Journal of Organometallic Chemistry, 437 (1992) 41–55
Elsevier Sequoia S.A., Lausanne
JOM 22842

Reactions of sterically hindered organozinc and organocadmium compounds containing functional silicon centres. Crystal structures of $Zn[C(SiMe_3)_2(SiMe_2OCOCF_3)]_2$ and $Cd[C(SiMe_3)_2(SiMe_2OMe)]_2$ *

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(Received May 2, 1992)

Abstract

The compound $(Me_3Si)_2CCl_2$ was converted by treatment with BuLi/Et_2O/THF and then with Me_2HSiCl into $(Me_3Si)_2CCl(SiMe_2H)$. Further lithiation with BuLi gave $LiC(SiMe_3)_2(SiMe_2H)$, which reacted with $ZnBr_2$ to yield $Zn[C(SiMe_3)_2(SiMe_2H)]_2$. Thence, several new organozinc compounds $Zn[C(SiMe_3)_2(SiMe_2X)]_2$, with X = Cl, Br, I, F, OH, OMe, O_2CCF_3, O_2CH, or NCS, were obtained by substitutions at silicon without cleavage of Zn–C bonds. The compounds $Cd[C(SiMe_3)_2(SiMe_2X)]_2$, with X = H, OMe, and Ph, were obtained similarly, but subsequent substitutions at Si were accompanied by reactions at Cd. The crystal structure of the trifluoroacetato derivative $Zn[C(SiMe_3)_2(SiMe_2OCOCF_3)]_2$ shows that the molecules are centrosymmetric, with the O_2CCF_3 groups forced outwards by steric hindrance away from the metal centre. In $Cd[C(SiMe_3)_2(SiMe_2OMe)]_2$, the methoxy groups are folded in towards cadmium but the Cd $\cdots$ O distance is only slightly shorter than the sum of the van der Waals radii.

Introduction

Bis[tris(trimethylsilyl)methyl]zinc (**1**) melts without decomposition at about 300°C and may be distilled unchanged in steam [1]. The extraordinary thermal and hydrolytic stability of this organozinc compound seems to be associated with the replacement of all six hydrogens in Me_2Zn by trimethylsilyl groups, since the compounds $Zn[CH_2SiMe_3]_2$ and $Zn[CH(SiMe_3)_2]_2$ are, like dimethylzinc itself, pyrophoric and hydrolytically unstable [2]. We reported in a preliminary communication [3] that the Zn–C bonds in the related compounds (**2**) are so resistant to

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* Dedicated by C.E. and J.D.S. to their good friend Alwyn G. Davies in recognition of his outstanding contribution to organometallic chemistry.

attack by electrophiles that a wide range of substitutions can be made at silicon without degradation of the molecule as a whole. We now present preparative details and spectroscopic data for a range of new compounds and describe the crystal structure of the compound $Zn[C(SiMe_3)_2(SiMe_2OCOCF_3)]_2$. (The structures of the hydroxy and methoxy compounds $Zn[C(SiMe_3)_2(SiMe_2X)]_2$, with X = OH and OMe, have been published elsewhere [4].) The unsymmetrical derivative $[(ClMe_2Si)(Me_3Si)_2C]Zn[C(SiMe_3)_2(SiMe_2I)]$ has been detected by NMR spectroscopy but not isolated pure.

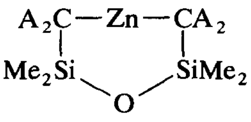
$Zn[C(SiMe_3)_2]_2$
(**1**)

$Cd[C(SiMe_3)_2(SiMe_2X)]_2$
(**4a**) X = H
(**4b**) X = OMe
(**4c**) X = Ph
(**4d**) X = $CH{=}CH_2$

$Zn[C(SiMe_3)_2(SiMe_2X)]_2$
(**2a**) X = H
(**2b**) X = OMe
(**2c**) X = Cl
(**2d**) X = I
(**2e**) X = OH
(**2f**) X = Br
(**2g**) X = F
(**2h**) X = O_2CCF_3
(**2i**) X = O_2CH
(**2j**) X = NCS
(**2k**) X = O_2CCH_3
(**2l**) X = $OSiMe_2Cl$

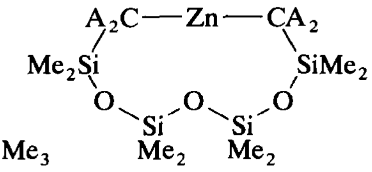
$(Me_3Si)_2CCl_2$
(**5**)
$(HMe_2Si)(Me_3Si)_2CCl$
(**6**)
$(HMe_2Si)_2(Me_3Si)_2C$
(**7**)
$(PhMe_2Si)(Me_3Si)_2CCl$
(**8**)
$(BrMe_2Si)(Me_3Si)_2CH$
(**11**)
$(BrMe_2Si)(Me_3Si)_2CBr$
(**12**)

$[(ClMe_2Si)(Me_3Si)_2C]Zn[C(SiMe_3)_2(SiMe_2I)]$ (**3**)



(**9**)

A = $SiMe_3$



(**10**)

The cadmium analogues proved to be less accessible than the organozinc compounds but three compounds $Cd[C(SiMe_3)_2(SiMe_2X)]_2$ (**4**), with X = H, OMe, or Ph, have been obtained. The crystal structure of the methoxy-compound is compared with those of the corresponding zinc and mercury derivatives described previously.

Experimental

Air and moisture were excluded by vacuum line and Schlenk tube techniques. Except where indicated, samples for NMR spectroscopy were dissolved in $CDCl_3$. Chemical shifts, all in ppm, are relative to $SiMe_4$ for ^1H and ^{13}C, $CFCl_3$ for ^{19}F, and $CdMe_2$ for ^{113}Cd. Mass spectra (relative intensities in parentheses) were by EI at 70 eV, unless otherwise stated. Mass numbers refer to ^1H, ^{13}C, ^{28}Si, ^{64}Zn, ^{79}Br and ^{114}Cd; in all cases, metal-containing species had the expected isotope patterns.

The compound $(HMe_2Si)(Me_3Si)_2CCl$ was made in 79% yield by the reaction between $(Me_3Si)_2CCl_2$ (**6**), BuLi, and HMe_2SiCl, at −110°C [4]. It was purified by sublimation at 100°C/10 Torr, and had ν(Si–H) 2125 cm^{-1} and δ(C) −1.98 ($SiMe_3$) and 0.49 ($SiMe_2$). ^1H NMR spectral data have been presented previously [4].

$(PhMe_2Si)(Me_3Si)_2CCl$ (8)

This was first made by Dr. K.L. Jones [5]. A solution of BuLi (0.096 mol) in hexane (38.5 cm^3) at −80°C was added to a mixture of $(Me_3Si)_2CCl_2$ (22 g, 0.096 mol), THF (160 cm^3), Et_2O (15 cm^3), and pentane (20 cm^3) at −110°C. The resulting mixture was stirred for 2 h, and after dropwise addition of $SiMe_2PhCl$ (16.3 g, 0.096 mol) left to warm overnight and then treated with saturated aqueous NH_4Cl. The organic layer was separated, washed with water, and dried ($MgSO_4$), and solvent removed under vacuum. The residual oil was distilled and the fraction distilling at 110°C/0.05 Torr was $(PhMe_2Si)(Me_3Si)_2CCl$ (11 g, 33%), m.p. 58°C.

$Zn[C(SiMe_3)_2(SiMe_2H)]_2$ (2a)

A solution of BuLi (16 mol) in hexane (10 cm^3) was added dropwise to a stirred solution of $(Me_3Si)_2C(Cl)SiMe_2H$ (3.7 g, 14.6 mmol) in THF (100 cm^3), Et_2O (15 cm^3), and pentane (15 cm^3) at −110°C. The mixture was stirred for 2 h then allowed to warm to −85°C, and finely ground anhydrous $ZnBr_2$ (1.64 g, 7.3 mmol) was added slowly with vigorous stirring. The suspension was left to warm to 20°C overnight, solvent was removed under vacuum, and the residue was extracted with hot heptane in a Soxhlet extractor. The heptane was removed from the extract under reduced pressure and the solid residue was fractionally sublimed (100°C at 0.05 Torr) by use of an air condenser. The most volatile fraction was a trace of $(Me_3Si)_2C(SiMe_2H)_2$ (7) (ν(SiH) 2104 cm^{-1}; m/z 261 $[M-Me]^+$), a common impurity in the starting material. The main fraction was $Zn[C(SiMe_3)_2(SiMe_2H)]_2$ (2.8 g, 78%), m.p. 160°C. Anal. Found: C, 43.8; H, 10.2. $C_{18}H_{50}ZnSi_6$ calc.: C, 43.3; H, 10.0%. δ(H) 0.21 (36H, s, $SiMe_3$); 0.28 (12H, d, $J = 3.7$ Hz, $SiMe_2$); 4.3 (1H, m, Si*H*). δ(C) 1.15 (CSi_3); 2.6 ($SiMe_2$); 5.7 ($SiMe_3$) J(CSi) 50.4 Hz. δ(Si) −5.6 ($SiMe_3$); 17.2 ($SiMe_2$). m/z 498 (80, M^+); 483 (80, $[M-Me]^+$); 281 (25, $[ZnC(SiMe_3)_2(SiMe_2H)]^+$); 202 (100, $[(Me_3Si)_2C(SiMe_2H)-Me]^+$); 129 (44); 73 (68).

$Zn[C(SiMe_3)_2(SiMe_2OMe)]_2$ (2b)

A solution of BuLi (10.6 mmol) in hexane (4.1 cm^3) at −78°C was added to a stirred solution of $(Me_3Si)_2C(Cl)SiMe_2OMe$ (3.0 g, 10.6 mmol) [4] in a mixture of

THF (60 cm^3), Et_2O (3 cm^3) and pentane (3 cm^3) at −110°C. The mixture was stirred for 1 h and a solution of $ZnBr_2$ (1.2 g, 5.3 mmol) in THF (15 cm^3) at −78°C was then added dropwise. The mixture was allowed to warm to 20°C overnight, the solvent was removed under vacuum, and the residue was extracted into pentane. Evaporation of the pentane left a solid, which was recrystallized from methanol to give $Zn[C(SiMe_3)_2(SiMe_2OMe)]_2$ (2.4 g, 50%), m.p. 233°C. Anal. Found: C, 43.1; H, 10.2. $C_{20}H_{54}O_2Si_6Zn$ calc.: C, 43.0; H, 9.7%. δ(H) 0.18 (36H, s, $SiMe_3$); 0.23 (12H, s, $SiMe_2$); 3.3 (3H, s, OMe). δ(C) 2.8 ($SiMe_3$); 5.9 ($SiMe_2$). δ(Si) −5.2, 17.1. *m/z* 558 (8, $[M^+]$); 543 (10, $[M-Me]^+$); 311 (26, $[ZnC(SiMe_3)_2(SiMe_2OMe)]^+$); 232 (100, $[(Me_3Si)_2C(SiMe_2OMe)-Me]^+$); 187 (18); 73 (28).

$Zn[C(SiMe_3)_2(SiMe_2Cl)]_2$ (2c)

A solution of ICl (0.8 mmol) in CCl_4 (8 cm^3) was added dropwise to one of $Zn[C(SiMe_3)_2(SiMe_2H)]_2$ (**2a**) (0.1 g, 0.2 mmol) in CH_2Cl_2 (5 cm^3) and the mixture was stirred for 0.75 h at 20°C. The solvent was taken off under vacuum and the residue recrystallized from heptane to give $Zn[C(SiMe_3)_2(SiMe_2Cl)]_2$ (0.1 g, 90%). Sublimed at 230°C/0.01 Torr; decomposed without melting at 265°C. Anal. Found: C, 37.1; H, 8.5. $C_{18}H_{48}ZnCl_2Si_6$ calc.: C, 37.6; H, 8.8%. δ(H) 0.29 (36H, s, $SiMe_3$); 0.62 (12H, s, $SiMe_2$). δ(C) 1.15 (CSi_3); 2.83 ($SiMe_2$); 5.92 ($SiMe_3$). δ(Si) −5.4 ($SiMe_3$); 17.2 ($SiMe_2$). *m/z* 568 (20, $[M]^+$); 553 (10, $[M-Me]^+$).

In similar reactions with smaller quantities of ICl, the products identified by ^1H NMR spectroscopy were as follows. With ICl (0.4 mmol): $Zn[C(SiMe_3)_2(SiMe_2I)]_2$ (**2d**) 60% (δ(H) 0.35, 1.06 ppm); (**2c**) 5% (δ(H) 0.27, 0.62 ppm); and $Zn[C(SiMe_3)_2(SiMe_2Cl)][C(SiMe_3)_2(SiMe_2I)]$ (**3**) 33% (δ(H) 0.30, 0.33, 0.64, 1.02 ppm). With ICl (0.2 mmol): (**2d**) 47% (δ(H) 0.36, 1.06 ppm); (**2a**) 21% (δ(H) 0.16, 0.19 ($J = 3.6$ Hz) and 4.3 m ppm); and (**3**) 30% (δ(H) 0.29, 0.31, 0.63, 1.02).

$Zn[C(SiMe_3)_2(SiMe_2I)]_2$ (2d)

Powdered I_2 (0.17 g, 2.8 mmol) was added to a solution of **2a** (0.70 g; 1.4 mmol) in CCl_4 (80 cm^3) and the mixture was stirred for 2 h at 20°C. The solvent was removed *in vacuo* and the residual solid crystallized from heptane to give $Zn[C(SiMe_3)_2(SiMe_2I)]_2$ (0.95 g, 95%). Anal. Found: C, 27.1; H, 6.7. $C_{18}H_{48}I_2Si_6Zn$ requires: C, 28.8, H, 6.4%. δ(H) 0.37 (36H, s, $SiMe_3$); 1.06 (12H, s, $SiMe_2$). δ(C) 3.2 (CSi_3); 6.6 ($SiMe_3$); 12.5 ($SiMe_2$). *m/z* 735 (22, $[M-Me]^+$); 699 (5); 661 (10); 623 (40, $[M-I]^+$); 571 (60); 435 (40); 421 (65); 217 (90); 73 (100).

$Zn[C(SiMe_3)_2(SiMe_2OH)]_2$ (2e)

A mixture of $Zn[C(SiMe_3)_2(SiMe_2Cl)]_2$ (**2e**) (0.25 g 0.46 mmol), THF (80 cm^3), water (20 cm^3), and hexane (7 cm^3) was shaken for 5 min in a separating funnel with $NaHCO_3$ (0.03 g) and the organic layer was separated and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to leave a white solid, which was recrystallized from hexane to give $Zn[C(SiMe_3)_2(SiMe_2OH)]_2$ (0.24 g, 98%), m.p. 175–178°C (decomposed at 235°C). Anal. Found: C, 41.3; H, 9.6. $C_{18}H_{50}Si_6O_2Zn$ calc.: C, 40.7; H, 9.4%. δ(H) 0.21 (36H, s, $SiMe_3$); 0.30 (12H, s, $SiMe_2$); 2.67 (1H, br, OH). δ(C) 1.02 (CSi_3); 6.08 ($SiMe_3$); 6.5 ($SiMe_2$). δ(Si) 6.0 ($SiMe_3$); 13.5 ($SiMe_2OH$). ν(Si–OH) (Nujol) 3367 (m) (CCl_4); 3360 (w); 3311 (m) cm^{-1}. *m/z* 530 (100, $[M]^+$); 515 (50, $[M-Me]^+$); 449 (85, $[M-OMe]^+$); 485 (20); 403 (40); 297 (80, $[(Me_3Si)_2C(SiMe_2OH)Zn]^+$); 218 (62, $[(Me_3Si)_2C(SiMe_2OH)-Me]^+$); 203 (100, $[(Me_3Si)_2C(SiMe_2OH)-2Me]^+$); 187 (90).

$Zn[C(SiMe_3)_2(SiMe_2Br)]_2$ (2f)

A solution of Br_2 (2 mmol) in CCl_4 (2 cm^3) was added to one of **2a** (0.1 g, 0.2 mmol) in CH_2Cl_2 (3 cm^3) and the mixture stirred for 5 min. Solvents and volatiles were removed *in vacuo* and the solid residue was recrystallized from heptane to give white crystals of $Zn[C(SiMe_3)_2(SiMe_2Br)]_2$ (**2f**) (0.15 g, 95%), which decomposed without melting at 230–240°C. Anal. Found: C, 32.7; H, 7.9. $C_{18}H_{48}BrSi_6Zn$ requires: C, 32.9; H, 7.3%. δ(H) 0.32 (36H, s, $SiMe_3$); 0.79 (12H, s, $SiMe_2$). δ(C) 6.3 ($SiMe_3$); 10.3 ($SiMe_2$). m/z 654 (1, $[M]^+$); 575 (40, $[M-Br]^+$).

$Zn[C(SiMe_3)_2(SiMe_2F)]_2$ (2g)

A solution of **2d** (0.10 g, 0.13 mmol) in CH_2Cl_2 (5 cm^3) was stirred with $AgBF_4$ (0.05 g, 0.25 mmol) for 2 h. The solution was filtered and solvent removed from the filtrate under reduced pressure to leave a residue, which was sublimed (100°C/0.05 Torr) to give $Zn[C(SiMe_3)_2(SiMe_2F)]_2$ (0.06 g, 90%), m.p. 184°C. δ(H) (CCl_4/CH_2Cl_2): 0.31 (36H, s, $SiMe_3$); 0.45 (12H, d, $^3J(FH) = 9$ Hz, $SiMe_2$). δ(F) -133.

$Zn[C(SiMe_3)_2(SiMe_2CO_2CF_3)]_2$ (2h)

A mixture of CF_3CO_2H (5 cm^3) (**2d**) (0.2 g, 0.27 mmol), CCl_4 (2 cm^3) and Ag_2O (0.25 g, 1.08 mmol) was stirred for 5 min. The mixture was filtered and the filtrate added to a mixture of ice-water and pentane. The organic layer was separated, dried ($MgSO_4$), and filtered, and the solvent evaporated to leave a solid, which was recrystallized from hexane to give $Zn[C(SiMe_3)_2(SiMe_2CO_2CF_3)]_2$ (0.17 g, 90%), m.p. 118°C. δ(H) 0.34 (36H, s, $SiMe_3$); 0.66 (12H, s, $SiMe_2$).

$Zn[C(SiMe_3)_2(SiMe_2O_2CH)]_2$ (2i)

Formic acid (10 cm^3) and Ag_2CO_3 (0.30 g, 12 mmol) were added to a solution of **2d** (0.20 g, 0.27 mmol) in CCl_4 (5 cm^3) and the mixture was stirred for 30 min at 20°C and filtered. The solvent was removed from the filtrate under reduced pressure and the residue extracted into pentane. The extract was washed with distilled water, and dried over $MgSO_4$, and the solvent evaporated to leave a white solid, which was recrystallized from hexane to give $Zn[C(SiMe_3)_2(SiMe_2O_2CH)]_2$ (0.13 g, 82%), m.p. 202–204°C. δ(H) (CH_2Cl_2/CCl_4): 0.28 (36H, s, $SiMe_3$); 0.52 (12H, s, $SiMe_2$). ν(CO): 1658 (vs).

$Zn[C(SiMe_3)_2(SiMe_2NCS)]_2$ (2j)

Freshly prepared and carefully dried AgNCS (0.05 g, 0.3 mmol) was added to a solution of **2d** (0.10 g, 0.13 mmol) in CH_2Cl_2 (20 cm^3) and the mixture was stirred for 3 h and then filtered. Solvent was evaporated from the filtrate to leave an oil, which upon addition of methanol gave a white solid. This was dissolved in hot heptane and the solution left at -20°C for several days to give white crystals of $Zn[C(SiMe_3)_2(SiMe_2NCS)]_2$ (50%), m.p. 165°C. δ(H) 0.30 (36H, s, $SiMe_3$); 0.51 (12H, s, $SiMe_2$). ν(NCS): 2066 cm^{-1}. m/z 612 (10, $[M^+]$); 597 (3, $[M-Me^+]$); 338 (60, $[ZnC(SiMe_3)_2(SiMe_2NCS)]^+$); 201 (100). The methanol washings were evaporated in air to leave a white solid, identified as **2b**.

$Zn[C(SiMe_3)_2(SiMe_2O_2CMe)]_2$ (2k)

A solution of **2e** (0.2 g, 0.38 mmol) in CCl_4 (3 cm^3) was stirred with CH_3COCl (10 cm^3, 190 mmol) for 2 h at 20°C, then the solvent and excess of CH_3COCl were removed under vacuum. The solid residue showed peaks in the NMR spectrum (δ(H) (CCl_4/CH_2Cl_2): 0.31 (36H, s, $SiMe_3$); 0.57 (12H, s, $SiMe_2$); 2.5 (3H, s, COMe)) and a strong band at 1717 cm^{-1} in the IR spectrum suggesting the formation of Zn[C(SiMe$_3$)$_2$(SiMe$_2$CO$_2$Me)]$_2$ (**2k**), but attempts to obtain a pure sample of this compound were unsuccessful.

*Cd[C(SiMe$_3$)$_2$(SiMe$_2$H)]$_2$ (**4a**)*

A solution of BuLi (10 mmol) in hexane (7 cm^3) at −78°C was added dropwise to one of (HMe$_2$Si)(Me$_3$Si)$_2$CCl (**6**) (2.17 g, 10 mmol) in THF (100 cm^3), Et$_2$O (15 cm^3), and pentane (10 cm^3) at −110°C. The mixture was stirred for 2 h then allowed to warm to −85°C, and a solution of $CdCl_2$ (0.60 g, 5 mmol) in THF (10 cm^3) was added dropwise. The mixture was allowed to warm to 20°C overnight, the solvent taken off under vacuum, and the solid residue extracted into pentane. The pentane was taken off under reduced pressure and the residue sublimed (100°C/0.05 Torr) to give Cd[C(SiMe$_3$)$_2$(SiMe$_2$H)]$_2$ (40%), m.p. 164°C. Anal. Found: C, 40.5; H, 9.7. $C_{18}H_{50}CdSi_6$ calc.: C, 39.6; H, 9.2%. ν(SiH): 2087 cm^{-1}. δ(H) 0.25 (36H, s, $SiMe_3$); 0.33 (12H, d, $^3J(HH) = 3.6$ Hz, $SiMe_2$); 4.4 (1H, m, SiH). δ(C) (C_6D_6): 3.4 ($J(CdC) = 21.4$ Hz ($SiMe_2$)); 6.0 ($J(CdC) = 14.8$ Hz ($SiMe_3$)). δ(Si) (C_6D_6): −4.2 ($J = 47$ Hz ($SiMe_3$)); −20.5 ($J = 50$ Hz ($SiMe_2$)). δ(Cd) (C_6D_6): −174. m/z 548 (50, $[M]^+$); 533 (64, $[M-Me]^+$); 331 (12, [CdC(SiMe$_3$)$_2$(SiMe$_2$H)]$^+$); 217 (100, [(Me$_3$Si)$_2$C(SiMe$_2$H)]$^+$). When **4a** was treated with Br_2 in CCl_4, a precipitate, insoluble in hydrocarbons and believed to be $CdBr_2$, formed immediately. This was filtered off and solvent removed from the filtrate under vacuum to give a solid, which was shown by GLC to consist of two components in the ratio 1:3. The first was judged to be (BrMe$_2$Si)(Me$_3$Si)$_2$CH (**11**) (δ(H) 0.28 (18H, s, $SiMe_3$); 0.71 (6H, s, $SiMe_2$)), and the second (BrMe$_2$Si)(Me$_3$Si)$_2$CBr (**12**) (δ(H) 0.38 (18H, s, $SiMe_3$); 0.88 (6H, s, $SiMe_2$)), in each case by comparison of the NMR data with those of authentic samples.

*Cd[C(SiMe$_3$)(SiMe$_2$OMe)] (**4b**)*

A solution of BuLi (20 mmol) in hexane (13 cm^3) at −78°C was added dropwise to one of (Me$_3$Si)$_2$C(Cl)(SiMe$_2$OMe) [4] (5.0 g, 20 mmol) in THF (90 cm^3), Et$_2$O (15 cm^3), and pentane (10 cm^3) at −110°C. The mixture was stirred for 1 h then allowed to warm to −85°C, and a cold (−78°C) solution of $CdCl_2$ (1.2 g, 10 mmol) in THF (20 cm^3) was added. The mixture was allowed to warm to 20°C overnight, the solvent was taken off under reduced pressure, and the solid residue extracted with pentane. The extract was filtered through Celite and the solvent evaporated from the filtrate to leave an oily residue, from which crystals of Cd[C(SiMe$_3$)$_2$(SiMe$_2$OMe)]$_2$ (1.0 g) were sublimed at 120°C/0.1 Torr. Yield 66%, m.p. 220°C. Anal. Found: C, 40.0; H, 9.1. $C_{20}H_{48}CdO_2Si_6$ calc.: C, 39.7; H, 8.9%. δ(H) 0.20 (36H, s, $SiMe_3$); 0.27 (12H, s, $SiMe_2$); 3.44 (3H, s, OMe). δ(C) (C_6D_6): 1.3 (CSi_3); 2.7 ($SiMe_2$); 6.3 ($SiMe_3$); 49.6 (OMe). δ(Si) (C_6D_6): −5.0 ($SiMe_3$); 16.8 ($SiMe_2$). δ(Cd) (C_6D_6): −226.1. m/z 608 (10, $[M]^+$); 593 (15, $[M-Me]^+$); 316 (70, [CdC(SiMe$_3$)$_2$(SiMe$_2$OMe)]$^+$); 232 (100); 201 (85); 73 (35).

*Cd[C(SiMe$_3$)$_2$(SiMe$_2$Ph)]$_2$ (**4c**)*

A cold (−78°C) solution of BuLi (8 mmol) in hexane (6 cm^3) was added dropwise to a stirred solution of (Me$_3$Si)$_2$C(Cl)(SiMe$_2$Ph) (2.6 g, 8 mmol) in THF

Table 1

X-Ray crystallographic details for **4b** and **2h**

Formula	$C_{20}H_{54}CdO_2Si_6$	$C_{22}H_{48}F_6O_4Si_6Zn$
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	16.896(13)	9.131(4)
b (Å)	9.352(5)	9.230(6)
c (Å)	23.879(8)	12.404(3)
α (°)	90	96.42(4)
β (°)	114.22(4)	93.34(3)
γ (°)	90	119.07(5)
Z	4	1
D_{calc} (g cm^{-3})	1.17	1.3
$F(000)$	1288	380
μ(Mo-K_α) (cm^{-1})	8.5	9.5
Unique reflections	3298	3153
Significant reflections	2179	2711
R	0.069	0.052
R'	0.077	0.070
Max shift/e.s.d.	0.01	0.22
Max difference density (e Å^{-3})	0.5	0.9

(80 cm^3), Et_2O (10 cm^3), and pentane (8 cm^3) at −110°C. After 1 h the mixture was allowed to warm to −90°C, finely powdered $CdCl_2$ (0.8 g, 4 mmol) was added, and the mixture allowed to warm to 20°C overnight. The solvent was removed and the oily residue washed with cold methanol to leave a white solid $Cd[C(SiMe_3)_2(SiMe_2Ph)]_2$ (1.6 g, 30%), m.p. 145°C. Anal. Found: C, 40.5; H, 9.3.

Table 2

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses for **4b**

	x	y	z
Cd	0	0	0
Si(1)	1842(3)	925(5)	978(2)
Si(2)	797(2)	−1217(4)	1396(2)
Si(3)	240(3)	2003(5)	1183(2)
O	1985(8)	−235(9)	407(4)
C(1)	788(5)	452(8)	955(3)
C(2)	2834(6)	567(14)	1751(5)
C(3)	1816(7)	2951(12)	677(5)
C(4)	2628(11)	−357(29)	306(10)
C(5)	1091(7)	−850(15)	2239(4)
C(6)	−283(6)	−2152(13)	1094(4)
C(7)	1580(8)	−2557(12)	1273(5)
C(8)	−186(6)	3368(12)	530(4)
C(9)	1119(9)	3025(13)	1887(5)
C(10)	−709(6)	1209(18)	1354(5)
Si(1a)	1857(4)	−490(8)	1055(3)
Si(2a)	257(5)	−423(9)	1384(3)
Si(3a)	877(5)	2390(8)	982(3)

Table 3

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for **4b**

(a) *Bonds*			
Cd–C(1)	2.159(6)	Si(1)–O	1.834(12)
Si(1)–C(1)	1.814(10)	Si(1)–C(2)	1.947(10)
Si(1)–C(3)	2.021(13)	Si(2)–C(1)	1.879(9)
Si(2)–C(5)	1.897(10)	Si(2)–C(6)	1.881(11)
Si(2)–C(7)	1.931(14)	Si(3)–C(1)	1.916(9)
Si(3)–C(8)	1.912(11)	Si(3)–C(9)	1.974(11)
Si(3)–C(10)	1.957(14)	O–C(4)	1.21(3)
(b) *Angles*			
O–Si(1)–C(1)	105.1(5)	O–Si(1)–C(2)	106.2(5)
O–Si(1)–C(3)	106.3(5)	C(1)–Si(1)–C(2)	116.1(5)
C(1)–Si(1)–C(3)	109.9(5)	C(2)–Si(1)–C(3)	112.5(5)
C(1)–Si(2)–C(5)	112.5(5)	C(1)–Si(2)–C(6)	112.8(4)
C(1)–Si(2)–C(7)	107.6(5)	C(5)–Si(2)–C(6)	106.4(6)
C(5)–Si(2)–C(7)	112.4(5)	C(6)–Si(2)–C(7)	104.9(5)
C(1)–Si(3)–C(8)	109.8(5)	C(1)–Si(3)–C(9)	109.1(5)
C(1)–Si(3)–C(10)	107.7(6)	C(8)–Si(3)–C(9)	105.8(5)
C(8)–Si(3)–C(10)	110.9(5)	C(9)–Si(3)–C(10)	113.6(6)
Si(1)–O–C(4)	127.1(1)	Cd–C(1)–Si(1)	104.6(4)
Cd–C(1)–Si(2)	106.8(3)	Cd–C(1)–Si(3)	106.7(3)
Si(1)–C(1)–Si(2)	113.8(4)	Si(1)–C(1)–Si(3)	112.9(4)
Si(2)–C(1)–Si(3)	111.3(5)		

Table 4

Fractional atomic coordinates (×10^4) with estimated standard deviations in parentheses for **2h**

	x	*y*	*z*
Zn	0	0	0
Si(1)	1155(1)	−1436(1)	1782(1)
Si(2)	−595(1)	694(1)	2417(1)
Si(3)	3020(1)	2414(1)	1760(1)
F(1)	5872(5)	1426(4)	4260(3)
F(2)	7540(4)	3886(5)	4894(3)
F(3)	5028(6)	2809(8)	5144(3)
O(1)	4042(3)	2297(3)	2934(2)
O(2)	6578(4)	4614(4)	3086(3)
C(1)	968(4)	466(4)	1547(3)
C(2)	−663(6)	−3400(5)	968(4)
C(3)	1170(6)	−1769(5)	3245(3)
C(4)	3121(5)	−1333(5)	1331(4)
C(5)	−1428(5)	1965(5)	1822(4)
C(6)	375(6)	1701(6)	3862(4)
C(7)	−2539(5)	−1349(6)	2481(4)
C(8)	3025(5)	4424(4)	2038(4)
C(9)	4397(5)	2611(6)	668(4)
C(10)	5568(5)	3384(5)	3405(4)
C(11)	5997(7)	2905(6)	4457(4)

Table 5

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for **2h**

(a) *Bonds*			
Zn–C(1)	1.974(3)	Si(1)–C(1)	1.896(4)
Si(1)–C(2)	1.880(3)	Si(1)–C(3)	1.874(5)
Si(1)–C(4)	1.873(5)	Si(2)–C(1)	1.916(4)
Si(2)–C(5)	1.869(6)	Si(2)–C(6)	1.872(4)
Si(2)–C(7)	1.874(4)	Si(3)–O(1)	1.726(3)
Si(3)–C(1)	1.838(2)	Si(3)–C(8)	1.847(5)
Si(3)–C(9)	1.865(5)	F(1)–C(11)	1.306(8)
F(2)–C(11)	1.289(6)	F(3)–C(11)	1.244(8)
O(1)–C(10)	1.306(4)	O(2)–C(10)	1.192(5)
C(10)–C(11)	1.513(8)		
(b) *Angles*			
C(1)–Si(1)–C(2)	110.3(2)	C(1)–Si(1)–C(3)	114.2(2)
C(1)–Si(1)–C(4)	112.5(2)	C(2)–Si(1)–C(3)	106.9(2)
C(2)–Si(1)–C(4)	106.2(2)	C(3)–Si(1)–C(4)	106.2(2)
C(1)–Si(2)–C(5)	111.1(2)	C(1)–Si(2)–C(6)	112.3(2)
C(1)–Si(2)–C(7)	113.6(2)	C(5)–Si(2)–C(6)	108.5(2)
C(5)–Si(2)–C(7)	104.0(2)	C(6)–Si(2)–C(7)	106.9(2)
O(1)–Si(3)–C(1)	103.9(1)	O(1)–Si(3)–C(8)	105.5(2)
O(1)–Si(3)–C(9)	106.5(2)	C(1)–Si(3)–C(8)	117.8(2)
C(1)–Si(3)–C(9)	115.1(2)	C(8)–Si(3)–C(9)	107.0(2)
Si(3)–O(1)–C(10)	126.9(3)	Zn–C(1)–Si(1)	105.5(1)
Zn–C(1)–Si(2)	107.1(2)	Zn–C(1)–Si(3)	108.5(2)
Si(1)–C(1)–Si(2)	111.2(2)	Si(1)–C(1)–Si(3)	112.8(2)
Si(2)–C(1)–Si(3)	111.2(2)	O(1)–C(10)–O(2)	127.4(5)
O(1)–C(10)–C(11)	111.9(3)	O(2)–C(10)–C(11)	120.7(4)
F(1)–C(11)–F(2)	104.2(6)	F(1)–C(11)–F(3)	106.4(5)
F(1)–C(11)–C(10)	110.0(4)	F(2)–C(11)–F(3)	109.6(4)
F(2)–C(11)–C(10)	113.1(4)	F(3)–C(11)–C(10)	113.0(6)

$C_{18}H_{50}Si_{16}Cd$ calc.: C, 39.6, H, 9.1%. δ(C) 6.2 (J(CdC) = 18 Hz (SiMe$_2$)); 7.4 (J(CdC) = 14.3 Hz (SiMe$_3$)). δ(Si) −4.8 (SiMe$_3$); −8.5 (SiMe$_2$). δ(Cd) −206. m/z positive FAB (Xe) (toluene–Nujol): 700 (10, $[M]^+$); 685 (18, $[M-\text{Me}]^+$); 623 (12, $[M-\text{Ph}]^+$); 559 (15); 407 (30, $[\text{CdC(SiMe}_3)_2(\text{SiMe}_2\text{Ph})]^+$); 279 (70); 262 (70); 135 (100).

X-Ray structure determinations

Suitable crystals of **4b** were obtained by sublimation in a sealed evacuated tube with a small temperature gradient, and crystals of **2h** were obtained by recrystallization from pentane. Data were collected on an Enraf–Nonius CAD4 diffractometer. Intensities for unique reflections with $2 < \theta < 25°$ were measured in the θ–2θ scan mode. Reflections with $|F^2| > \sigma(F^2)$ where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, were regarded as significant. Structure solution was by routine heavy atom methods and non-hydrogen atoms were refined with anisotropic thermal parameters by full matrix least squares. For **4b**, the Si atoms were disordered over two sites with occupancies of 0.64 and 0.36, and hydrogen atoms were omitted. For **2h** the hydrogen atoms were located on a difference map and refined with isotropic thermal parameters. Further details are given in Tables 1–5.

Results and discussion

The complex reactions between butyllithium, dichloromethane, and chlorosilanes have been studied in considerable detail [6]. With careful control of reaction conditions, *viz.* $CH_2Cl_2/BuLi$ in 1:2 molar ratio at −110°C, $(Me_3Si)_2CCl_2$ (**5**), the key starting material for the present work, may be conveniently obtained in 50% yield (eq. 1).

$$CH_2Cl_2 \xrightarrow[2Me_3SiCl]{2BuLi} \underset{(\mathbf{5})}{(Me_3Si)_2CCl_2} \xrightarrow[HMe_2SiCl]{BuLi} \underset{(\mathbf{6})}{(HMe_2Si)(Me_3Si)_2CCl} \qquad (1)$$

Metallation of **5** and reaction with HMe_2SiCl at −110°C yields typically **6** (79%), **5** (10%) and $(HMe_2Si)_2(Me_3Si)_2C$ (**7**) (8%). Good temperature control is essential. If the temperature is allowed to fluctuate, or if the reaction is conducted at −78°C, yields of **5** and **7** increase and **7** becomes the major product (60% yield), presumably as a result of lithium–halogen exchange (eq. 2).

$$(Me_3Si)_2CClLi + (HMe_2Si)(Me_3Si)_2CCl \longrightarrow$$

$$\underset{(\mathbf{5})}{(Me_3Si)_2CCl_2} + (HMe_2Si)(Me_3Si)_2CLi \qquad (2a)$$

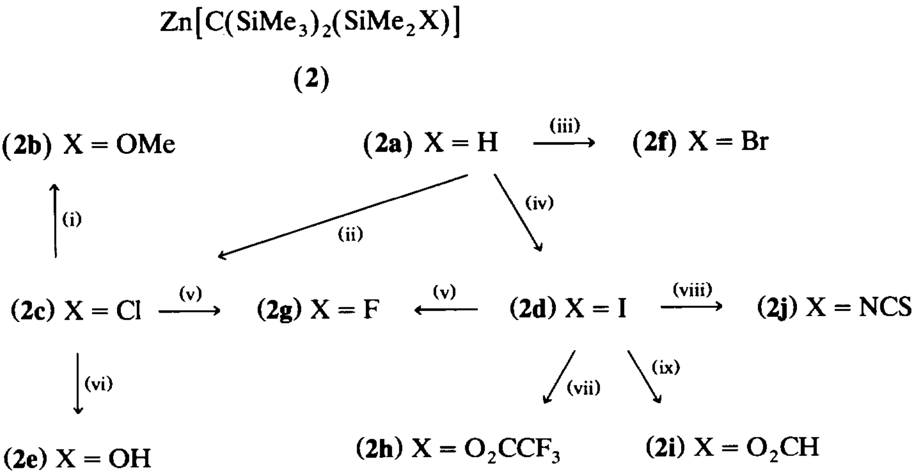
$$(HMe_2Si)(Me_3Si)_2CLi + HMe_2SiCl \longrightarrow \underset{(\mathbf{7})}{(HMe_2Si)_2(Me_3Si)_2C} \qquad (2b)$$

Attempts to separate **6** and **7** by recrystallization from methanol were unsuccessful; better results were obtained by careful fractional sublimation but samples of **6** were nearly always contaminated with traces of **7**. The amount of the latter could not be easily estimated by 90 MHz NMR spectroscopy because of overlapping peaks, but when the samples were treated with a few drops of a solution of Br_2 in CCl_4 the corresponding bromo-derivatives were formed and these gave well separated signals.

The compound $(PhMe_2Si)(Me_3Si)_2CCl$ (**8**) was also made from **5** by a metallation-alkylation sequence at −110°C. In this case, there was no evidence for formation of $(PhMe_2Si)_2(Me_3Si)_2C$ by reactions similar to those observed for $BuLi/HMe_2SiCl$ mixtures.

$$\underset{(\mathbf{5})}{(Me_3Si)_2CCl_2} \xrightarrow[\text{(ii) } PhMe_2SiCl]{\text{(i) } BuLi} \underset{(\mathbf{8})}{(PhMe_2Si)(Me_3Si)_2CCl} \qquad (3)$$

The silane **6** is an extremely useful starting material: metallation with BuLi followed by treatment with $ZnBr_2$ gives the dihydride $Zn[C(SiMe_3)_2(SiMe_2H)]_2$ (**2a**) in *ca.* 80% yield. This, like **1**, is stable towards air and moisture and is recovered unchanged when a solution in THF/H_2O is stirred for 20 h at 20°C. Crucially, the lack of reactivity at zinc allows a wide range of high yield reactions to be developed at the silicon centre. These reactions (see Scheme 1) are remarkable by the standards of organometallic chemistry since Zn–C bonds are normally cleaved by powerful electrophiles such as CF_3CO_2H, HCO_2H, water, or the hydrogen halides formed by reaction of Si–H bonds with halogens or interhalogens. The inertness of the ZnC_2 skeleton in the dialkyls **2** is without doubt a consequence of the protection afforded by the triply-substituted methyl groups,



Scheme 1. (i) MeOH; (ii) ICl (2.5 mol); (iii) Br_2/CCl_4; (iv) I_2/CCl_4; (v) $AgBF_4$; (vi) H_2O/THF; (vii) AG_2O/CF_3CO_2H; (viii) AgNCS; (ix) Ag_2CO_3/HCO_2H.

which is apparent from the results of the X-ray structural studies of **1** [2], **2b**, **2e** [4], and **2h** (see below).

In contrast, reactions at the Si–X bonds of the zinc alkyls are rapid compared with those in silanes bearing the $(Me_3Si)_3C$ or related ligands. Thus the iodo derivative **2d** is converted into the hydroxy compound **2e** or the methoxy derivative **2b** by a few minutes' treatment with water or methanol whereas methanolyses of $(Me_3Si)_3CSiMe_2I$ or $(Me_2PhSi)_3CSiMe_2I$ have half-lives of 12 days and 21 h, respectively at 50°C [7]. It can reasonably be assumed that the differences in reaction rates at the Si–X bonds in $XMe_2Si{-}C(SiMe_2Y)_3$ and $XMe_2Si{-}C(SiMe_2Y)_2ZnC(SiMe_2Y)_3$ are due very predominantly to steric rather than electronic effects, the $ZnC(SiMe_2Y)_3$ substituent at carbon shielding the adjacent silicon less than a $SiMe_2Y$ substituent alone.

The hydroxy compound **2e** is remarkably stable both chemically and thermally. It decomposes only above 235°C. When a solution in toluene was subjected to prolonged boiling in an attempt to remove water by azeotropic distillation and perhaps form a cyclic compound **9**, only unchanged **2e** was recovered. Likewise, no reaction was observed with Me_3SiCl, but Me_2SiCl_2 reacted to give a compound tentatively formulated as $[(ClMe_2SiOSiMe_2)(Me_3Si)_2C]_2Zn$ (**2k**); with water, this gave an oil that had an NMR spectrum consistent with its being a mixture of cyclic siloxanes, such as **10**, but the species present have not been fully characterized. Nevertheless, the results indicate that it should be possible to develop this chemistry to make linear or cyclic polysiloxanes incorporating stable Si–C–Zn–C–Si linkages. Compound **2e** reacted with CH_3COCl to give the acetato compound **2l**, which was characterized by ^1H NMR and IR spectroscopy (ν(CO) 1717 cm^{-1}) but not isolated pure.

The organolithium derivative made by metallation of **6** reacted with $CdCl_2$ at −85°C to give the cadmium dialkyl **4a**. This, like the zinc analogue **2a** was remarkably stable thermally; decomposition was apparent only above *ca.* 175°C. The Cd–C bond was, however, considerably more susceptible to attack by halogens than the Zn–C bond of **2a**. With Br_2 in CCl_4, **4a** gave an immediate precipitate of

$CdBr_2$, and analysis by GLC and NMR spectroscopy showed formation of $(BrMe_2Si)(Me_3Si)_2CH$ (**11**) and $(BrMe_2Si)(Me_3Si)_2CBr$ (**12**). With an excess of Br_2/CCl_4 only **12** was formed. Similarly, **4a** also gave a precipitate with ICl and the NMR spectra of the reaction mixture suggested that Cd–C bonds had been cleaved. It was thus not possible to use **4a** to make a wide range of new cadmium alkyls by reactions analogous to those in Scheme 1. It was necessary first to assemble the relevant ligands as halides and then convert these into cadmium alkyls by lithiation and reaction with cadmium halides at −85°C (eq. 4)

$$(XMe_2Si)(Me_3Si)_2CCl \xrightarrow[\text{(ii) CdCl}_2]{\text{(i) BuLi}} \underset{(\mathbf{4})}{Cd[C(SiMe_3)_2(SiMe_2X)]_2} \qquad (4)$$

$X = H, OMe, Ph$

The methoxy and phenyl compounds **4b** and **4c** were made in this way. The methoxy derivative **4b** melted without decomposition at 220°C but reacted with Br_2/CCl_4 to give a white precipitate and a soluble product tentatively identified as $(Me_3Si)_2C(Br)(SiMe_2OMe)$. The phenyl-substituted compound **4c** was also decomposed by electrophilic reagents. For example, with one molar equivalent of ICl (0.01 *M* in CCl_4), a precipitate formed immediately and the ^1H NMR spectrum of the solution suggested that Cd–C bonds were broken. Reaction with Br_2 in CCl_4 gave similar results. It was found some years ago that even $Cd[C(SiMe_3)_3]_2$, in contrast to the zinc analogue **1**, was attacked by ICl, but the products were incompletely characterized [8].

The ^{113}Cd NMR signals for $Cd[C(SiMe_3)_2(SiMe_2X)]_2$ are at lower frequency than that for $CdMe_2$: chemical shifts are as follows: for $X = H$, −170; $X = Me$, −175; $X = Ph$, −206; $X = OMe$, −226 ppm.

In order to explore more fully the reasons for the differences between the reactivities of the closely related zinc and cadmium alkyls, we decided to determine the X-ray structures of a cadmium compound and chose the methoxy-substituted derivative **4b**, since the structures of the corresponding zinc and mercury compounds had already been determined [4]. The crystal packing of the cadmium compound resembles that of the mercury derivative: both compounds have the same space group and similar cell dimensions. The molecules lie on inversion centres, so that the C–M–C skeleton (M = Cd or Hg) is linear. In both compounds the silicon atoms are disordered between alternative sites, as found for many compounds containing the $(Me_3Si)_3C$ ligand [9], including $Zn[C(SiMe_3)_3]_2$ (**1**) [2], and so the molecular parameters (Table 5) have large estimated standard deviations. Considerable caution is therefore necessary in drawing detailed conclusions, *e.g.* the long Si–O and Si–Me bonds in **4b** may be crystallographic artefacts. However, it seems that the molecular conformation of the cadmium compound **4b** (Fig. 1) is more like that of the zinc than that of the mercury analogue, in that the lone pairs of the methoxy oxygens of the OMe groups point towards the metal, rather than outwards as in $Hg[C(SiMe_3)_2(SiMe_2OMe)]_2$. The $Cd \cdots O$ distance (3.09 Å) is only slightly less than the sum of the van der Waals radii (3.10 Å). In **2b**, the $Zn \cdots O$ distance (2.932(4) Å) is also close to the sum of the van der Waals radii (2.90 Å). Evidence for internal coordination, as suggested for $Zn[(CH_2)_3X]_2$ with $X = OMe$, SMe, NMe_2 [10], and found in $\{Li[C(SiMe_2OMe)_3]\}_2$ and related compounds [1], is therefore weak in **2b** and **4b**, and the solid state structures may well be determined mainly by steric factors.

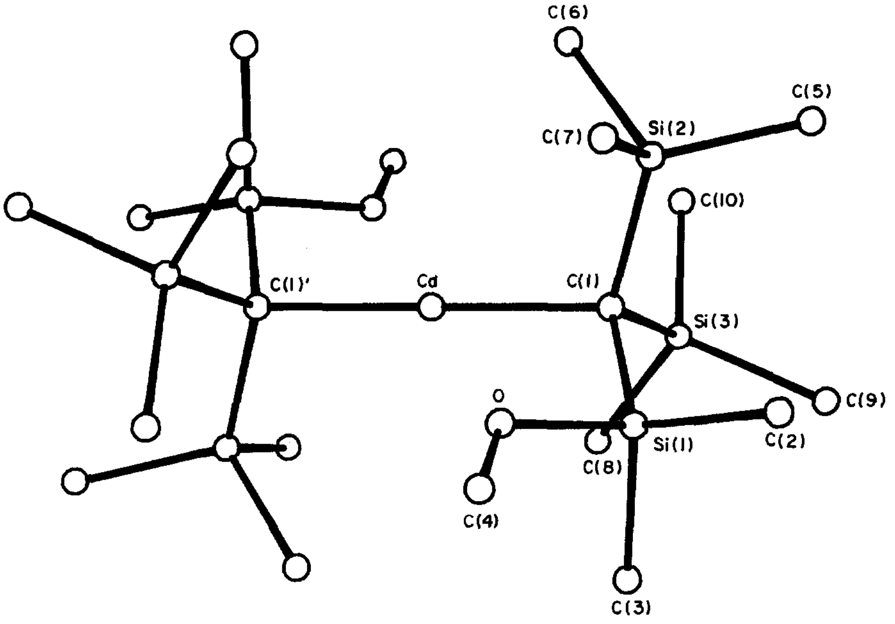


Fig. 1. Molecular structure of **4b**.

It occurred to us that a change of structure might be induced by replacement of the methoxy by a carboxylate substituent, since interaction between the central metal atom and the carbonyl oxygen would involve a five- rather than a more strained four-membered ring. We were unable to obtain suitable crystals of the acetato derivative **2k**. The formato compound **2c** gave good crystals, but the structure could not be solved because of crystallographic disorder. Of the carboxylate compounds so far isolated, only the trifluoroacetato derivative could be obtained in a form suitable for a structural study. The structure determined by X-ray diffraction shows that molecules lie at inversion centres, so the C–Zn–C chain is linear (Fig. 2). However, the Si_3C groups make internal coordination impossible and the bulky CF_3CO_2 groups are forced to lie out towards the ends of the molecule to minimize strain. Table 6 shows that data for **1**, **2b**, **2e**, and **2h** are remarkably consistent. In zinc derivatives there is little difference between bond lengths from silicon to the central carbon and those to the peripheral methyl groups. In **2b** and **2e** the bond lengths and angles at the silicon bearing the oxygen substituent are not significantly different from those in the rest of the molecule. This is not the case in **2h**. The Si(3)–C bond lengths, 1.838(2), 1.847(5) and 1.865(5) Å, are all short, and the Si–O bond (1.726(3) Å) is long (Si–O bonds are usually about 1.62 Å [12]). The flattening of the SiC_3 system (sum of angles 340°) from the tetrahedral is consistent with a strongly polarized Si–O bond. Similar, long Si-$OCOCF_3$ distances (1.719(4) and 1.713(3) in two independent molecules) are found in $(Me_3Si)_3CSi(OH)_2(O_2CCF_3)$ [13]. The distance between the carbonyl oxygen O(2) and the silicon atom Si(3) to which the CF_3CO_2 group is attached is 3.099(3) Å, well below the sum (3.60 Å) of the relevant van der Waals radii. A

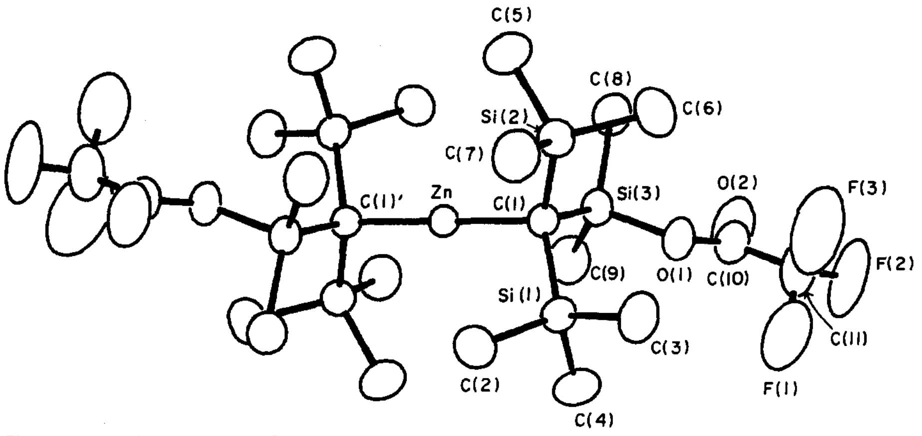


Fig. 2. Molecular structure of **2h**.

mean value of 3.025 Å for the corresponding distance in the diol $(Me_3Si)_3CSi(OH)_2(O_2CCF_3)$ was considered to indicate weak O ··· Si interaction.

A very interesting finding from the present work is that of the marked difference between the chemistry of the zinc and cadmium derivatives. Substitution at silicon in the zinc compounds can be effected without attack at the metal, but not in the case of the cadmium analogues. The protection of the central metal–carbon bonds by the surrounding alkyl ligands is thus very sensitive to the metal–carbon bond distance. Table 6 shows that Zn–C distances in silyl-substituted derivatives of dimethylzinc (1.96–1.98 Å) are slightly larger than those in $ZnMe_2$, $ZnEt_2$, or $ZnPr_2$, *viz.* 1.93–1.95 Å [14,15], the terminal bonds in dimeric $ZnPh_2$ (1.946(5) Å) [16] or in compounds in which only one alkyl group is bound to each zinc. In the silyl-substituted derivatives of dimethylcadmium, **4b** and **4d** [17], the Cd–C distances are 2.16–2.17 Å, again significantly longer than the distance (2.11(4) Å) in $CdMe_2$ [15]. Thus the distance between the two sets of protecting methyl groups on either side of the central atom (C(2), C(5), and C(9) in Fig. 2 and the symmetry-related set) is *ca.* 0.3 Å greater in the cadmium than in the zinc analogue. In the light of the reactions observed, it seems that this must be sufficient to allow electrophiles to approach the cadmium atom, even though they cannot attack the zinc atom. The compounds $M[C(SiMe_3)_2(SiMe_2X)]_2$ with M = Zn, for which M–C < 2.0 Å, seem to be protected from attack at the metal; the

Table 6

Mean bond lengths (Å) and angles (°)

	1 [a]	**2b** [b]	**2e** [b]	**2h** [c]
Zn–C	1.982(2)	1.980(4)	1.968(2)	1.974(3)
Si–O		1.674(3)	1.660(2)	1.726(3)
C–Si	1.890(3)	1.864(4)	1.881(1)	1.883(4)
Si–Me	1.885(3)	1.868(6)	1.866(7)	1.868(4)
Me–Si–Me	106.7(2)	105.9(3)	105.8(12)	106.5(2)
Si–C–Si	111.1(1)	112.6(2)	112.5(2)	111.7(2)

[a] Ref. 2. [b] Ref. 4. [c] This work.

Cd, Mn, and Mg compounds (M–C 2.10–2.17 Å) are not. It would be interesting to have further examples, perhaps involving other metals, to see whether this observation can be generalized.

Acknowledgement

We thank the S.E.R.C. for financial support and for the award of a research studentship (to A.H.) and the Ministry of Higher Education of Saudi Arabia for a postgraduate scholarship (to S.S. Al-J.).

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