O_2CCF_3 addition). With $PhHgO_2CCH_3$, first the complex $PtMe_2(O_2CCH_3)(HgO_2CCH_3)(bpy)$ formed according to eq 8. Subsequent phenylation of the platinum compound by

$$PtMe_2(bpy) + 2HgPhO_2CCH_3 \rightarrow PtMe_2(O_2CCH_3)(HgO_2CCH_3)(bpy) + HgPh_2 \quad (8)$$

$HgPh_2$ resulted in a partial formation of $PtMe_2Ph(O_2CCH_3)(bpy)$ and mercury. With MeHgCl the reaction proceeded similarly as with $MeHgO_2CCF_3$ although small amounts of other products were formed besides $PtMe_3Cl(bpy)$.

Analogous reactions were performed with $PtMe_2(Ph_2Me_2phen)$ and MeHgCl, $MeHgO_2CCF_3$, $PhHgO_2CCF_3$, and $PhHgO_2CCH_3$. In all cases unidentifable intermediate compounds were formed; however, surprisingly in all cases the formation of Me_2Hg was observed, which did not react further.

In conclusion it can be said that the mechanism of the methyl or phenyl transfer still remains uncertain; however, most likely a Pt(IV) intermediate is always involved in this process.

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Registry No. $PtMe_3(O_2CCF_3)(bpy)$, 65915-46-0; $PtMe_2(O_2CCH_3)(HgO_2CCH_3)(bpy)$, 65915-45-9; $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$, 65915-44-8; $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$, 65915-43-7; $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4$, 65915-42-6; $PtMe_2Cl(HgCl)(Ph_2Me_2phen)$, 65915-41-5; $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$, 65915-40-4; $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$, 65956-96-9; *trans*-$PtMe_2Ph(O_2CCF_3)(bpy)$, 66007-12-3; *cis*-$PtMe_2Ph(O_2CCF_3)(bpy)$, 65915-55-1; $PtMe_2(O_2CCH_3)(HgO_2CCH_3)(Ph_2Me_2phen)$, 65915-54-0; $PtMe_2Br(HgBr)(Ph_2Me_2phen)$, 65915-53-9; $PtMe_2I(HgI)(Ph_2Me_2phen)$, 65915-52-8; Ph_2Hg, 587-85-9; Me_2Hg, 593-74-8; $MeHgO_2CCF_3$, 21502-74-9; $PhHgO_2CCF_3$, 332-11-6; PhHgCl, 100-56-1; MeHgCl, 115-09-3; AgO_2CCF_3, 2966-50-9; $Hg(O_2CCF_3)_2$, 13257-51-7; $Hg(O_2CCH_3)_2$, 1600-27-7; $PtMe_2(bpy)$, 52594-52-2; $HgCl_2$, 7487-94-7; $PtMe_2(Ph_2Me_2phen)$, 63133-64-2; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; $PtMe_3I(bpy)$, 38194-05-7; $PhHgO_2CCH_3$, 62-38-4; $PtMe_2Ph(O_2CCH_3)(bpy)$, 65915-51-7.

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Aspects of Organocadmium Chemistry. 1. Bis[(trimethylsilyl)methyl]cadmium and Relationship with Homoleptic Zinc and Mercury Compounds

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Bis[(trimethylsilyl)methyl]cadmium (I) has been synthesized by reaction of anhydrous CdI_2 with Me_3SiCH_2MgCl in diethyl ether. It exhibits high thermal stability but reacts immediately with oxygen to give peroxo derivatives and with water yielding $Cd(OH)_2$ and $SiMe_4$. A yellow 1:1 complex, II, is formed with 1,10-phenanthroline, while with 2,2′-bipyridyl a yellow, volatile adduct, III, is isolated the composition of which has been shown by elemental analysis and x-ray crystallography to be $[Cd(bpy)(CH_2SiMe_3)_2]\cdot 0.5bpy$. Reaction between Zn powder and $Hg(CH_2SiMe_3)_2$ gives the zinc analogue of I quantitatively. IR, Raman, and mass spectra for I have been measured and assigned, and ^1H and ^{13}C NMR data for I and its zinc and mercury analogues are reported and compared.

Kinetic stabilization of alkylmetal compounds by incorporation of either the trimethylsilylmethyl group (Me_3SiCH_2-) or one of several closely related ligands continues to attract very active interest.[1-3] Although first reported as long ago as 1961 by Seyferth and Freyer,[4] it was not until recently that bis[(trimethylsilyl)methyl]mercury was shown to possess enhanced thermal and photochemical stability over simple mercury dialkyls.[5] The subsequent synthesis of the corresponding zinc compound and investigation of its utility as an alkylating agent by Moorhouse and Wilkinson[6] has led us to undertake the preparation of the cadmium analogue, thereby completing a family of homoleptic alkyls for the group 2 metals. Formation of $Cd(CH_2SiMe_3)_2$ and comparison of its spectroscopic and chemical properties with those of the zinc and mercury analogues form the substance of the present paper.

Experimental Section

Elemental microanalyses were performed by the Schwarzkopf Laboratory, Woodside, N.Y. IR spectra were recorded using a Beckman IR20 instrument, mass spectra with a Perkin-Elmer Hitachi RMU 7E unit, and NMR measurements with Perkin-Elmer R12 or R32 (^1H, at 60.0 or 90.0 MHz, respectively) and Nicolet TT-14 Fourier transform (^{13}C, at 15.09 MHz) spectrometers. The Raman spectrum of $Cd(CH_2SiMe_3)_2$ was obtained on a Spex Ramalog 4

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instrument through kind cooperation of the Department of Chemistry, University of British Columbia.

By analogy with other cadmium alkyls, $Cd(CH_2SiMe_3)_2$ was assumed to be very toxic, and rigorous precautions were adopted for handling of the compound and its derivatives and for disposal of unwanted material. Diethyl ether was distilled from $LiAlH_4$ under an atmosphere of dry dinitrogen gas immediately before use. Solid reagents were dried where necessary by prolonged pumping (48 h, 10^{-4} mmHg). [(Trimethylsilyl)methyl]magnesium chloride was synthesized by the Grignard procedure.[1-4]

(a) Synthesis of Compounds: Bis[(trimethylsilyl)methyl]cadmium. To a solution of Me_3SiCH_2MgCl (100 mmol) in dry diethyl ether (75 cm^3) was added dry CdI_2 (16.5 g, 45 mmol) during 4 h with constant stirring. Reaction was evidenced by slow disappearance of CdI_2 which is insoluble in ether. Further stirring for 16 h at 25 °C was followed by removal of ether under vacuum; prolonged pumping at ambient temperature (72 h, 10^{-4} mmHg) into a trap held at −196 °C followed by refractionation afforded pure *product* (ca. 7 g, 24 mmol, 53%), condensed as a colorless, air-sensitive liquid in a trap held at 0 °C. Anal. Calcd for $C_8H_{22}CdSi_2$: C, 33.48; H, 7.73. Found: C, 33.23; H, 7.60.

Bis[(trimethylsilyl)methyl]mercury. This compound was prepared as described earlier[5] and its purity checked by IR and ^1H NMR measurements.

Reaction of Bis[(trimethylsilyl)methyl]mercury with Zinc. Excess powdered zinc and $Hg(CH_2SiMe_3)_2$ (ca. 0.5 g) were sealed in a glass breakseal and heated at 45 °C for 15 h. After a further 11 days at ambient temperature, volatile material was transferred directly to an NMR tube, diluted with an equal volume of $CDCl_3$, and subsequently identified by ^1H NMR spectroscopy[6] as bis[(trimethylsilyl)methyl]zinc, formed in quantitative yield.

(b) Reactions of Bis[(trimethylsilyl)methyl]cadmium. Thermal Decomposition. The dialkyl (ca. 0.5 g, 1.75 mmol) was sealed in an evacuated breakseal. Heating at 140 °C for 6 h resulted in extensive deposition of a fine gray deposit. After a further 30 days at 25 °C the tube was opened yielding a small pressure of noncondensable material, tetramethylsilane (ca. 1 mmol) and a much less volatile liquid shown by mass spectroscopy to be mainly unchanged $Cd(CH_2SiMe_3)_2$ (ca. 1.2 mmol) containing traces of material showing ions at higher mass with m/e 360–370.

Oxidation. A stream of dry air was drawn through a solution of the dialkyl (0.67 g, 2.35 mmol) in dry benzene (ca. 4 cm^3). A white precipitate formed immediately. Removal of volatiles left a white solid (0.72 g), 105 °C dec. Anal. Found: C, 18.6; H, 4.2.

Hydrolysis. Treatment of the dialkyl (ca. 2 mmol) with degassed H_2O afforded $Cd(OH)_2$ and $Si(CH_3)_4$, identified by IR spectroscopy. Repetition using D_2O gave $Cd(OD)_2$ and $Si(CH_3)_3CH_2D$ (IR).

With 2,2′-Bipyridyl. To the dialkyl (1.12 g, 3.91 mmol) was added 2,2′-bipyridyl (0.61 g, 3.88 mmol) in dry benzene (10 cm^3). The solution became bright yellow immediately; removal of volatiles after 60 min left the air-sensitive, yellow *adduct* (1.08 g), purified by sublimation in vacuo. Anal. Calcd for $C_8H_{22}CdSi_2{\cdot}1.5C_{10}H_8N_2$: C, 52.98; H, 6.53; N, 8.06. Found: C, 52.51; H, 6.53; N, 7.95. Careful resublimation at 30 °C (10^{-4} mmHg) afforded beautiful, lemon yellow crystals, mp 42–43 °C.

With 1,10-Phenanthroline. Anhydrous 1,10-phenanthroline (0.46 g, 2.54 mmol) in dry benzene (10 cm^3) was added to the dialkyl (0.67 g, 2.55 mmol) resulting in an immediate orange-yellow coloration. Removal of solvent left a bright yellow, air-sensitive solid (1.12 g); sublimation at 70 °C in vacuo gave the crystalline yellow *adduct*, 110 °C dec. Anal. Calcd. for $C_8H_{22}CdSi_2{\cdot}C_{12}H_8N_2$: C, 51.41; H, 6.47; N, 6.00. Found: C, 51.29; H, 6.78; N, 6.04.

Reaction of Bis[(trimethylsilyl)methyl]mercury with 1,10-Phenanthroline. In dry tetrahydrofuran (15 cm^3), $Hg(CH_2SiMe_3)_2$ (0.44 g, 1.16 mmol) and 1,10-phenanthroline (0.21 g, 1.15 mmol) were refluxed for 24 h under a stream of dry dinitrogen gas. A slight yellow color was observed which did not intensify in a further 24 h; after removal of volatiles, a white solid remained (0.205 g), identified (IR) as unreacted base, and unchanged mercurial was isolated virtually quantitatively.

Results and Discussion

Reaction between solid cadmium iodide and an ether solution of [(trimethyl)silylmethyl]magnesium chloride (eq 1) followed by removal of solvent afforded a soft, translucent gelatinous residue. Prolonged evacuation was required to

$$2Me_3SiCH_2MgCl + CdI_2 \xrightarrow[25\,°C]{Et_2O} Cd(CH_2SiMe_3)_2 \qquad (1)$$

collect the product in approximately 53% yield, suggesting a relatively strong interaction with diethyl ether.

Bis[(trimethylsilyl)methyl]cadmium(I) is a colorless liquid, just volatile at 25 °C (10^{-4} mmHg) which decomposes very rapidly but does not inflame in air. It is thermally relatively stable, being recovered in about 70% yield after 9 h at 140 °C. Decomposition products under these conditions were methane, $SiMe_4$, and probably $Me_3SiCH_2CdCH_2SiMe_2(CH_2)_2SiMe_3$, the mercury analogue of which was identified earlier.[5] Rapid oxidation of cadmium dialkyls is a general reaction (2) giving mono- and diperoxide compounds.[7] With

$$CdR_2 \xrightarrow{O_2} RCdOOR \xrightarrow{O_2} Cd(OOR)_2 \qquad (2)$$

dry dioxygen immediate precipitation of a white solid from I was observed, the IR spectrum of which resembled that of I but contained a strong absorption at 1600 cm^{-1} and a weaker band in the 800–900-cm^{-1} range. Plausible assignments for these features would be ν(C–O) and ν(O–O) of peroxo complexes but the relatively low carbon content suggests contamination by CdO. Hydrolysis using oxygen-free water was very rapid giving $SiMe_4$ and $Cd(OH)_2$ as the only products and deuteriolysis confirmed the direct fracture of metal carbon bonds as in eq 3.

$$Cd(CH_2SiMe_3)_2 + 2D_2O \rightarrow Cd(OD)_2 + 2SiMe_3(CH_2D) \qquad (3)$$

Changes in the Lewis acid character of the dialkyls of the group 2 metals and the factors on which they may depend have been discussed by Coates et al.[8] Relative behavior is typified by the interaction of bipyridyl with the dimethyl derivatives: $ZnMe_2$ forms a stable yellow complex [$ZnMe_2{\cdot}$bpy], $CdMe_2$ forms a yellow compound with a high dissociation pressure at ambient temperature, while with $HgMe_2$ no reaction occurs. Instant formation of a bright yellow coloration was observed on addition of either 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bpy) to a solution of I in dry benzene, removal of which left yellow microcrystalline products. By contrast, we have obtained no evidence for complex formation between the mercury analogue of I and phen even after 48 h although before removal of solvent a faint yellow color was detected, consistent with a very weak acid–base interaction.

Unlike the adducts of bis[(trimethylsilyl)methyl]zinc with phen and bpy which are stable in air for several days,[6] those formed with I rapidly lose their color although decomposition is slower than that of the uncomplexed dialkyl. Conversely, the latter reacts in air less vigorously than its zinc relative which[6] ignites spontaneously resembling other volatile ZnR_2 compounds. These observations support the view that while the MR_2 species become more stable to oxidation on coordination, the cadmium compounds form weaker complexes with higher dissociation constants facilitating oxidative decomposition via reaction of free alkyl. However, by contrast with the unstable adducts described previously[9] in the absence of air the new complexes exhibit high thermal stability; they may be purified by sublimation in vacuo and undergo no detectable decomposition during many months in a dry nitrogen atmosphere or when sealed in evacuated ampules.

Proton NMR data for the complexes with phen, II, and bpy, III, are compared in Table I with those for I, and show an upfield displacement in the methylene resonance accompanying complexation as was observed for the zinc analogues.[6] While the reaction of I with phen affords a 1:1 adduct (II, [$Cd(C_{12}H_8N_2)(CH_2SiMe_3)_2$]) as was found with the zinc compound,[6] with bpy a different situation was encountered. Elemental analysis was consistent with a formulation $Cd(CH_2SiMe_3)_2{\cdot}1.5$bpy for III; the novel stoichiometry and the curiously volatile character of the complex (sublimes even at

Table I. ^{1}H NMR Data ($CDCl_3$ Solution) for Adducts with bpy[a] and phen

Compound	$\tau(CH_2)$	$\tau(CH_3)$
CdR_2	10.38	9.98
$[CdR_2 \cdot 1.5bpy]$[b]	10.52	10.00
$[CdR_2 \cdot phen]$	10.60	10.02

[a] bpy = 2,2'-bipyridyl; phen = 1,10-phenanthroline; R = CH_2SiMe_3. [b] For structure see text; no distinction resolved in low-field region between bound and uncoordinated bpy.

ambient temperature, more readily than bpy itself) invited structural characterization by crystallographic methods. Pale yellow translucent crystals belonging to the monoclinic space group $P2_1/c$ were obtained by sublimation in vacuo. Data collection was difficult owing to the volatility of the complex and instability to x rays; currently $R = 0.14$ for 1230 independent reflections. The structure consists of (a) molecular $[Cd(bpy)(CH_2SiMe_3)_2]$ units with highly distorted tetrahedral geometry and (b) uncoordinated bipyridyl molecules, one per two cadmium-containing units, located at a crystallographic center of symmetry and well away from the metal atoms. Two significant features emerge concerning coordination at cadmium: first, the two alkyl groups are separated by a very wide angle of 160°, with Cd–C distances in the expected range (mean 2.11 Å); second, the two Cd–N bonds are long (2.53, 2.55 Å) making an angle of only 65° at the metal atom. These data are consistent with a relatively weak interaction with the base and a structure derived from a linear C–Cd–C configuration in the free dialkyl.

To provide comparative ^{13}C NMR data for the homoleptic alkyls $M(CH_2SiMe_3)_2$ samples of the zinc and mercury analogues of I were required. The mercury compound was isolated as reported before,[5] but the inconvenience associated with its pyrophoric nature led us to seek an alternative route to the zinc derivative. Reaction between $Hg(CH_2SiMe_3)_2$ and Zn powder at ambient temperature was conducted in an evacuated, all-glass apparatus and afforded the desired product in quantitiative yield (eq 4). In this respect bis[(tri-

$$Hg(CH_2SiMe_3)_2 + Zn \xrightarrow[11\ days]{25\ ^\circ C} Zn(CH_2SiMe_3)_2 + Hg \qquad (4)$$

methylsilyl)methyl]mercury resembles other mercury dialkyls and its reactivity as an alkylating agent may have been underestimated during the course of earlier work.[5]

Vibrational Spectrum. The infrared spectrum of liquid I closely resembles that of its mercury relative[5] in appearance. Observed wavenumbers and corresponding Raman data are listed in Table II.

The most prominent feature in the Raman effect is an intense shift at 485 cm^{-1}. This has no IR counterpart as demanded for an A_g vibration under the idealized C_{2h} symmetry associated with a linear R–Cd–R configuration and is identified as the symmetric Cd–C stretching mode. A medium intensity IR absorption at 520 cm^{-1} with no coincident Raman shift is assigned as the corresponding B_u component, ν_{asym}(Cd–C). Gutowsky[10] has reported ν_{sym}(Cd–C) and ν_{asym}(Cd–C), respectively, at 465, 538 cm^{-1} for dimethylcadmium. For $Hg(CH_2SiMe_3)_2$ the ν(Hg–C) vibrations were assigned[5] at 522 (A_g, Raman active) and 530 cm^{-1} (B_u, IR active) while for the zinc compound a Raman shift detected[6] at 508 cm^{-1} must be due to the A_g fundamental. Thus the latter shows a significant shift to lower energy in the order Hg > Zn > Cd, contrary to predictions based on the mass of the central metal atom and similar to the situation encountered for the analogous dimethyl compounds.[11] This is consistent with a substantially stronger M–C bond for M = Hg over M = Zn or Cd, a conclusion supported by mass spectral fragmentation data (see below), and paralleling the substantial decrease in chemical

Table II. Vibrational Spectrum (cm^{-1}) of Liquid $Cd(CH_2SiMe_3)_2$

IR	Raman	Approx descripn
2950 s	2958 m	ν_{asym}(CH)
2880 m	2898 vs	ν_{sym}(CH)
1405 w	1423 w, sh	
1360 w, br	1354 m	
	1320 vw	$\delta(CH_3) + \delta(CH_2)$
1260 s, sh		
1246 vs	1258, 1249 m	
1130 w		
1052 w		
932 s	933 s, br	$\delta(CH_2)$
848 vs, br	849 m	
825 vs	825 w	$\rho(CH_3)$
	753 vw	
748 s		
	723 vw	
712 s		ν_{asym}(SiC)
680 s	688 m	
602 w	607 vs	
572 m		ν_{sym}(SiC)
520 m		ν_{asym}(CdC)
	485 vs	ν_{sym}(CdC)
	269, 209 m	
	164 m	skeletal deformn

Table III. Mass Spectrum of $Cd(CH_2SiMe_3)_2$ (70 eV)

m/e[a]	% ion current	Formula or probable structure
288	1.8	$(Me_3SiCH_2)_2Cd^{\cdot +}$
273	6.2	$Me_3SiCH_2CdCH_2SiMe_2^+$
216	<0.1	$Me_3SiCH_2CdMe^{\cdot +}$
201	2.5	$Me_3SiCH_2Cd^+$
187	<0.1	Me_3SiCd^+
186	<0.1	$Me_2SiCH_2Cd^{\cdot +}$
171	1.1	$MeSiCH_2Cd^+$
145	1.7	$C_6H_{17}Si_2^+$
131	6.1	$C_5H_{15}Si_2^+$
129	4.1	$C_5H_{13}Si_2^+$
115	1.7	$C_4H_{11}Si_2^+$
114	0.3	$Cd^{\cdot +}$
87	6.1	$C_4H_{11}Si^+$
86	0.5	$C_4H_{10}Si^{\cdot +}$
85	5.2	$C_4H_9Si^+$
73	15.2	Me_3Si^+
72	8.9	$Me_2SiCH_2^{\cdot +}$
59	13.1	Me_2SiH^+
58	5.4	$C_2H_6Si^{\cdot +}$
57	2.1	$C_2H_5Si^+$
45	2.5	CH_5Si^+
44	5.0	$CH_4Si^{\cdot +}$
43	5.4	CH_3Si^+
31	2.3	H_3Si^+
29	1.1	HSi^+

[a] For ^{114}Cd and ^{28}Si.

reactivity (particularly in relation to Lewis acidity) of MR_2 observed between M = Zn or Cd and M = Hg. For MMe_2 (M = Zn, Cd, or Hg), while the *mean* bond dissociation energy $\bar{D}$(M–Me) decreases as M = Zn > Cd > Hg, it has long been known[17] that D_1, the energy required to initiate disruption by the fracture of the first M–C bond, changes in the order Hg > Zn > Cd, in precise agreement with the above discussion.

The IR spectra for the adducts II and III were also recorded but were very complicated owing to absorptions arising from vibrations of the ligands phen or bpy. In particular the latter precluded detection of IR activity for both Cd–C stretching modes as would result on distortion of the centrosymmetric (C_{2h}) structure of I.

Mass Spectrum. Abundances of ion fragments in the mass spectrum of I are listed in Table III. Peaks due to cadmium-containing ions were immediately recognizable due to the

Table IV. NMR Data for $M(CH_2SiMe_3)_2$ (M = Zn, Cd, or Hg)

Compound	Chemical shift δ, ppm[a]			
	$\mathit{C}H_2$	$\mathit{C}H_3$	CH_2	CH_3
$Zn(CH_2SiMe_3)_2$	−0.69[b]	−0.02[b]	3.61	3.10
$Cd(CH_2SiMe_3)_2$[c]	−0.38	0.02	7.53	3.45
$Hg(CH_2SiMe_3)_2$[c]	0.16[d]	0.10[d]	28.13	2.60

[a] From internal Me_4Si, downfield measured positive, 10% v/v (^1H) or 50% v/v solution (^{13}C) in $CDCl_3$. [b] Data from ref 6. [c] Coupling constants (Hz): $^2J_{av}$(Cd–H), 65 (^{111}Cd, ^{113}Cd components not resolved); $^2J(^{199}Hg–H)$, 130.4; $^1J(^{111}Cd–^{13}C)$, 402; $^1J(^{113}Cd–^{13}C)$, 420; $^1J(^{199}Hg–^{13}C)$, 546. [d] Data from ref 5.

polyisotopic nature of the metal. For $Hg(CH_2SiMe_3)_2$ about 50% of the ion current was carried by mercury-containing fragments,[5] and the most important ion could be identified as $Me_3SiCH_2HgCH_2SiMe_2^+$. By contrast, for I only about 10% of the summed ion abundances arises from cadmium-containing fragments although of these latter that due to loss of methyl remains the most prominent. These observations indicate that the Hg–C bond in $Hg(CH_2SiMe_3)_2$ is of similar strength to the Si–C bond while the Cd–C bond in I is considerably weaker, substantiating the interpretation of the vibrational data for ν(M–C) (M = Zn, Cd, or Hg).

NMR Parameters. The ^1H NMR spectrum of compound I consisted of two singlets at τ 9.98 and 10.38, in the ratio 9:2 and attributable to methyl and methylene protons, respectively. Spin coupling with cadmium nuclei having $I = {}^1/_2$ was observed giving rise to "satellites" around the CH_2 resonance but was incompletely resolved, ^{111}Cd (12.75% natural abundance) and ^{113}Cd (12.26%) components not being distinguishable. The average coupling constant of 65 ± 3 Hz compares with $^2J(^{111}Cd–H)$ = 47 Hz and $^2J(^{113}Cd–H)$ = 49 Hz in dimethylcadmium,[12] satellite broadening being tentatively ascribed to intermolecular exchange.[5] A similar increase in coupling constant occurs in the related mercury compounds, where replacement of methyl[13] by the trimethylsilylmethyl group[5] results in alteration of $^2J(^{199}Hg–H)$ from 104 to 128 Hz.

To extend the comparison made possible between the ^1H NMR data for I and its zinc[6] and mercury[5] analogues, ^{13}C NMR spectra have been obtained for all three compounds. Results are presented in Table IV. Due to its proximity to the central metal atom, the chemical shifts for the nuclei of the methylene group are much more sensitive to the nature of the metal than are those of the more remote methyl substituents. A paramagnetic shift in $\delta(\mathit{C}H_2)$ is observed in the order of M = Zn > Cd > Hg while $\delta(\mathit{C}H_3)$ is altered only very slightly in the same sense. As expected changes in carbon frequencies are much more pronounced, and $\delta(\mathit{C}H_2)$ shifts downfield over a 25 ppm range between M = Zn and Hg. In both cases the trend is regular and follows the pattern predicted in terms of the Pauling electronegativities for the three metals which are[14] 1.65 (Zn), 1.69 (Cd), and 2.00 (Hg).

Coupling between the methylene ^{13}C spin and metal nuclei having $I = {}^1/_2$ was also resolved for the cadmium and mercury dialkyls. For the former, $^1J(^{111}Cd–^{13}C)$ = 402 Hz with $^1J(^{113}Cd–^{13}C)$ = 420 Hz (Table IV). The only available data with which to compare these values are from the work of Weigert,[15] who reported $^1J(^{111}Cd–^{13}C)$ = 512 Hz and $^1J(^{113}Cd–^{13}C)$ = 537 Hz for $CdMe_2$. A similar increase in $^1J(^{199}Hg–^{13}C)$ occurs between $Hg(CH_2SiMe_3)_2$ (546 Hz, Table IV) and $HgMe_2$ for which a value of 689 Hz has been measured.[16]

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Registry No. I, 63835-91-6; II, 65982-71-0; III, 66008-61-5; $Hg(CH_2SiMe_3)_2$, 13294-23-0; $Zn(CH_2SiMe_3)_2$, 41924-26-9; Me_3SiCH_2MgCl, 13170-43-9; CdI_2, 7790-80-9.

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