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PREPARATION AND SOME REACTIONS OF THE COMPOUNDS $HgVsi_2$, $CdVsi_2$, AND Hg(Vsi)Br [Vsi = $(Me_3Si)_2(CH_2{=}CHMe_2Si)C$]. CRYSTAL STRUCTURE OF $CdVsi_2$

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Summary

Treatment of MBr_2 (M = Hg or Cd) with a 2 molar proportion of VsiLi [Vsi = $(Me_3Si)_2(CH_2{=}CHMe_2Si)C$] gave $MVsi_2$. Use of a 1 molar proportion of VsiLi in the reaction with $HgBr_2$ gave VsiHgBr. The $MVsi_2$ compounds are stable towards HCl in Et_2O, boiling MeCOCl containing a little LiBr, or MBr_2 in boiling THF, and $CdVsi_2$ is also stable towards MeOH in PhMe under reflux. $HgVsi_2$ reacts with CF_3CO_2H at 60°C to give $Hg[C(SiMe_3)_2(SiMe_2O_2CCF_3)]_2$.

An X-ray diffraction study has shown that $CdVsi_2$ has a linear structure very similar to those of $Hg[C(SiMe_3)_3]_2$ and $Mn[C(SiMe_3)_3)]_2$.

Introduction

The compounds $MTsi_2$ (Tsi = $(Me_3Si)_3C$; M = Zn, Cd, or Hg) have been shown to be remarkably thermally stable (decomposing only at ca. 300°C, ca. 15°C above their melting points) and chemically resistant [1,2]. (The mercury compound is, however, readily decomposed by UV light [3].) We describe here the preparation and some properties of the related compounds $MVsi_2$ (Vsi = $(Me_3Si)_2(CH_2{=}CHMe_2Si)C$ with M = Hg and Cd, and of VsiHgBr.

Results and discussion

The reaction of $HgBr_2$ with a 2 molar proportion of VsiLi (made from VsiCl at low temperature) in THF/Et_2O/pentane (THF = tetrahydrofuran) gave $HgVsi_2$ (though only in 20% isolated yield). When a one molar proportion of VsiLi was used the isolated product was VsiHgBr; an attempt to determine its structure by X-ray diffraction was frustrated by considerable disorder in the crystal. Reaction of $CdBr_2$ with a 2 molar proportion of VsiLi gave $CdVsi_2$, the crystal structure of which was determined.

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Both HgVsi$_2$ and CdVsi$_2$ apparently undergo some decomposition at their melting points of 155 and 160°C, respectively, since the samples go black. The reasons for this marked difference in stability between the MTsi$_2$ and MVsi$_2$ species merit investigation.

Both of the MVsi$_2$ compounds were recovered unchanged after (i) passage of HCl for 1 h through the refluxing solutions in Et$_2$O and subsequent refluxing of the solutions for 1 h, (ii) boiling for 24 h with MeCOCl containing a catalytic amount of LiBr, and (iii) boiling with the corresponding MBr$_2$ in THF for 5 (M = Hg) or 10 h (M = Cd). No reaction took place when a solution of CdVsi$_2$ in 8/2 v/v PhMe/MeOH was kept at 60°C for 3 d, or when a solution of VsiHgBr in 1 *M* NaOMe/MeOH was kept at room temperature for 24 h or one in 20/1 v/v THF/H$_2$O was refluxed for 24 h.

Cleavage of the Si–vinyl bonds took place when a solution of HgVsi$_2$ in CF$_3$CO$_2$H was kept at 60°C; ca. 65% of the HgVsi$_2$ had disappeared after 4 h, and after 14 h work-up gave exclusively Hg[C(SiMe$_3$)$_2$(SiMe$_2$O$_2$CCF$_3$)]$_2$; the rate of cleavage of the Si–vinyl bonds appears to be rather similar to that for TsiSiMe$_2$CH=CH$_2$ [4]. The exclusive cleavage of the Si–vinyl bonds demonstrates the remarkable resistance to attack of the C–Hg bonds in this type of compound.

The crystal structure of CdVsi$_2$

The molecular structure of CdVsi$_2$ is shown in Fig. 1, and details of bond lengths

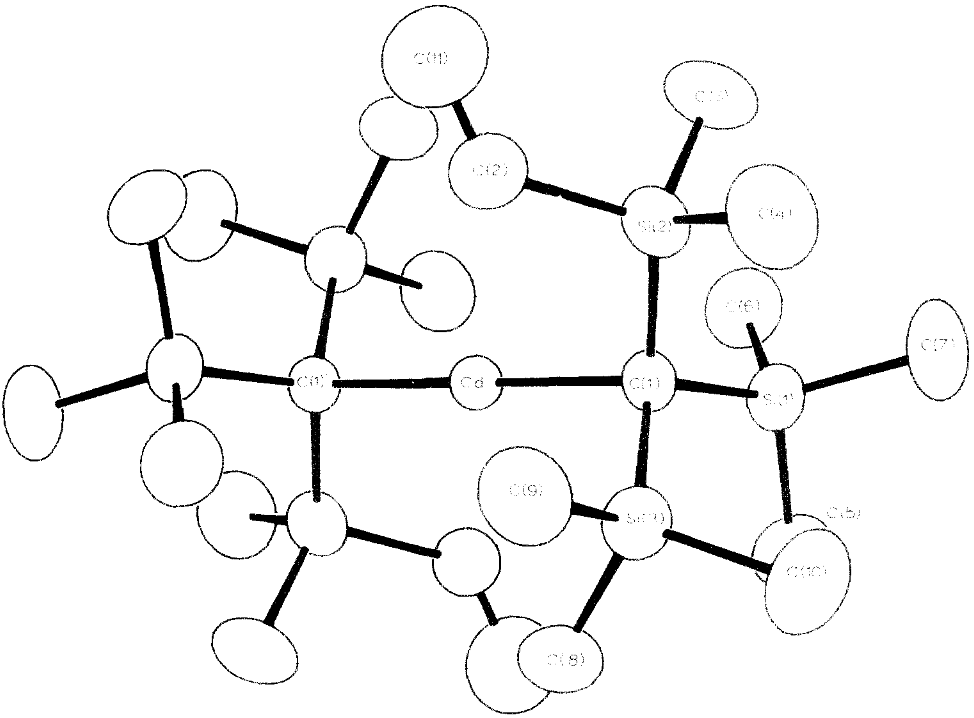

Fig. 1. An ORTEP drawing showing the molecular structure and atom numbering. The atoms are shown as 50% thermal vibrational ellipsoids.

TABLE 1

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) (with estimated standard deviations in parentheses)

Cd–C(1)	2.172(3)	Si(1)–C(1)	1.881(3)
Si(1)–C(5)	1.864(6)	Si(1)–C(6)	1.865(6)
Si(1)–C(7)	1.879(5)	Si(2)–C(1)	1.869(4)
Si(2)–C(2)	1.854(5)	Si(2)–C(3)	1.873(6)
Si(2)–C(4)	1.869(6)	Si(3)–C(1)	1.884(4)
Si(3)–C(8)	1.876(6)	Si(3)–C(9)	1.873(5)
Si(3)–C(10)	1.879(6)	C(2)–C(11)	1.311(10)
C(1)–Si(1)–C(5)	113.3(2)	C(1)–Si(1)–C(6)	112.5(2)
C(1)–Si(1)–C(7)	112.8(2)	C(5)–Si(1)–C(6)	104.9(3)
C(5)–Si(1)–C(7)	105.7(2)	C(6)–Si(1)–C(7)	107.0(2)
C(1)–Si(2)–C(2)	110.8(2)	C(1)–Si(2)–C(3)	113.4(2)
C(1)–Si(2)–C(4)	112.8(3)	C(2)–Si(2)–C(3)	106.1(3)
C(2)–Si(2)–C(4)	106.3(2)	C(3)–Si(2)–C(4)	106.8(3)
C(1)–Si(3)–C(8)	111.8(2)	C(1)–Si(3)–C(9)	113.2(2)
C(1)–Si(3)–C(10)	113.1(2)	C(8)–Si(3)–C(9)	104.6(2)
C(8)–Si(3)–C(10)	106.9(3)	C(9)–Si(3)–C(10)	106.7(3)
Cd–C(1)–Si(1)	107.0(2)	Cd–C(1)–Si(2)	106.2(2)
Cd–C(1)–Si(3)	104.2(2)	Si(1)–C(1)–Si(2)	112.6(2)
Si(1)–C(1)–Si(3)	113.0(2)	Si(2)–C(1)–Si(3)	113.1(2)
Si(2)–C(2)–C(11)	125.0(5)		

and angles appear in Table 1. This represents the second determination of the solid-state structure of a simple diorganocadmium compound; in the first such structurally characterized species, $[\overline{\mathrm{Cd\{NC_5H_4C}}\mathrm{(SiMe_3)_2\text{-}2\}_2}]$, however, there may be a weak interaction between Cd and N [5], as in the 4-coordinate Cd complex $[\mathrm{Cd(bipy)(CH_2SiMe_3)_2}] \cdot 0.5 \sim$ bipy (bipy = 2,2′-bipyridyl) studied earlier [6]. Dimethylcadmium is known from Raman spectral studies to be linear in the vapour phase [7].

The two Vsi groups lie across an inversion centre, so that the coordination at Cd is strictly linear, and the two Vsi groups are fully staggered about the C–Cd–C direction. The Cd–C(1) distance, viz. 2.172(3) Å, is significantly longer than the Cd–C distance, 2.112(44) Å, derived spectroscopically for gaseous $\mathrm{CdMe_2}$ [7], possibly a little longer than the mean Cd–C distance in the four-coordinate species $[\mathrm{Cd(bipy)(CH_2SiMe_3)_2}] \cdot 0.5$bipy, viz. 2.14(6) [6] and significantly shorter than that in $[\overline{\mathrm{Cd\{NC_5H_5C}}\mathrm{(SiMe_3)_2\text{-}2\}_2}]$, viz. 2.27 Å [5]. The structure is closely similar to those of $\mathrm{HgTsi_2}$ [1] and $\mathrm{MnTsi_2}$ [8], as can be seen by comparing the corresponding structural parameters listed in Table 2. The distance between the planes C(2), C(6), C(8) and C(2′), C(6′), and C(8′) is ca. 3.2 Å, and so, as noted for $\mathrm{Mn(Tsi)_2}$ (in which the corresponding distance is ca. 3.0 Å [8]), the two Vsi groups must interlock, effectively filling the space around the metal atom. The structure is also similar overall to those of the linear anions $[\mathrm{MTsi_2}]^-$, where M = Li [9], Cu [10] or Ag [11], but there is one seemingly significant difference in detail, namely that the central $\mathrm{Me_3Si}$–C bonds in the anions are apparently substantially shorter than the peripheral Si–Me bonds, (e.g. in $[\mathrm{AgTsi_2}]^-$ the mean distances are 1.83(3) and 1.90(4) Å, respectively), whereas in $\mathrm{CdVsi_2}$ and $\mathrm{MTsi_2}$ with M = Hg and Mn the two sets of bonds have similar lengths within the uncertainty limits. In contrast, in

TABLE 2

MEAN BOND LENGTHS (Å) AND ANGLES (°) IN $CdVsi_2$, $HgTsi_2$, AND $MnTsi_2$

Parameter [a]	$CdVsi_2$	$HgTsi_2$	$MnTsi_2$
M–C	2.172(3)	2.142(4)	2.102(4)
C–$SiMe_2R$	1.878(8)	1.887(4)	1.881(8)
Si–Me	1.872(6)	1.871(3)	1.883(9)
Si–C–Si	112.9(3)	112.5(21)	112.3(2)
Me–Si–R	106.1(9)	106.0(12)	105.6(17)
M–C–Si	105.8(14)	106.2(5)	106.5(8)
C(M)–Si–R	112.9(5)	112.7(6)	113.1(16)

[a] M denotes the central metal; R = Me or $CH{=}CH_2$.

compounds such as $TsiSiMe_2Ph$ [12], and $TsiBPh_2$ [13], in which the presence of a fourth bulky ligand on the central carbon increases the congestion, the C–$SiMe_3$ bonds are longer than the Si–Me bonds; in $TsiSiMe_2Ph$ the respective mean distances are 1.915(9) and 1.876(15), and in $TsiBPh_2$ they are 1.934(3) and 1.873(6) Å.

In $CdVsi_2$ the strain within the Vsi groups is relieved mainly by opening of the Si–C–Si angles (mean 112.6(8)°) and closing of the Me–Si–R (R = Me or $CH{=}CH_2$) angles (mean 106.1(9)°).

Experimental

Spectra

The ^1H and ^{19}F NMR spectra of isolated compounds refer to solutions in CCl_4, (δ(F) shifts are relative to external $CFCl_3$ in $CDCl_3$), and IR spectra to KBr discs, unless otherwise indicated. Mass spectra (electron impact) were recorded at 70 eV.

Preparation

(a) A solution of VsiLi was made by treatment of VsiCl (2.0 g, 7.2 mmol) in a mixture of THF (60 cm^3) and Et_2O (8 cm^3) at −100°C with n-BuLi (8.0 mmol) in pentane (5 cm^3) [4], and was then added dropwise to a stirred mixture of $CdBr_2$ (0.96 g, 3.5 mmol) and THF (2 cm^3) cooled in a bath at −80°C. The mixture was then allowed to warm to room temperature and the solvents were evaporated off under vacuum. The residue was extracted with pentane, and the extract was filtered and evaporated to leave a solid, which was recrystallized from MeOH to give $CdVsi_2$ (0.77 g, 18% based on VsiCl taken), m.p. 160°C (with darkening); δ(H) 0.14 (36H, s, $SiMe_3$), 0.21 (12H, s, $SiMe_2$), 5.5–6.5 (6H, m, $CH{=}CH_2$); ν(C=C) 1585, ν(Cd–C) 525, 400, 345 cm^{-1}; *m/z* 600 (5%, ($[M]^+$), 585 (35, $[M-Me]^+$), 551 (30), 357 (90, $[M-Vsi]^+$), 243 (100, $[Vsi]^+$), 213 (85), 169 (85), 155 (80), 141 (20), 129 (30), 85 (40, $[SiMe_2CH{=}CH_2]^+$), 73 (Found: C, 43.9, H, 8.4. $C_{22}H_{54}CdSi_6$ calc: C, 44.0; H, 9.0%).

(b) The procedure described under (a) but with $HgBr_2$ in place of $CdBr_2$ gave $HgVsi_2$ (20%), m.p. 155°C (with darkening); δ(H) 0.21 (36H, s, $SiMe_3$), 0.27 (12H, s, $SiMe_2$), and 5.4–6.6 (6H, m, $CH{=}CH_2$); ν(C=C) 1585 cm^{-1}, ν(Hg–C) 525, 395, 345 cm^{-1}; *m/z* 673 (40%, $[M-Me]^+$), 661 (5, $[M-CH{=}CH_2]^+$), 243 (100), 228 (50), 213 (100), 202 (80, $[Hg]^+$), 185 (20), 169 (100), 155 (95), 129 (40), 73 (Found: C, 37.8; H, 7.9. $C_{22}H_{54}HgSi_6$ calc: C, 38.4; H, 7.85%).

(c) A solution of VsiLi was prepared by treatment of VsiCl (1.20 g, 4.30 mmol) in THF (40 cm^3) and Et_2O (5 cm^3) at $-100\,°C$ with n-BuLi (4.8 mmol), then added dropwise to a stirred solution of $HgBr_2$ (1.73 g, 4.8 mmol) in THF (20 cm^3) cooled in a bath at $-80\,°C$. The mixture was allowed to warm to room temperature during 5 h, and the solvents were removed under vacuum. The residue was extracted with pentane, and the extract was evaporated to leave VsiHgBr (0.57 g, 25%), m.p. 100°C; δ(H) 0.14 (18H, s, $SiMe_3$), 0.21 (6H, s, $SiMe_2$), and 5.5–6.55 (3H, m, $CH{=}CH_2$); ν(C=C) 1585, ν(Hg–C) 520; ν(Hg–Br) 310 cm^{-1}; m/z 526 (5%, $[M]^+$), 511 (50, $[M-Me]^+$), 497 (10, $[M-CH{=}CH_2]^+$), 355 (20), 333 (20), 313 (20), 229 (10), 213 (10), 175 (13), 155 (162), 141 (25), 129 (10), 85 (40), 73 (100). (Found: C, 25.3; 5.8. $C_{11}H_{27}BrHgSi_3$ calc: C, 25.1; H, 5.7%).

Reactions

(a) A mixture of $CdVsi_2$ (0.05 g), MeOH (2 cm^3), and toluene (8 cm^3) was stirred at 60°C for 3 d. The solvents were taken off under reduced pressure to leave unchanged $CdVsi_2$.

(b) A solution of $MVsi_2$ (M = Cd or Hg) (0.05 g) in MeCOCl (10 cm^3) containing a catalytic amount of LiBr was refluxed for 24 h. Evaporation under reduced pressure left a residue which was extracted with heptane. Filtration and evaporation of the extract left unchanged $MVsi_2$.

(c) A solution of $MVsi_2$ (M = Cd or Hg) (0.08 mmol) and MBr_2 (0.08 mmol) in THF (10 cm^3) was refluxed for 10 h then added to hexane. The organic layer was separated, washed, dried ($MgSO_4$), and evaporated to leave exclusively unchanged $MVsi_2$.

(d) Hydrogen chloride was bubbled for 1 h through a solution of $MVsi_2$ (0.1 mmol) in Et_2O at room temperature and the mixture then refluxed for 1 h. Evaporation followed by extraction of the residue with heptane and filtration and evaporation of the extract left only unchanged $MVsi_2$.

(1) Trifluoroacetic acid (0.5 cm^3) was added to a solution of $HgVsi_2$ (0.14 mg, 0.02 mmol) in a drop (ca. 0.02 cm^3) of CCl_4 in an NMR tube. The tube was capped then kept at 60°C. The ^1H NMR spectrum of the solution indicated that reaction was ca. 65% complete after 4 h and > 95% after 14 h. The solvent was evaporated under reduced pressure to leave a solid (0.10 mg, 55%), m.p. 85°C, which was judged to be $Hg[C(SiMe_3)_2(SiMe_2O_2CCF_3)]_2$; δ(H) 0.28 (36H, s, $SiMe_3$) and 0.59 (12H, s, $SiMe_3$); δ(F) -70.9 ppm; ν(C=O) 1765 cm^{-1}; m/z 844 (85%, $[M-MeH]^+$), 746 (30, $[M-CF_3CO_2H]^+$), 329 (10, $[Me_3Si)_2(CF_3CO_2Me_2Si)C]^+$), 314 (100, $[(Me_3Si)_2(CF_3CO_2Me_2Si)C-Me]^+$).

Crystal structure of $CdVsi_2$

A crystal, ca. 0.28 × 0.23 × 0.28 mm, obtained by recrystallization from heptane, was used.

Crystal data. $C_{22}H_{54}CdSi_6$, M 559.6, monoclinic, a 9.151(1), b 17.730(4), c 10.548(2) Å, β 103.57(1)°, U 1663.5 $Å^3$, Z 2, D_c 1.12 g cm^{-3}, $F(000)$ 636. Monochromated Mo-K_α radiation, λ 7.1069 Å, μ 8.74 cm^{-1}. Space group $P2_1/n$.

Data were obtained with an Enraf–Nonius CAD4 diffractometer. Preliminary cell dimensions were found by use of the SEARCH and INDEX routines of the CAD4, and final values calculated from the setting angle for 25 reflections with $\theta = 13°$. Intensities for $hk \pm l$ reflections, with $2 < \theta < 25°$ were measured by a

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) (with estimated standard deviations in parentheses)

Atom	x	y	z
Cd	0	0	0
Si(1)	2441(1)	345(1)	2732(1)
Si(2)	1935(1)	1544(1)	508(1)
Si(3)	−583(1)	1256(1)	2012(1)
C(1)	1035(4)	847(2)	1416(3)
C(2)	761(6)	1697(3)	−1160(5)
C(3)	3826(5)	1238(5)	303(6)
C(4)	2195(7)	2492(3)	1308(6)
C(5)	1561(6)	−185(3)	3887(5)
C(6)	3544(6)	−376(3)	2066(5)
C(7)	3832(6)	1004(3)	3770(5)
C(8)	−1952(5)	509(3)	2238(5)
C(9)	−1738(5)	1941(3)	838(5)
C(10)	29(7)	1763(4)	3613(5)
C(11)	1258(8)	1691(5)	2229(7)

$\theta/2\theta$ scan with scan width $\Delta\theta = (0.8 + 0.35\tan\theta)^\circ$. The scan rate was determined by a rapid prescan at 10 min^{-1}, and any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were rescanned at such a speed as to give a minimum value of $\sigma(I)I$ of 0.05 subject to a maximum scan time of 60 s. Two standard reflections were monitored hourly but showed no significant variation. Data were corrected for Lp effects but not for absorption, and after averaging of equivalent reflections 2278 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

The structure was solved by routine heavy atom methods. Refinement was by full matrix least squares with Cd, Si, and C atoms anisotropic. Hydrogen atoms were located on a difference map, and included in the refinement with a common isotropic temperature factor. The terminal hydrogen atoms of the vinyl group did not refine successfully, and were fixed at their original positions with $B = 4.0$ Å^2. Refinement converged at $R = 0.032$, $R' = 0.042$ when the maximum shift/error was 0.9 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless.

The structure solution and refinement were carried out on a PDP11/34 computer using the Enraf–Nonius Structure Determination Package. Scattering factors for the neutral atoms were taken from ref. 14. The atom coordinates are listed in Table 3, and lists of temperature factors, hydrogen atom positions, and final structure factors are available from the authors.

References

1 F. Glockling, N.S. Hosmane, V.B. Mahale, J.J. Swindall, L. Magos, and T.J. King, J. Chem. Res., (1977) (S) 116, (M) 1201.

2 C. Eaborn, N. Retta, and J.D. Smith, J. Organomet. Chem., 190 (1980) 101.

3 A.R. Bassindale, A.J. Bowles, M.A. Cook, C. Eaborn, A. Hudson, R.A. Jackson, and A.E. Jukes, J. Chem. Soc., Chem. Commun., (1970) 559.

4 G.A. Ayoko and C. Eaborn, J. Chem. Soc., Perkin Trans. 2, in press

5 M.J. Henderson, R.I. Papasergio, C.L. Raston, A.H. White, and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1986) 672.
6 G.W. Bushnell and S.R. Stobart, Canad. J. Chem., 58 (1980) 574.
7 K.S. Rao, B.P. Stoicheff, and R. Turner, Canad. J. Phys., 38 (1960) 1516.
8 N.H. Buttrus, C. Eaborn, P.B. Hitchcock, J.D. Smith, and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1985) 1380.
9 C. Eaborn, P.B. Hitchcock, J.D. Smith, and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1983) 827.
10 C. Eaborn, P.B. Hitchcock, J.D. Smith, and A.C. Sullivan, J. Organomet. Chem., 263 (1984) C23.
11 C. Eaborn, P.B. Hitchcock, J.D. Smith, and A.C. Sullivan, J. Chem. Soc., Chem. Commun., (1984) 870.
12 C. Eaborn, P.B. Hitchcock, and P.D. Lickiss, J. Organomet. Chem., 221 (1981) 13; P.B. Hitchcock, ibid., 228 (1982) C83.
13 C. Eaborn, M.N. El-Kheli, P.B. Hitchcock, and J.D. Smith, J. Organomet. Chem., 272 (1984) 1.
14 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.