to halogen. The differences between the two bond lengths (0.059 Å at Cd(1) and 0.042 Å at Cd(2)) are slightly larger than those for the zinc compound. The Cd–Cl bond lengths are significantly shorter than the mean Cd–Cl bond length (2.626(7) Å) in $[(Me_3Si)_3CCdCl]_4$ [3]. The Cl–M–Cl angles in the cadmium compound are slightly smaller and the M–Cl–M angles corresponding slightly larger than those in the zinc analogue (see Table 2).

The mean Cd–C bond length (2.193(8) Å) is similar to those in the corresponding bromide (2.195(8) Å) [3] * and $[(Me_3Si)_2\{(CH_2=CH)Me_2Si\}Cl_2]Cd$ (2.172(3) Å) [17]. It is also not significantly different, when account is taken of the estimated standard deviations, from those in the four coordinate cadmium compounds $[Cd\{(C(SiMe_3)_2(C_5H_4N)_2\} (2.27 \text{ Å})$ [1], $[(Me_3Si)_3CCd-$

weak coordination from the donor atoms in the γ -position [13], or in $[(MeZnOMe)_4]$ (1.946(28) Å) in which the zinc is four-coordinate [14]. Slightly shorter bonds are found in the two-coordinate zinc species Me_2Zn (1.930(2) Å in the gas-phase [15] and in $(MeZnNPh_2)_2$ (1.948(17) Å), in which the metal is three-coordinate. The insensitivity of the Zn–C bond length to the coordination number of Zn has been noted elsewhere [16].

The structure of the cadmium chloride, $TpsiCdCl$, is shown in Fig. 2, and the bond lengths and angles are

TABLE 2. Some bond lengths (Å) and angles ($^\circ$) in the dimeric species $(TpsiMCl)_2$

M	Zn	Cd	Hg
M–Cl	2.303(3), 2.304(3)	2.499(2), 2.515(2)	2.326(3), 2.317(3)
	2.335(3), 2.365(3)	2.558(2), 2.557(2)	3.194(3), 3.392(3)
M–C	1.970(8), 1.984(9)	2.192(6), 2.199(6)	2.089(9), 2.109(9)
Cl–M–Cl	87.5(1), 88.2(1)	85.69(6), 86.02(6)	75.6(1), 79.8(1)
M–Cl–M	91.5(1), 92.3(1)	93.86(5), 94.27(6)	99.3(1), 105.2(1)

* We previously suggested [3] that the difference in the molecular complexities of the chloride $(Me_3Si)_3CCdCl$, which forms a tetramer containing four-coordinate cadmium, and the bromide $TpsiCdBr$, which forms a dimer, with three-coordinate cadmium, might arise from the different sizes of the halogen atoms, but it is evident from the results for $TpsiCdCl$ that difference is actually attributable to the change in the organic ligand, probably because of the change in the effective bulk of that ligand.

Cl₄] (2.19(2) Å) [3], and [Cd(CH₂SiMe₃)₂(bipy)]_{0.5} bipy (2.14(6) Å) [18], but may possibly be longer than those in [Cd(2-Me₂NCH₂Ph)₂] (2.154(8) Å [19]).

The mercury compound TpsiHgCl also forms dimers in the crystal, as can be seen from Fig. 3 and Table 4.

TABLE 3. Intramolecular distances (Å) and angles (°) in [(TpsiCdCl)₂], with estimated standard deviations in parentheses

(a) Bonds			
Cd(1)–Cl(1)	2.558(2)	Cd(1)–Cl(2)	2.499(2)
Cd(1)–C(1)	2.192(6)	Cd(2)–Cl(1)	2.515(2)
Cd(2)–Cl(2)	2.557(2)	Cd(2)–C(26)	2.199(6)
Si(1)–C(1)	1.893(5)	Si(1)–C(2)	1.853(8)
Si(1)–C(3)	1.876(8)	Si(1)–C(4)	1.900(6)
Si(2)–C(1)	1.902(6)	Si(2)–C(10)	1.869(6)
Si(2)–C(11)	1.864(8)	Si(2)–C(12)	1.894(5)
Si(3)–C(1)	1.883(5)	Si(3)–C(18)	1.865(8)
Si(3)–C(19)	1.857(9)	Si(3)–C(20)	1.898(6)
Si(4)–C(26)	1.882(5)	Si(4)–C(27)	1.876(7)
Si(4)–C(28)	1.870(8)	Si(4)–C(29)	1.895(6)
Si(5)–C(26)	1.902(6)	Si(5)–C(35)	1.857(6)
Si(5)–C(36)	1.862(8)	Si(5)–C(37)	1.902(5)
Si(6)–C(26)	1.880(5)	Si(6)–C(43)	1.875(8)
Si(6)–C(44)	1.875(8)	Si(6)–C(45)	1.879(6)
C(4)–C(5)	1.389(10)	C(4)–C(9)	1.387(9)
C(5)–C(6)	1.375(10)	C(6)–C(7)	1.365(11)
C(7)–C(8)	1.358(13)	C(8)–C(9)	1.371(10)
C(12)–C(13)	1.407(9)	C(12)–C(17)	1.389(9)
C(13)–C(14)	1.411(8)	C(14)–C(15)	1.347(11)
C(15)–C(16)	1.367(12)	C(16)–C(17)	1.391(9)
C(2)–C(21)	1.388(10)	C(20)–C(25)	1.392(10)
C(21)–C(22)	1.378(10)	C(22)–C(23)	1.372(13)
C(23)–C(24)	1.380(13)	C(24)–C(25)	1.378(9)
C(29)–C(30)	1.389(9)	C(29)–C(34)	1.398(10)
C(30)–C(31)	1.404(10)	C(31)–C(32)	1.348(13)
C(32)–C(33)	1.361(11)	C(33)–C(34)	1.384(10)
C(37)–C(38)	1.393(9)	C(37)–C(42)	1.397(8)
C(38)–C(39)	1.390(8)	C(39)–C(40)	1.374(10)
C(40)–C(41)	1.367(11)	C(41)–C(42)	1.382(8)
C(45)–C(46)	1.397(9)	C(45)–C(50)	1.403(10)
C(46)–C(47)	1.393(9)	C(47)–C(48)	1.366(12)
C(48)–C(49)	1.383(11)	C(49)–C(50)	1.392(9)

(b) Angles			
Cl(1)–Cd(1)–Cl(2)	86.02(6)	Cl(1)–Cd(1)–C(1)	133.6(1)
Cl(2)–Cd(1)–C(1)	139.5(2)	Cl(1)–Cd(2)–Cl(2)	85.69(6)
Cl(1)–Cd(2)–C(26)	144.3(2)	Cl(2)–Cd(2)–C(26)	129.5(1)
Cd(1)–Cl(1)–Cd(2)	93.86(5)	Cd(1)–Cl(2)–Cd(2)	94.27(6)
C(1)–Si(1)–C(2)	114.4(3)	C(1)–Si(1)–C(3)	114.1(3)
C(1)–Si(1)–C(4)	109.1(2)	C(2)–Si(1)–C(3)	105.1(3)
C(2)–Si(1)–C(4)	110.3(3)	C(3)–Si(1)–C(4)	103.2(3)
C(1)–Si(2)–C(10)	112.9(3)	C(1)–Si(2)–C(11)	113.2(3)
C(1)–Si(2)–C(12)	113.3(2)	C(10)–Si(2)–C(11)	106.1(3)
C(10)–Si(2)–C(12)	104.7(3)	C(11)–Si(2)–C(12)	106.0(3)
C(1)–Si(3)–C(18)	110.5(3)	C(1)–Si(3)–C(19)	113.3(3)
C(1)–Si(3)–C(20)	114.0(3)	C(18)–Si(3)–C(19)	108.2(4)
C(18)–Si(3)–C(20)	106.5(3)	C(19)–Si(3)–C(20)	103.9(3)
C(26)–Si(4)–C(27)	114.2(3)	C(26)–Si(4)–C(28)	113.9(3)
C(26)–Si(4)–C(29)	109.7(2)	C(27)–Si(4)–C(28)	104.6(3)
C(27)–Si(4)–C(29)	103.9(3)	C(28)–Si(4)–C(29)	110.0(3)
C(26)–Si(5)–C(36)	113.2(3)	C(26)–Si(5)–C(36)	112.6(3)

TABLE 3 (continued)

(b) Angles			
C(26)–Si(5)–C(37)	112.2(2)	C(35)–Si(5)–C(36)	107.4(3)
C(35)–Si(5)–C(37)	103.9(3)	C(36)–Si(5)–C(37)	106.9(3)
C(26)–Si(6)–C(43)	112.1(3)	C(26)–Si(6)–C(44)	114.4(3)
C(26)–Si(6)–C(45)	111.4(3)	C(43)–Si(6)–C(44)	106.9(3)
C(43)–Si(6)–C(45)	107.3(3)	C(44)–Si(6)–C(45)	104.2(3)
Cd(1)–C(1)–Si(1)	100.2(3)	Cd(1)–C(1)–Si(2)	104.3(2)
Cd(1)–C(1)–Si(3)	109.8(3)	Si(1)–C(1)–Si(2)	115.6(3)
Si(1)–C(1)–Si(3)	112.6(3)	Si(2)–C(1)–Si(3)	113.0(3)
Si(1)–C(4)–C(5)	118.7(4)	Si(1)–C(4)–C(9)	125.4(5)
C(5)–C(4)–C(9)	115.8(6)	C(4)–C(5)–C(6)	122.1(6)
C(5)–C(6)–C(7)	120.1(8)	C(6)–C(7)–C(8)	119.2(7)
C(7)–C(8)–C(9)	120.8(7)	C(4)–C(9)–C(8)	121.9(7)
Si(2)–C(12)–C(13)	122.1(4)	Si(2)–C(12)–C(17)	121.0(5)
C(13)–C(12)–C(17)	116.8(5)	C(12)–C(13)–C(14)	120.3(6)
C(13)–C(14)–C(15)	120.2(7)	C(14)–C(15)–C(16)	121.2(6)
C(15)–C(16)–C(17)	119.3(7)	C(12)–C(17)–C(16)	122.2(6)
Si(3)–C(20)–C(21)	121.0(5)	Si(3)–C(20)–C(25)	122.5(5)
C(21)–C(20)–C(25)	116.3(6)	C(20)–C(21)–C(22)	122.4(7)
C(21)–C(22)–C(23)	120.1(8)	C(22)–C(23)–C(24)	119.1(7)
C(23)–C(24)–C(25)	120.4(8)	C(20)–C(25)–C(24)	121.8(7)
Cd(2)–C(26)–Si(4)	101.8(3)	Cd(2)–C(26)–Si(5)	103.5(2)
Cd(2)–C(26)–Si(6)	108.3(2)	Si(4)–C(26)–Si(5)	114.7(3)
Si(4)–C(26)–Si(6)	113.4(3)	Si(5)–C(26)–Si(6)	113.7(3)
Si(4)–C(29)–C(30)	124.1(6)	Si(4)–C(29)–C(34)	119.6(4)
C(30)–C(29)–C(34)	116.3(6)	C(29)–C(30)–C(31)	120.8(7)
C(30)–C(31)–C(32)	120.6(7)	C(31)–C(32)–C(33)	120.4(7)
C(32)–C(33)–C(34)	119.6(8)	C(29)–C(34)–C(33)	122.2(6)
Si(5)–C(37)–C(38)	120.5(4)	Si(5)–C(37)–C(42)	123.0(4)
C(38)–C(37)–C(42)	116.4(5)	C(37)–C(38)–C(39)	122.1(6)
C(38)–C(39)–C(40)	119.6(6)	C(39)–C(40)–C(41)	119.8(6)
C(40)–C(41)–C(42)	120.6(6)	C(37)–C(42)–C(41)	121.5(6)
Si(6)–C(45)–C(46)	121.0(5)	Si(6)–C(45)–C(50)	122.9(5)
C(46)–C(45)–C(50)	116.2(5)	C(45)–C(46)–C(47)	122.4(7)
C(46)–C(47)–C(48)	119.7(7)	C(47)–C(48)–C(49)	120.1(7)
C(48)–C(49)–C(50)	119.9(7)	C(45)–C(50)–C(49)	121.6(6)

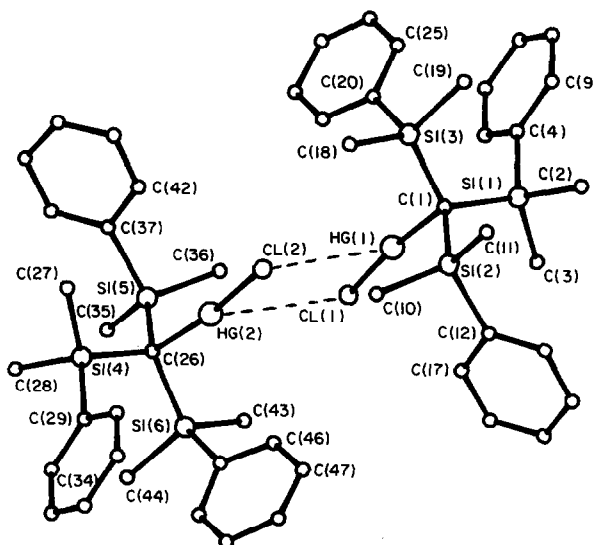


Fig. 3. Molecular structure of [(TpsiHgCl)₂].

TABLE 4. Intramolecular distances (Å) and angles (°) in [(TpsiHgCl)₂]. (with estimated standard deviations in Parentheses)

(a) Bonds			
Hg(1)–Cl(1)	2.328(3)	Hg(1)–Cl(1)	2.105(9)
Hg(2)–Cl(2)	2.320(3)	Hg(2)–Cl(2)	2.092(9)
Si(1)–C(1)	1.920(10)	Si(1)–C(2)	1.876(13)
Si(1)–C(3)	1.857(11)	Si(1)–C(4)	1.880(11)
Si(2)–C(1)	1.917(10)	Si(2)–C(10)	1.853(13)
Si(2)–C(11)	1.860(12)	Si(2)–C(12)	1.869(11)
Si(3)–C(1)	1.890(10)	Si(3)–C(18)	1.882(12)
Si(3)–C(19)	1.901(13)	Si(3)–C(20)	1.889(11)
Si(4)–C(26)	1.909(10)	Si(4)–C(27)	1.886(12)
Si(4)–C(28)	1.861(11)	Si(4)–C(29)	1.877(10)
Si(5)–C(26)	1.899(10)	Si(5)–C(35)	1.855(13)
Si(5)–C(36)	1.869(13)	Si(5)–C(37)	1.895(12)
Si(6)–C(26)	1.915(10)	Si(6)–C(43)	1.878(13)
Si(6)–C(44)	1.860(12)	Si(6)–C(45)	1.867(10)
C(4)–C(5)	1.40(2)	C(4)–C(9)	1.41(2)
C(5)–C(6)	1.41(2)	C(6)–C(7)	1.35(2)
C(7)–C(8)	1.38(2)	C(8)–C(9)	1.40(2)
C(12)–C(13)	1.395(15)	C(12)–C(17)	1.39(2)
C(13)–C(14)	1.38(2)	C(14)–C(15)	1.38(2)
C(15)–C(16)	1.35(2)	C(16)–C(17)	1.38(2)
C(20)–C(21)	1.39(2)	C(20)–C(25)	1.40(2)
C(21)–C(22)	1.39(2)	C(22)–C(23)	1.41(2)
C(23)–C(24)	1.34(2)	C(24)–C(25)	1.39(2)
C(29)–C(30)	1.414(15)	C(29)–C(34)	1.380(15)
C(30)–C(31)	1.39(2)	C(31)–C(32)	1.36(2)
C(32)–C(33)	1.39(2)	C(33)–C(34)	1.40(2)
C(37)–C(38)	1.37(2)	C(37)–C(42)	1.40(2)
C(38)–C(39)	1.43(2)	C(39)–C(40)	1.35(2)
C(40)–C(41)	1.34(2)	C(41)–C(42)	1.39(2)
C(45)–C(46)	1.40(2)	C(45)–C(50)	1.408(15)
C(46)–C(47)	1.42(2)	C(47)–C(48)	1.36(2)
C(48)–C(49)	1.39(2)	C(49)–C(50)	1.38(2)
Hg(1)–Cl(2)	3.195(3)	Hg(2)–Cl(1)	3.393(3)

(b) Angles

Cl(1)–Hg(1)–Cl(1)	171.0(3)	Cl(2)–Hg(2)–Cl(2)	171.3(3)
C(1)–Si(1)–C(2)	112.0(5)	C(1)–Si(1)–C(3)	112.5(5)
C(1)–Si(1)–C(4)	111.5(5)	C(2)–Si(1)–C(3)	107.2(5)
C(2)–Si(1)–C(4)	107.9(5)	C(3)–Si(1)–C(4)	105.3(5)
C(1)–Si(2)–C(10)	114.9(5)	C(1)–Si(2)–C(11)	110.4(5)
C(1)–Si(2)–C(12)	110.4(5)	C(10)–Si(2)–C(11)	106.7(6)
C(10)–Si(2)–C(12)	104.0(5)	C(11)–Si(2)–C(12)	110.1(5)
C(1)–Si(3)–C(18)	113.0(5)	C(1)–Si(3)–C(19)	111.5(5)
C(1)–Si(3)–C(20)	111.6(4)	C(18)–Si(3)–C(19)	105.1(6)
C(18)–Si(3)–C(20)	106.4(5)	C(19)–Si(3)–C(20)	108.9(5)
C(26)–Si(4)–C(27)	112.4(5)	C(26)–Si(4)–C(28)	112.3(5)
C(26)–Si(4)–C(29)	111.7(4)	C(27)–Si(4)–C(28)	107.5(5)
C(27)–Si(4)–C(29)	105.1(5)	C(28)–Si(4)–C(29)	107.6(5)
C(26)–Si(5)–C(35)	112.5(5)	C(26)–Si(5)–C(36)	114.2(5)
C(26)–Si(5)–C(37)	109.3(5)	C(35)–Si(5)–C(36)	106.6(6)
C(35)–Si(5)–C(37)	108.9(6)	C(36)–Si(5)–C(37)	105.0(5)
C(26)–Si(6)–C(43)	112.5(5)	C(26)–Si(6)–C(44)	111.2(5)
C(26)–Si(6)–C(45)	112.0(4)	C(43)–Si(6)–C(44)	106.9(5)
C(43)–Si(6)–C(45)	105.9(5)	C(44)–Si(6)–C(45)	108.1(5)
Hg(1)–Cl(1)–Si(1)	101.5(4)	Hg(1)–Cl(1)–Si(2)	105.4(4)
Hg(1)–Cl(1)–Si(3)	108.1(5)	Si(1)–Cl(1)–Si(2)	112.7(5)
Si(1)–Cl(1)–Si(3)	114.0(5)	Si(2)–Cl(1)–Si(3)	113.9(5)
Si(1)–C(4)–C(5)	119.7(8)	Si(1)–C(4)–C(9)	122.1(9)
C(5)–C(4)–C(9)	118(1)	C(4)–C(5)–C(6)	121(1)
C(5)–C(6)–C(7)	119(1)	C(6)–C(7)–C(8)	122(1)
C(7)–C(8)–C(9)	119(1)	C(4)–C(9)–C(8)	121(1)

TABLE 4 (continued)

(b) Angles			
Si(2)–C(12)–C(13)	125.3(8)	Si(2)–C(12)–C(17)	119.0(8)
C(13)–C(12)–C(17)	116(1)	C(12)–C(13)–C(14)	123(1)
C(13)–C(14)–C(15)	119(1)	C(14)–C(15)–C(16)	120(1)
C(15)–C(16)–C(17)	121(1)	C(12)–C(17)–C(16)	122(1)
Si(3)–C(20)–C(21)	121.0(8)	Si(3)–C(20)–C(25)	121.7(8)
C(21)–C(20)–C(25)	117(1)	C(20)–C(21)–C(22)	122(1)
C(21)–C(22)–C(23)	119(1)	C(22)–C(23)–C(24)	119(1)
C(23)–C(24)–C(25)	122(1)	C(20)–C(25)–C(24)	120(1)
Hg(2)–C(26)–Si(4)	101.9(4)	Hg(2)–C(26)–Si(5)	106.5(5)
Hg(2)–C(26)–Si(6)	105.7(4)	Si(4)–C(26)–Si(5)	113.7(5)
Si(4)–C(29)–Si(6)	113.5(5)	Si(5)–C(26)–Si(6)	114.2(5)
Si(4)–C(29)–C(30)	121.0(8)	Si(4)–C(29)–C(34)	123.1(8)
C(30)–C(29)–C(34)	115.6(9)	C(29)–C(30)–C(31)	123(1)
C(30)–C(31)–C(32)	119(1)	C(31)–C(32)–C(33)	120(1)
C(32)–C(33)–C(34)	120(1)	C(29)–C(34)–C(33)	122(1)
Si(5)–C(37)–C(38)	125.9(9)	Si(5)–C(37)–C(42)	118.1(8)
C(38)–C(37)–C(42)	116(1)	C(37)–C(38)–C(39)	121(1)
C(38)–C(39)–C(40)	118(1)	C(39)–C(40)–C(41)	123(2)
C(40)–C(41)–C(42)	118(1)	C(37)–C(42)–C(41)	123(1)
Si(6)–C(45)–C(46)	120.5(8)	Si(6)–C(45)–C(50)	124.7(8)
C(46)–C(45)–C(50)	115(1)	C(45)–C(46)–C(47)	122(1)
C(46)–C(47)–C(48)	119(1)	C(47)–C(48)–C(49)	121(1)
C(48)–C(49)–C(50)	119(1)	C(45)–C(50)–C(49)	124(1)
Hg(1)–Cl(1)–Hg(2)	99.4(1)	Hg(1)–Cl(2)–Hg(2)	105.3(1)
Cl(1)–Hg(1)–Cl(2)	79.7(1)	Cl(1)–Hg(2)–Cl(2)	75.5(1)
C(1)–Hg(1)–Cl(2)	109.1(3)	C(26)–Hg(2)–Cl(1)	113.1(3)

As for the cadmium analogue, the geometries of the two molecules in the dimer are very similar, and the dimers again almost centrosymmetric. The dimers are, however, markedly different from those of the analogous zinc and cadmium chlorides in that the interaction between the two monomers is very weak. The geometry at the metal is not far from linear (the C–Hg–Cl angles are 171.0(3) and 171.3(3) Å) and the intermolecular Hg...Cl distances (3.194(3) and 3.392(3) Å) are little if any below the sum of the Van der Waals radii (3.2–3.6 Å, depending on which data are used [20,21]). A comparable situation is found in HgCl₂, in which the mean covalent Hg–Cl bond length is 2.291(9) Å, and the lengths of the weak coordinate Hg...Cl linkages are 3.37–3.48 Å [22], and also in various other chlorides RHgCl where R is an organic group [21]. The covalent Hg–Cl bonds (2.326(3) and 2.317(3) Å) in TpsiHgCl are possibly longer than those in gaseous (monomeric) HgCl₂ (2.252(5) Å) [23], and MeHgCl (2.28(5) Å) [26]. The Hg–C bond lengths (2.102(9) and 2.089(9) Å) are comparable with those in *e.g.* Me₂Hg in the gas phase (2.083(5) Å) [25], (PhCH₂)₂Hg (2.065(17) Å) [28], and a range of other diorganomercurials [21], but may be slightly shorter than those in [(Me₃Si)₃C]₂Hg (2.142(4) Å) [27]. The Hg–Cl–Hg angles are distinctly larger and the Cl–Hg–Cl angles distinctly smaller than the corresponding angles in the cadmium analogue.

We have previously pointed out that in compounds of the type $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{M}$ the Me groups in one of the $(\text{Me}_3\text{Si})_3\text{C}$ ligands are interlocked with those in the other [1,28], and it seemed possible that the repulsion between the two sets of Me groups might result in lengthening of the C–M bond, but the similarity in the lengths of the C–M bonds in TpsiHgCl and $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{Hg}$, both involving essentially sp hybridization at mercury, suggests that such an effect, if it operates at all, must be very small.

The results described here neatly show the consequences of relativistic effects for the elements of the sixth period [29]. In the compounds TpsiMCl both the M–C and M–Cl bond lengths vary in the sequence $\text{Zn} < \text{Cd} > \text{Hg}$ (Table 2), showing clearly the smaller size of Hg compared with Cd as the $6p_{1/2}$ electrons contract. (For further examples see refs. 1 and 30). The weakness of the interactions between the monomers in the mercury compound is the result of the much smaller contraction, and hence higher energy, of the $6p_{3/2}$ subshell.

2.3. Conformations of the $(\text{PhMe}_2\text{Si})_3\text{C}$ ligands

Changes in the size and symmetry of the central M_2X_2 ring ($M = \text{Zn}, \text{Cd}, \text{or Hg}; \text{X} = \text{Cl}$) result in changes in the conformation of the Tpsi groups, as shown by the torsion angles about Si–C bonds (Table 5). If all the adjacent bonds were in fully staggered positions the inter-methyl distances would be as low as 3.14–3.22 Å, but significant increases in these distances can be brought about by quite small rotations. For example, in $(\text{TpsiZnCl})_2$ rotations of 10° – 20° from the staggered positions will result inter-methyl distances of 3.47–4.31 Å. There are similar twists in the Cd and Hg analogues, but the directions differ in a subtle way.

In $(\text{TpsiZnCl})_2$ the three Me_2PhSi groups of the Tpsi fragment containing C(1) are twisted in the same direction, taking the Ph groups away from the metal as in Fig. 4(a), to give a propeller-type configuration like that in TpsiH [31] and other compounds in which the adjacent group is small [32,33]. In the Tpsi group containing C(26), however, two Ph groups are twisted

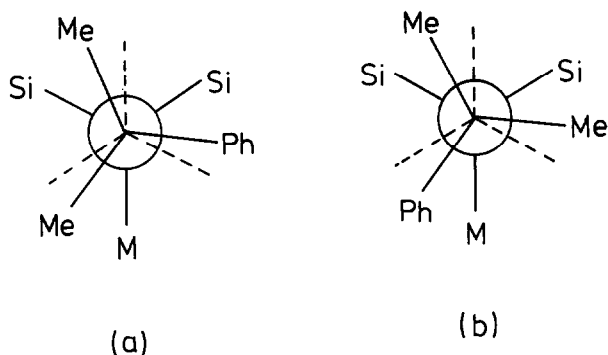


Fig. 4. Conformations of the Tpsi groups.

away from the Zn (Fig. 4(a)) but the third is twisted towards it (Fig. 4(b)); similar arrangements are found in $\text{TpsiSnMe}_2\text{F}$ [34], TpsiPCl_2 [35] and $(\text{TpsiZnOH})_2$ [36]. The dimer $(\text{TpsiZnCl})_2$ thus has no symmetry overall. In $(\text{TpsiCdCl})_2$ and $(\text{TpsiHgCl})_2$ the dimers are almost centrosymmetrical, though the space groups do not require them to be so. Again the Me_2Ph groups are twisted by 10° – 20° from staggered positions about Si–C bonds, but in all the Tpsi fragments two of the Ph groups are twisted away from the metal (Fig. 4(a)) and the third towards it (Fig. 4(b)). We have previously described the conformations of Tpsi groups in terms of the dihedral angles between the planes of the Ph groups and the Si_3 planes [32,37]. For the TpsiMCl compounds these are: $M = \text{Zn}$, 86, 90, 82 and 89, 86, 54; $M = \text{Cd}$, 68, 80, 88 and 69, 84, 82; $M = \text{Hg}$, 72, 89, 88 and 70, 86, 94. The above discussion of the conformations of Tpsi ligands represents an extension of an analysis based on NMR data [38].

The factors leading to the differences in the configurations of the Tpsi groups are not at present understood. Although there is no evidence that the differences persist in solution they could affect the molecular complexities. For example, in $(\text{TpsiCdCl})_2$ the Ph groups attached to Si(1) and Si(4) that twist towards the metal effectively shield both sides of the Cd_2Cl_2 ring; we have suggested that this shielding may prevent

TABLE 5. Torsion angles ($^\circ$) about Si–C bonds

	M = Zn			M = Cd			M = Hg		
CSi(1)C(1)M(1)	68 ^a	–48	–170	153	–86	29 ^a	–161	–40	78 ^a
CSi(2)C(1)M(1)	80 ^a	–160	–40	45	166	–73 ^a	–52	–173	65 ^a
CSi(3)C(1)M(1)	72 ^a	–43	–166	161	40	–79 ^a	84	–158	–36 ^a
CSi(4)C(26)M(2)	74 ^a	–43	–164	87	–153	29 ^a	43	164	–75 ^a
CSi(5)C(26)M(2)	74 ^a	–167	–45	–48	–170	69 ^a	170	49	–69 ^a
CSi(6)C(26)M(2)	–18 ^a	–140	98	–167	–45	73 ^a	–82	158	37 ^a

^a Denotes C of Ph.

the formation of tetramers like those observed for [(Me₃Si)₃CCdCl]₄ [3].

3. Experimental details

Solvents were carefully dried and distilled immediately before use. Reactions involving organolithium reagents were conducted under argon.

The ¹H NMR were recorded at 90 MHz on a Perkin Elmer R32 spectrometer or at 360 MHz on a Bruker WM360 FT spectrometer, the ¹³C, ²⁹Si, ¹¹³Cd, and ¹⁹⁹Hg NMR spectra at 90.5, 71.5, 79.9, and 64.4 MHz, respectively, on the Bruker WM 360 spectrometer, and ⁷Li NMR spectra at 31.14 MHz on a Bruker WP80 FT spectrometer. Chemical shifts for ¹H, ¹³C, and ²⁹Si are relative to internal SiMe₄, those for ¹¹³Cd to CdMe₂, those for ¹⁹⁹Hg to HgMe₂, and those for ⁷Li to external aqueous LiNO₃; all shifts are in ppm. The solvent was toluene-*d*₈ unless otherwise indicated. The DEPT CH only technique was used to remove interfering solvent peaks in the aryl region of the ¹³C spectra.

Mass spectra were obtained by electron impact at 70 eV unless otherwise indicated. Where relevant the *m/z* values refer to ions containing ³⁵Cl, ⁶⁴Zn, ¹¹⁴Cd, or ²⁰²Hg isotopes. The assignments of ions are meant only to indicate possible identities and not fragmentation pathways.

3.1. Preparation of (PhMe₂Si)₃CH

A 2.5 M solution of ⁿBuLi in hexane (360 cm³, 0.90 mol), cooled to -78°C, was added dropwise with vigorous stirring to a mixture of PhMe₂SiCl (141 g, 0.83 mol) and CHBr₃ (25 cm³, 0.28 mol) in THF (400 cm³) maintained at -78°C. When addition was complete the stirred mixture was allowed to warm to room temperature then cautiously treated with water. The organic layer was washed with dilute hydrochloric acid until the washings were colourless, then dried (MgSO₄) and filtered. The solvent was removed under vacuum, methanol was added to the residue, and the solution kept at -20°C. The white crystals were filtered off, dried, and shown to be (PhMe₂Si)₃CH (79 g, 71%), m.p. 106–107°C (*c.f.* ref. 2); δ (H) (CCl₄/CH₂Cl₂) 0.4 (s) and 7.3–7.5 (m). (The signal from the central, quaternary, carbon atom was not observed.)

3.2. Preparation of (the probable) [(PhMe₂Si)₃CZn(μ-Cl)₂Li(THF)₂]

A 0.90 M solution of MeLi in Et₂O (20 cm³, 18.3 mmol) was added to a solution of (PhMe₂Si)₃CH (7.62 g, 18.3 mmol) in THF (50 cm³) and the ether then distilled off. The remaining solution was heated under reflux for 3 h then cooled to room temperature, transferred to a pressure-equalizing dropping funnel, and

added dropwise to a stirred suspension of ZnCl₂ (2.5 g, 18.3 mmol) in THF (60 cm³). The mixture was stirred at room temperature for 70 h and the solvent then taken off under reduced pressure. The solid residue was washed with cold pentane (20 cm³) to remove (PhMe₂Si)₃CH, and then extracted with hot toluene (*ca.* 40 cm³). The extract was filtered, diluted with THF (15 cm³), and kept at -10°C. White crystals separated, and these were filtered off and judged probably to be [(Me₂PhSi)₃CZn(μ-Cl)₂Li(THF)₂] (7.5 g, 59%), m.p. *ca.* 85°C (with decomposition); δ(H) 0.50 (18H, s, SiMe₂), 1.36 (8H, m, CH₂), 3.52 (8H, m, OCH₂), 7.10–7.57 (15H, m, Ph); δ(C) 2.68 (quaternary C), 8.26 (SiMe₂), 25.6 (CH₂), 68.4 (OCH₂), 133.6 (*p*-C of Ph), 135.1 (*m*-C), 137.5 (*o*-C), 144.1 (*ipso*-C); δ(Si) -7.46; δ (⁷Li) 0.26; *m/z* (positive FAB (xenon; toluene/3-nitrobenzyl alcohol (3NBA)) 523 (1%, (PhMe₂Si)₃CZnCl₂Li-Cl); 481 (1, (PhMe₂Si)₃CZn), 403 (1, (PhMe₂Si)₃CH-Me), 309 (15), 175 (15), 135 (100, PhMe₂Si), 105 (25) 73 (35, Me₃Si). Ions containing Li, Zn and/or Cd showed the expected isotope patterns.

3.3. Preparation of (PhMe₂Si)₃CZnCl

A sample of the compound [(PhMe₂Si)₃CZn(μ-Cl)₂Li(THF)₂] (3.0 g, 4.3 mmol) was placed in a small round-bottomed flask fitted with an air condenser, the outlet of which led to a trap cooled in liquid nitrogen. The flask was evacuated to 0.05 Torr and heated at 200°C to generate THF, which was collected in the trap and identified from its ¹H NMR spectrum, and leave a white residue, which was sublimed under reduced pressure to give (PhMe₂Si)₃CZnCl (1.70 g, 79%), m.p. 170°C (no decomposition below 350°C) (Found: C, 56.8; H, 6.6. Calc. for C₂₅H₃₃ClSi₃Zn; C, 58.1; H, 6.4%); δ(H) 0.40 (18H, s, SiMe₂), 7.10–7.54 (15H, m, SiMe₂), 7.10–7.54 (15H, m, Ph); δ(C) 5.43 (SiMe₂), 127.8 (*m*-C), 129.5 (*p*-C), 133.2 (*o*-C), 144.3 (*ipso*-C); *m/z* (positive FAB (xenon), toluene/3NBA) 481 (55%, M-Cl), 420 (45), 403 (40, (PhMe₂Si)₃CH-Me), 387 (30), 371 (25), 341 (45, (PhMe₂Si)₃CH-Ph), 325 (100, (PhMe₂Si)₃C-Ph-Me).

3.4. Preparation of (the probable) [(PhMe₂Si)₃CCd(μ-Cl)₂Li(THF)₂]

A 0.95 M solution of MeLi in Et₂O [5.5 cm³, 5.22 mmol) was added to one of (PhMe₂Si)₃CH (2.0 g, 4.77 mmol) in THF (20 cm³). The ether was distilled off and the remaining solution heated under reflux for 3 h then cooled to room temperature and added dropwise with stirring to a suspension of CdCl₂ (1.0 g, 5.45 mmol) in THF (60 cm³). The mixture was stirred at room temperature for 19 h and the solvent then removed under reduced pressure. The residue was washed with hep-

tane (30 cm³) (to remove (Me₂PhSi)₃CH) then extracted twice with hot toluene. The hot extracts were filtered, concentrated, and combined, and THF (10 cm³) was added. The white crystals that separated were filtered off, dried under vacuum, and judged

TABLE 6. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for [(TpsiZnCl)₂].

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
Zn(1)	2424.3(5)	3813.7(10)	4961.4(5)	47(1)
Zn(2)	3312.9(5)	4884.9(10)	6099.8(5)	48(1)
Cl(1)	2645(1)	3262(2)	5929(1)	68(2)
Cl(2)	3163(1)	5313(2)	5106(1)	82(2)
Si(1)	2422(1)	3245(2)	3622(1)	50(2)
Si(2)	1556(1)	1811(2)	4475(1)	51(2)
Si(3)	1207(1)	4400(3)	4199(1)	53(2)
Si(4)	4226(1)	4061(2)	7154(1)	44(2)
Si(5)	4520(1)	6363(2)	6487(1)	42(1)
Si(6)	3230(1)	6107(2)	7246(1)	47(2)
C(1)	1879(4)	3294(7)	4280(3)	35(5)
C(2)	3039(4)	2065(8)	3728(4)	50(6)
C(3)	3534(4)	2188(8)	4160(4)	64(6)
C(4)	4023(5)	1371(9)	3267(5)	72(7)
C(5)	4008(5)	416(9)	3922(5)	82(8)
C(6)	3543(5)	249(9)	3489(5)	83(8)
C(7)	3067(5)	1055(8)	3404(4)	70(7)
C(8)	2926(4)	4548(8)	3518(4)	62(6)
C(9)	1972(5)	3026(10)	2906(4)	72(7)
C(10)	833(4)	1869(8)	4986(4)	53(6)
C(11)	833(4)	1869(8)	4986(4)	53(6)
C(11)	211(4)	1590(8)	4781(4)	64(6)
C(12)	-306(4)	1601(9)	5169(5)	75(7)
C(13)	-213(5)	1896(10)	5755(5)	81(7)
C(14)	382(5)	2203(11)	5958(4)	90(8)
C(15)	913(5)	2140(10)	5590(4)	81(8)
C(16)	1282(5)	976(8)	3808(4)	70(7)
C(17)	2175(5)	888(8)	4882(4)	65(6)
C(18)	1510(4)	5798(8)	3891(4)	58(6)
C(19)	1390(5)	6146(8)	3299(4)	64(6)
C(20)	1594(5)	7218(10)	3104(5)	84(8)
C(21)	1938(5)	7941(9)	3474(5)	97(8)
C(22)	2079(5)	7642(9)	4049(5)	85(8)
C(23)	1853(5)	6582(8)	4258(5)	74(7)
C(24)	871(5)	4823(9)	4923(5)	86(8)
C(25)	509(4)	3938(9)	3704(5)	73(7)
C(26)	3868(4)	5387(7)	6787(3)	32(5)
C(27)	4883(4)	3444(7)	6687(4)	41(5)
C(28)	5539(4)	3461(8)	6869(4)	49(6)
C(29)	6025(4)	3023(8)	6511(4)	55(6)
C(30)	5862(4)	2586(8)	5963(4)	62(6)
C(31)	5227(5)	2545(8)	5773(4)	66(7)
C(32)	4737(4)	2848(8)	7229(4)	63(6)
C(34)	4571(5)	4351(9)	7919(4)	65(6)
C(35)	4223(4)	7842(7)	6259(4)	46(5)
C(36)	3883(5)	7975(8)	5713(4)	61(6)
C(37)	3673(5)	9061(9)	5516(5)	78(7)
C(38)	3808(5)	10015(9)	5852(5)	87(8)
C(39)	4152(6)	9899(8)	6380(5)	90(8)
C(40)	4358(5)	8834(8)	6572(4)	71(7)
C(41)	5198(5)	6639(9)	7042(4)	67(7)
C(42)	4907(4)	5788(8)	5803(4)	51(6)

TABLE 6 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
C(43)	2500(4)	6407(8)	6745(4)	53(6)
C(44)	1973(5)	5694(10)	6720(5)	82(8)
C(45)	1428(5)	5914(10)	6366(6)	102(9)
C(46)	1387(5)	6905(10)	6058(5)	103(8)
C(47)	1900(5)	7670(12)	6050(5)	101(9)
C(48)	2450(5)	7421(10)	6399(4)	76(7)
C(49)	3484(5)	7462(9)	7616(4)	74(7)
C(50)	2896(5)	5222(10)	7862(5)	88(8)

^a *U*_{eq} is defined as one third of the trace of the orthogonalised *U*_{*ij*} tensor.

probably to be [(PhMe₂Si)₃CCd(μ-Cl)₂Li(THF)₂] (2.3 g, 64%), m.p. 123°C (with decomposition) (Found: C, 52.3; H, 6.7. C₃₃H₄₉CdCl₂LiO₂Si₃ calc.: C, 52.7; H, 6.6%); δ(H) 0.61 (18H, s, SiMe₂), 1.42 (8H, m, CH₂), 3.57 (8H, m, OCH₂), 7.02–7.74 (15H, m, Ph); δ(C) (C₆D₆) 5.9 (SiMe₂), 25.6 (CH₂) 68.2 (OCH₂), 127.9 (*m*-C of Ph), 128.7 (*p*-C), 135.3 (*o*-C), 143.7 (*ipso*-C) (DEPT CH only); δ(Si) (C₆D₆) -7.02; δ(⁷Li) -0.40; δ(Cd) (C₆D₆) -326; ν(Cd-C) 397 (w) cm⁻¹; *m/z* (EI) 566 (109, (PhMe₂Si)₃CCdCl), 551 (20, (PhMe₂-Si)₃CCdCl-Me), 402 (25, (PhMe₂Si)₃C-Me), 387 (15), 325 (55), 309 (100), 267 (10), 197 (20, Ph₂MeSi), 175 (15), 135 (95, PhMe₂Si), 105 (15).

3.5. Preparation of (PhMe₂Si)₃CdCl

(a) A sample of [(PhMe₂Si)₃Cd(μ-Cl)₂Li(THF)₂] (0.8 g, 1.07 mmol) was heated at 190°C at 0.01 Torr to give THF (which was collected in a liquid nitrogen trap and identified from its ¹H NMR spectrum) and leave white crystals of (PhMe₂Si)₃CdCl (0.46 g, 77%), m.p. 208–210°C (with decomposition) (Found: C, 52.6; H, 6.0. C₂₅H₃₃CdClSi₃ calc: C, 53.1; H, 5.9%); δ(H) 0.43 (18H, s, SiMe₂), 7.03–7.72 (15H, m, Ph); δ(C) (C₆D₆) 4.8 (SiMe₂); 128.8 (*m*-C of Ph), 129.3 (*p*-C), 134.1 (*o*-C); 144.4 (*ipso*-C) (DEPT CH only); δ(Si) (C₆D₆) -6.7; δ(Cd) (C₆D₆) -314; (Cd-C) 398 (w) cm⁻¹; *m/z* (EI) 566 (10%, M) 551 (45, M-Me), 403 (30, (PhMe₂-Si)₃CH-Me); 387 (20), 340 (20), 325 (80), 309 (100), 247 (15), 197 (25), 175 (40), 135 (95), 105 (25), 73 (40). Mol. wt. (in benzene) by freezing point method, 1047 (Calc. for dimer, 1131).

(b) The procedure described above for the preparation of [(PhMe₂Si)₃Cd(μ-Cl)₂Li(THF)₂] was repeated as far as the removal of the solvent from the reaction mixture under reduced pressure. The residue was then extracted with hot toluene and the extract filtered and cooled, to give crystals of (PhMe₂Si)₃CdCl in 35% yield.

3.6. Preparation of (PhMe₂Si)₃CHgCl

A solution of (PhMe₂Si)₃CH (7.0 g, 16.7 mmol) in THF (35 cm³) was added dropwise to a 1.5 M solution

of MeLi in ether (12.2 cm³, 18.3 mmol). The ether was distilled off and the mixture heated under reflux for 3 h. The solution was then added dropwise during 30 min to a solution of HgCl₂ (5.0 g, 18.4 mol) in THF (20 cm³) and the mixture heated under reflux. Monitoring

TABLE 7. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for [(TpsiCdCl)₂]

	x	y	z	U_{eq}^a
Cd(1)	1454.2(3)	720.9(2)	2944.8(2)	49.3(1)
Cd(2)	467.9(3)	1836.8(2)	4046.3(2)	49.3(1)
Cl(1)	1000(1)	534(1)	4020(1)	65(1)
Cl(2)	842(1)	1995(1)	2937(1)	75(1)
Si(1)	1264(1)	-492(1)	1840(1)	46(1)
Si(2)	2808(1)	769(1)	2005(1)	41(1)
Si(3)	3127(1)	-521(1)	3063(1)	51(1)
Si(4)	818(1)	3192(1)	5051(1)	43(1)
Si(5)	-682(1)	1985(1)	5113(1)	41(1)
Si(6)	-1129(1)	3127(1)	3908(1)	46(1)
C(1)	2246(4)	65(3)	2429(3)	37(3)
C(2)	1486(5)	-800(4)	1055(3)	72(4)
C(3)	972(5)	-1349(3)	2231(4)	76(4)
C(4)	135(4)	56(3)	1624(3)	44(3)
C(5)	-347(4)	86(4)	2094(3)	56(3)
C(6)	-1137(5)	508(4)	1993(4)	80(4)
C(7)	-1479(5)	907(4)	1413(4)	93(5)
C(8)	-1030(5)	883(4)	940(4)	80(4)
C(9)	-241(4)	466(4)	1040(3)	63(4)
C(10)	3349(4)	1550(3)	2575(3)	57(3)
C(11)	3754(4)	379(4)	1706(3)	64(4)
C(12)	1947(4)	1215(3)	1238(3)	44(3)
C(13)	1855(4)	989(3)	574(3)	56(3)
C(14)	1227(5)	1352(4)	16(3)	73(4)
C(15)	714(5)	1920(4)	115(4)	83(5)
C(16)	797(5)	2165(4)	753(4)	75(4)
C(17)	1409(5)	1810(3)	1308(3)	58(3)
C(18)	3526(5)	-1289(4)	2630(4)	79(4)
C(19)	2671(5)	-918(4)	3719(4)	78(4)
C(20)	4221(4)	-10(4)	3570(3)	56(3)
C(21)	4208(5)	461(4)	4091(4)	69(4)
C(22)	4999(5)	818(5)	4484(4)	85(5)
C(23)	5842(6)	704(5)	4376(4)	96(5)
C(24)	587(5)	216(5)	3880(4)	94(5)
C(25)	5090(5)	-130(4)	3483(4)	73(4)
C(26)	-201(4)	2605(3)	4566(3)	34(3)
C(27)	1051(5)	3990(4)	4558(3)	65(4)
C(28)	683(5)	3608(3)	5836(3)	64(4)
C(29)	1937(4)	2636(3)	5266(3)	48(3)
C(30)	2372(4)	2328(4)	5897(4)	63(4)
C(31)	3174(5)	1891(4)	6009(4)	84(4)
C(32)	3541(5)	1763(4)	5505(4)	92(5)
C(33)	3147(5)	2068(4)	4883(4)	80(4)
C(34)	2361(4)	2505(4)	4768(3)	60(4)
C(35)	-1340(4)	1186(3)	4645(3)	57(3)
C(36)	-1471(4)	2479(4)	5499(3)	64(4)
C(37)	283(4)	1555(3)	5835(3)	40(3)
C(38)	799(4)	966(3)	5716(3)	50(3)
C(39)	1486(5)	621(3)	6235(3)	59(3)
C(40)	1680(5)	871(4)	6888(4)	69(4)
C(41)	1175(5)	1439(4)	7024(3)	68(4)
C(42)	485(4)	1777(3)	6508(3)	55(3)

TABLE 7 (continued)

	x	y	z	U_{eq}^a
C(43)	-1558(5)	3940(4)	4275(4)	66(4)
C(44)	-753(5)	3472(4)	3184(3)	64(4)
C(45)	-2173(4)	2533(3)	3495(3)	46(3)
C(46)	-2157(4)	2027(4)	2995(3)	60(4)
C(47)	-2914(5)	1572(4)	2685(4)	74(4)
C(48)	-3717(5)	1630(4)	2855(4)	78(4)
C(49)	-3772(5)	2130(4)	3341(4)	70(4)
C(50)	-3008(4)	2574(4)	3657(3)	55(3)

^a U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

by ¹H NMR spectroscopy showed that reaction was complete after 2 h. The solvent was removed under vacuum. The residue was washed with a little heptane at room temperature (to remove the small amount of (PhMe₂Si)₃CH that had been shown by the NMR spectrum to be present) and then extracted with warm heptane. The extract was filtered, concentrated, and then kept at -10°C to give crystals of (PhMe₂Si)₃-CHgCl (7.3 g, 70%), m.p. 169–170°C. (Found: C, 44.6; H, 5.2. Calc. for C₂₅H₃₃ClHgSi₃: C 45.9; H 5.1%); δ (H) (C₆D₆) 0.21 (18 H, s, Me), 6.82–7.16 and 7.22–7.54 (15 H, m, Ph); δ (C) (C₆D₆) 3.76 (Me), 141.3 (*ipso*-C of Ph), 134.1 (*o*-C), 128.5 (*m*-C), 129.3 (*p*-C); δ (Si) (C₆D₆) -5.47; δ (Hg) -888; IR spectra: (Hg-Cl) 306, 319 (w); (Hg-C) 391(w) cm⁻¹. *m/z* 639 (1%, M-Me), 402 (25, (Me₂PhSi)₃C-Me), 340 (10), 325 (20), 329 (30), 267 (10), 247 (10), 202 (10, Hg), 197 (25, MePh₂Si), 175 (20), 135 (100, Me₂PhSi), 121 (20, MePhHSi), 105 (25), 85 (15), 73 (40), 43 (40); *m/z* Cl (NH₃) 672 (3%, M + NH₄), 434 (100), Me₂PhSi₃CH + NH₄, 403 (45), 340 (30), 325 (10), 309 (10), 280 (15), 264 (15), 202 (10), 197 (10), 175 (10), 135 (50), 105 (10), 90 (20), 73 (20), 43 (10).

3.7. Crystal structure determinations

All crystals were sealed in capillaries. Data were collected on an Enraf-Nonius CAD4 diffractometer.

3.7.1. Crystal data for [(TpsiZnCl)₂]

C₅₀H₆₆Cl₂Si₆Zn₂. monoclinic, $P2_1/n$ $M = 1037.2$, $a = 20.590(9)$, $b = 11.67(1)$, $c = 22.511(2)$ Å, $\beta = 91.75(2)^\circ$, $\mu = 5406.6$ Å³, $Z = 4$, $D_c = 1.3$ g cm⁻³, $F(000)$ 2176, monochromated MoK α radiation, $\lambda = 0.71069$ Å, $\mu = 11.7$ cm⁻¹.

A crystal of dimensions *ca.* 0.3 × 0.4 × 0.2 mm³ was used. Intensities of 10 262 unique reflections with $+h$, $+k$, $\pm l$ and $2 < \theta < 25^\circ$ were measured by a $\theta/2\theta$ scan with a scan width $\theta = (0.8 + 0.35 \tan \theta)^\circ$ and a maximum scan time of one minute. Corrections were made for Lorentz and polarization effects and for absorption using DIFABS (max. 1.09, min. 0.75); 4151

reflections with $F^2 > \sigma(F^2)$ were used for the structure analysis where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{0.5}/\text{Lp}$.

Non-hydrogen atoms were located by the direct method by use of the SHELXS86 program, and refined by full matrix least squares with anisotropic temperature

TABLE 8. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for [(TpsiHgCl)₂]

	x	y	z	U_{eq}^a
Hg(1)	1330.8(3)	982.9(2)	1287.2(1)	47.6(1)
Hg(2)	-1504.2(3)	281.4(2)	1173.5(1)	49.0(1)
Cl(1)	659.1(24)	424.0(15)	786.6(9)	84(2)
Cl(2)	-698.4(22)	806.1(16)	1651.4(9)	86(2)
Si(1)	3292(2)	1518(1)	1413(1)	51(2)
Si(2)	2227(2)	982(1)	2164(1)	52(2)
Si(3)	1543(2)	2170(1)	1786(1)	57(2)
Si(4)	-3519(2)	-184(1)	1107(1)	45(2)
Si(5)	-2508(2)	269(1)	319(1)	51(2)
Si(6)	-1861(2)	-914(1)	725(1)	51(2)
C(1)	2138(7)	1457(4)	1696(3)	40(6)
C(2)	4281(8)	1701(5)	1755(4)	80(9)
C(3)	3607(8)	843(5)	1148(3)	64(7)
C(4)	3238(7)	2086(5)	1012(3)	59(7)
C(5)	2735(9)	1981(5)	661(3)	72(8)
C(6)	2723(10)	2385(6)	346(4)	94(10)
C(7)	3236(11)	2871(6)	380(4)	110(11)
C(8)	3747(10)	2996(5)	719(5)	105(11)
C(9)	3768(8)	2594(5)	1032(4)	74(8)
C(10)	1104(9)	729(5)	2363(4)	76(8)
C(11)	2803(9)	1382(6)	2578(3)	82(9)
C(12)	2884(7)	308(5)	2049(3)	56(7)
C(13)	3768(7)	175(5)	2192(4)	70(8)
C(14)	4220(9)	-331(5)	2096(4)	92(10)
C(15)	3788(9)	-721(5)	1848(4)	89(9)
C(16)	2937(10)	-607(5)	1703(4)	82(9)
C(17)	2476(8)	-106(5)	1807(4)	69(8)
C(18)	611(9)	2128(5)	2179(3)	77(8)
C(19)	2390(9)	2735(5)	1977(4)	91(9)
C(20)	967(8)	2449(4)	1317(3)	54(6)
C(21)	179(9)	2187(5)	1164(3)	76(8)
C(22)	-263(9)	2386(6)	821(4)	95(9)
C(23)	126(9)	2855(6)	612(4)	107(10)
C(24)	878(9)	3114(6)	760(4)	100(10)
C(25)	1320(8)	2922(5)	1106(4)	74(8)
C(26)	-2408(6)	-170(4)	797(3)	40(5)
C(27)	-3763(8)	529(5)	1356(3)	66(7)
C(28)	-4553(8)	-373(5)	801(3)	65(7)
C(29)	-3444(7)	-717(4)	1528(3)	45(6)
C(30)	-2938(8)	-590(5)	1880(3)	64(7)
C(31)	-2917(10)	-950(5)	2214(3)	86(9)
C(32)	-3406(10)	-1451(6)	2204(4)	94(9)
C(33)	-3921(9)	-1594(5)	1867(4)	89(9)
C(34)	-3941(8)	-1225(5)	1536(3)	63(7)
C(35)	-3125(10)	-124(6)	-84(4)	85(9)
C(36)	-1371(9)	502(5)	105(3)	73(8)
C(37)	-3153(8)	962(5)	429(3)	64(7)
C(38)	-4052(9)	1083(6)	322(4)	85(9)
C(39)	-4490(9)	1611(6)	440(4)	132(10)
C(40)	-3982(12)	1999(7)	646(5)	161(14)
C(41)	-3101(11)	1908(5)	754(5)	119(12)
C(42)	-2688(9)	1393(5)	641(4)	78(9)

TABLE 8 (continued)

	x	y	z	U_{eq}^a
C(43)	-931(9)	-914(5)	331(3)	79(8)
C(44)	-2743(9)	-1453(5)	568(3)	72(8)
C(45)	-1295(7)	6181(4)	-3808(3)	51(6)
C(46)	-459(9)	5941(5)	-3676(4)	80(8)
C(47)	9(9)	6142(5)	-3330(4)	96(10)
C(48)	-354(10)	6588(6)	-3119(4)	106(10)
C(49)	-1163(9)	6857(5)	-3243(4)	87(9)
C(50)	-1606(8)	6655(5)	-3582(4)	68(7)

^a U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

factors by use of the programs in the Enraf-Nonius SDP package. The hydrogen atoms were fixed at calculated position with $U_{150} = 1.3 U_{\text{eq}}$ for the atoms to which they are bonded. Refinement converged at $R = 0.074$, $R' = 0.058$, with weighting scheme $w = \sigma^2(F)$. Atom coordinates are shown in Table 6.

3.7.2. Crystal data for [(TpsiCdCl)₂]

$\text{C}_{50}\text{H}_{66}\text{Cd}_2\text{Cl}_2\text{Si}_6$, monoclinic $P2_1/n$, $M = 1131.3$, $a = 15.048(6)$, $b = 18.248(9)$, $c = 20.807(21)$ Å, $\beta = 108.29(6)^\circ$, $U = 5424.9$ Å³, $Z = 4$, $D_c = 1.39$ g cm⁻³, $F(000)$, MoK α radiation, $\lambda = 0.71069$, $\mu = 10.4$ cm⁻¹.

A crystal of dimensions *ca.* $0.4 \times 0.4 \times 0.25$ mm³ was used. Intensities for 10 229 reflections with $+h$, $+k$, $\pm l$ and $2 < \theta < 25^\circ$ were measured by a $\theta/2\theta$ scan with scan width $\theta = (0.6 \pm 0.35 \tan \theta)^\circ$ and a maximum scan time of one minute. Corrections were made for Lorentz and polarization effects and for absorption using the DIFABS program (max. 144, min. 0.72). After averaging of equivalent reflections ($R_{\text{int}} = 0.038$) there were 9855 unique reflections, of which 5053 with $|F^2| > 3\sigma(F^2)$ were used in the structure refinement, where $\sigma(F^2) = [\sigma^2(I) + 0.04I]^2/\text{Lp}$.

The crystal was isomorphous with that of [(TpsiCdBr)₂] [3], the coordinates of which were taken as the starting point for full matrix least squares refinement with anisotropic temperature factors for non-hydrogen atoms. The hydrogen atoms were fixed at calculated position with $U_{\text{iso}} = 1.3U_{\text{eq}}$ for the atoms to which they are bonded. Refinement converged at $R = 0.039$, $R' = 0.042$, with weighting scheme $w = 1/\sigma^2(F)$. Atom coordinates are listed in Table 7

3.7.3. Crystal data for [(TpsiHgCl)₂]

$\text{C}_{50}\text{H}_{66}\text{Cl}_2\text{Hg}_2\text{Si}_6$, *Pbca*, $M = 1307.7$, $a = 14.421(9)$, $b = 23.226(4)$, $c = 33.391(6)$ Å, $U = 11184.0$ Å³, $Z = 8$, $D_c = 1.6$ g cm⁻³, $F(000) = 5152$, monochromated MoK α radiation, $\lambda = 0.71069$, $\mu = 57.4$ cm⁻¹.

A crystal of dimensions *ca.* $0.2 \times 0.3 \times 0.17$ mm³ was used. Intensities for 10 652 reflections with $+h$, $+k$, $+l$ and $2 < \theta < 25^\circ$ were measured by a $\theta/2\theta$

scan with scan width $\theta = (0.8 - 0.35 \tan \theta)^\circ$ and a maximum scan time of one minute. Corrections were made for Lorentz and polarization effects, for crystal decay of 13% during the data collection, and for absorption using the DIFABS program (max. 1.34, min. 0.64). 4540 reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + 0.04I]^2 / \text{Lp}$.

Non-hydrogen atoms were located by use of the SHELX80 program, and refined by full matrix least squares with anisotropic temperature factors using the programs of the Enraf-Nonius SDP package. Hydrogen atoms were fixed at calculated positions with $U_{\text{iso}} = 1.3 U_{\text{eq}}$ for the atoms to which they are bonded. Refinement converged at $R = 0.037$, $R' = 0.039$, with weighting scheme $w = \sigma^2(F)$. Atom coordinates are listed in Table 8).

Tables of thermal parameters and hydrogen atom coordinates for all three compounds have been deposited with the Cambridge Crystallographic Data Centre.

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