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Contribution from the IBM Research Laboratory,
San Jose, California 95193

Dimethyl Compounds of Platinum. 3. Oxidative-Addition and Methyl-Transfer Reactions with Mercury Compounds

JAN KUYPER*

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Novel binuclear compounds $PtMe_2X(HgX)(N\text{-}N)$ (N-N = Ph_2Me_2phen, X = Cl, Br, I, O_2CCH_3, O_2CCF_3; N-N = bpy, X = O_2CCH_3, O_2CCF_3) were obtained by reaction of equimolar amounts of $PtMe_2(N\text{-}N)$ and HgX_2. The compounds were formed by cis oxidative addition of HgX_2 to platinum. Reaction of $Hg(O_2CCF_3)_2$ with $PtMe_2(N\text{-}N)$ in a ratio 1:2 resulted in the formation of trinuclear compounds $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$ and $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$. Reaction with $PtMe_2(bpy)$ in a ratio 1:4 afforded a pentanuclear compound $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4$ which had a metallic appearance. The formation of $MeHgO_2CCF_3$ by a methyl-transfer reaction from $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(N\text{-}N)$ to $Hg(O_2CCF_3)_2$ was evidenced by ^1H NMR. Reaction of $MeHgO_2CCF_3$ with $PtMe_2(N\text{-}N)$ first gave Me_2Hg which reacted further (N-N = bpy) to form $PtMe_3(O_2CCF_3)(bpy)$. Similar reactions were observed with MeHgCl, $PhHgO_2CCF_3$, and $PhHgO_2CCH_3$.

Introduction

Many reactions of divalent mercury compounds with d^8 transition metals have been reported[1–5] and it has been shown that these reactions proceed differently. Reaction of Vaska's compound $IrCl(CO)(PPh_3)_2$ with HgX_2 (X = Cl, Br, I, O_2CCH_3, O_2CCF_3)[1,2] proceeded via a trans oxidative addition and $IrClX(HgX)(CO)(PPh_3)_2$ was formed. Reactions of mercury–triazenido compounds with $MCl(CO)(PPh_3)_2$ (M = Rh, Ir) resulted either in oxidative addition with the formation of a bimetallic five-membered ring or in oxidative addition followed by elimination of mercury.[2] Reaction of mercuric halides with dihalide compounds of palladium(II) and platinum(II) resulted in the formation of compounds with halides bridging between the mercury and palladium or platinum atom.[3] Reaction of $HgCl_2$ and $Hg(O_2CCH_3)_2$ with $PtMe_2(PPhMe_2)_2$ resulted in methyl transfer from platinum to mercury,[4,5] whereas reaction of $Hg(O_2CR)_2$ (R = CH_3, CF_3) with $[PtMe_2(Et_2S)]_2$ afforded binuclear compounds of platinum(III).[5] Both reactions possibly involved the formation of an intermediate platinum–mercury bonded compound.

In two previous papers[6,7] reactions of $PtMe_2(N\text{-}N)$ (N-N = bipyridine, phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) with carbon, silicon, germanium, tin, and lead compounds have been reported. Trans oxidative addition involving the metal–halogen bond was observed in the case of the germanium, tin, and lead compounds, and the substituents on the metals had a large effect on the stabilities of the product. In this paper reactions of divalent mercury compounds with $PtMe_2(N\text{-}N)$ are reported and it is shown that oxidative addition and/or methyl transfer can occur, depending upon the starting materials and the reaction conditions.

In addition, our interest in highly conducting compounds with linear chains of platinum atoms such as $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$[15] led us to investigate the possibility of partial oxidation of $PtMe_2(bpy)$. The first indication, that "one-dimensional" compounds with methyl substituents on platinum can exist, is presented in this paper.

Experimental Section

General Information. All compounds prepared in this study were stable in air. ^1H NMR spectra were recorded on a Varian HA100 NMR spectrometer, and for solubility reasons CH_2Cl_2 (ppm relative to CH_2Cl_2) was used as a solvent. Decomposition points were recorded on a DTA apparatus, du Pont Model 900, and were checked visually. Elemental analyses were performed by Childers Laboratories, Milford, N.J., and Chemical Analytical Services, University of California, Berkeley, Calif., and are summarized in Table I.

Chemicals. Reagent grade solvents were distilled prior to use. The mercury compounds HgX_2 (X = Cl, Br, I, O_2CCH_3, O_2CCF_3), MeHgCl, and $PhHgO_2CCH_3$ were commercially available. $PtMe_2(bpy)$[6,8] and $PtMe_2(Ph_2Me_2phen)$[6] (bpy = 2,2′-bipyridine, Ph_2Me_2phen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) were prepared according to the literature procedures.

Preparation of $RHgO_2CCF_3$ (R = Me, Ph). RHgCl (5.00 mol) and AgO_2CCF_3 (5.00 mmol) were added to a mixture of 10 mL of benzene and 10 mL of dichloromethane. The mixture was refluxed with stirring for 10 min and AgCl was removed by filtration. Evaporation of the solvent under vacuum gave $RHgO_2CCF_3$ as a white solid in quantitative yield.

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* Address correspondence to the author at the Koninklyke Shell Laboratorium, Shell Research BV, Badhuisweg 3, Amsterdam, The Netherlands.

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Table I. Analytical Data

Compd	% C		% H		% N		% Pt	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$PtMe_3(O_2CCF_3)(bpy)$	35.37	35.45	3.36	3.22	5.50	5.30	38.30	38.0
$PtMe_2Ph(O_2CCF_3)(bpy)$	42.03	41.88	3.35	3.25	4.90	4.95	34.14	33.9
$PtMe_2(O_2CCH_3)(HgO_2CCH_3)(bpy)$	27.45	27.35	2.88	2.96	4.00	3.99	27.87	27.6
$PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$	23.78	23.80	1.75	1.90	3.47	3.40	24.17	23.7
$Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$	28.28	28.18	2.37	2.39	4.71	4.59	32.8	32.9
$Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4\cdot{}^1/_2CH_2Cl_2$	31.61	31.44	2.88	2.98	5.62	5.50	39.12	38.9
$Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4\cdot CH_2Cl_2$[a]	31.25	30.87	2.87	2.87	5.50	5.48	38.31	38.3
$PtMe_2Cl(HgCl)(Ph_2Me_2phen)$	39.23	39.43	3.06	3.06	3.27	3.19	22.76	22.3
$PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$	37.97	38.22	2.59	2.60	2.77	2.58	19.82	19.5
$Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$	45.09	45.18	3.28	3.38	3.50	3.30	24.42	24.7

[a] In three different preparations using a Pt:Hg ratio 6:1, 5:1, and 4:1, the analytical data of the products were equal within 0.20%; % Cl = 3.60 (3.48).

Preparation of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$. $Hg(O_2CCF_3)_2$ (0.55 mmol) was added to a stirred solution of $[PtMe_2(bpy)]$ (0.5 mmol) in CH_2Cl_2 (5 mL). After 5 min the resulting light yellow solution was filtered, and ether was added until the solution started to cloud (~5 mL). Yellow-orange crystals of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$ were obtained at −20 °C in nearly quantiative yield. Occasionally a small white initial fraction was obtained which had a slightly higher content of $Hg(O_2CCF_3)_2$ and decomposed slowly at room temperature. The compound $PtMe_2(O_2CCH_3)(HgO_2CCH_3)(bpy)$ was prepared in an analogous manner.

Preparation of $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4\cdot CH_2Cl_2$. $Hg(O_2CCF_3)_2$ (0.125 mmol) was added to a stirred solution of $PtMe_2(bpy)$ (0.5 mmol) in CH_2Cl_2 (20 mL). The solution immediately turned dark red and was filtered after 2 min. The filtrate was set aside at −20 °C for 3 days. Black-brown needles, one facet of which had a golden metallic appearance, were obtained in 75% yield. The same compound $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4\cdot CH_2Cl_2$ was obtained if less than 0.125 mmol of $Hg(O_2CCF_3)_2$ was used, although in lower yield. When the reaction was carried out with a platinum:mercury ratio of 6:1, occasionally golden-bronze leaflets of $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4\cdot{}^1/_2CH_2Cl_2$ were obtained. In all cases the amount of lattice CH_2Cl_2 was determined by ^1H NMR (in addition to elemental analysis). The compounds were almost insoluble in benzene or chloroform but dissolved slowly with prolonged stirring in CH_2Cl_2. The compound could be prepared equally well from 1 equiv of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$ and 3 equiv of $PtMe_2(bpy)$.

Preparation of $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$. $Hg(O_2CCF_3)_2$ (0.25 mmol) was added to a stirred solution of $PtMe_2(bpy)$ (0.5 mmol) in CH_2Cl_2 (10 mL)/hexane (10 mL). The orange solution was set aside at −20 °C and after 1 day the orange-yellow crystals of $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$ were collected on a filter. The yield was 85%. The compound was soluble in CH_2Cl_2 only upon prolonged stirring. It slowly turned yellow in air.

Reaction of $PtMe_2$(N-N) with $n[Hg(O_2CCF)_2]$. These reactions (N-N = bpy, Ph_2Me_2phen; n = 0–1) were studied with ^1H NMR and are described in section II of the Results and Discussion.

Preparation of $PtMe_2Cl(HgCl)(Ph_2Me_2phen)$. $HgCl_2$ (0.25 mmol) was added to a stirred solution of $PtMe_2(Ph_2Me_2phen)$[6] (0.25 mmol) in CH_2Cl_2 (3 mL). After 10 min hexane was added to the light yellow solution until it started to cloud. The mixture was rapidly filtered and set aside at −20 °C. The white precipitate of $PtMe_2Cl(HgCl)(Ph_2Me_2phen)$ was collected on a filter and vacuum-dried for 4 h. The yield was 80%. The compounds $PtMe_2Br(HgBr)(Ph_2Me_2phen)$ and $PtMe_2I(HgI)(Ph_2Me_2phen)$ were prepared in an analogous manner.

Preparation of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$. $Hg(O_2CCF_3)_2$ (0.25 mmol) was added to a stirred solution of $PtMe_2(Ph_2Me_2phen)$ (0.25 mmol) in CH_2Cl_2 (3 mL). After 2 min the solvent was removed under vacuum and the residue dissolved in ether (~10 mL). Light yellow crystals of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$ were obtained at −20 °C in 90% yield. The compound $PtMe_2(O_2CCH_3)(HgO_2CCH_3)(Ph_2Me_2phen)$ was prepared in an analogous manner.

Preparation of $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$. $Hg(O_2CCF_3)_2$ (0.125 mmol) was added to a stirred solution of $PtMe_2(Ph_2Me_2phen)$ (0.25 mmol) in CH_2Cl_2/ether (1:1 mixture, 5 mL). As soon as all $Hg(O_2CCF_3)_2$ had reacted (1–2 min), the solution turned yellow and a yellow precipitate of $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$ slowly formed. After 1 h at ambient temperature the mixture was set aside at 0 °C overnight. The precipitate was collected on a filter and washed with ether; yield 70%. The compound was only slightly soluble in CH_2Cl_2, benzene, or acetone at room temperature. However, it dissolved readily in boiling benzene or chloroform.

Preparation of $PtMe_3(O_2CCF_3)(bpy)$ from $PtMe_3I(bpy)$. AgO_2CCF_3 (0.25 mmol) was added to a stirred solution of $PtMe_3I(bpy)$[8] (0.25 mmol in CH_2Cl_2 (5 mL)/benzene (5 mL). After 1 h the precipitate of AgI was removed by filtration and the filtrate was set aside in air to evaporate. Light yellow crystals of $PtMe_3(O_2CCF_3)(bpy)$ were obtained in a quantitative yield.

Preparation of $PtMe_3(O_2CCF_3)(bpy)$ with $MeHgO_2CCF_3$. $MeHgO_2CCF_3$ (0.25 mmol) was added to a solution of $PtMe_2(bpy)$ (0.25 mmol) in CH_2Cl_2 (3 mL). After 2 days ether was added (5 mL) and a gray precipitate (mercury) was removed by filtration. Evaporation in air afforded light yellow crystals of $PtMe_3(O_2CCF_3)(bpy)$ which were washed with a few milliliters of ether. The yield was 85%.

Preparation of $PtMe_2Ph(O_2CCF_3)(bpy)$. $PhHgO_2CCF_3$ (0.25 mmol) was added to a solution of $PtMe_2(bpy)$ (0.25 mmol) in CH_2Cl_2 (3 mL). After 1 day ether (5 mL) was added and the gray precipitate of Hg was removed by filtration. Evaporation in air afforded light yellow crystals of $PtMe_2Ph(O_2CCF_3)(bpy)$ which were washed with a few milliliters of ether. The yield was 85%. According to ^1H NMR, the product consisted of a mixture of the cis and trans isomers.

Reaction of $PtMe_2(bpy)$ with $PhHgO_2CCH_3$. Addition of 2 equiv of $PhHgO_2CCH_3$ to a dichloromethane solution of $PtMe_2(bpy)$ resulted in a rapid color change to yellow, and according to ^1H NMR, the compounds $HgPh_2$ and $PtMe_2(O_2CCH_3)(HgO_2CCH_3)(bpy)$ were formed almost quantitatively. Further reaction took place and after 1–2 days all resonances of the platinum compound had disappeared. There was evidence for the formation of $PtMe_2Ph(O_2CCH_3)(bpy)$ (resonances at −3.82 (68 Hz) (Me), −4.72 (63 Hz) (Me), −3.20 (6 Hz) (O_2CCH_3), and 1.40 (Ph) ppm relative to CH_2Cl_2, ^{199}Pt–H couplings in parentheses). However other unidentified products were also present. With 1 equiv of $PhHgO_2CCH_3$, half of the $PtMe_2(bpy)$ reacted in this manner.

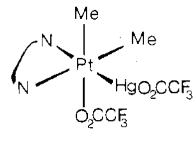
Reactions of $PtMe_2$(N-N) with RHgX (R = Me, X = Cl, O_2CCF_3; R = Ph, X = O_2CCF_3, O_2CCH_3). These reactions were studied with ^1H NMR and are described in section III of the Results and Discussion.

Results and Discussion

I. Compounds of Formula $PtMe_2X(HgX)$(N-N). Reaction of $PtMe_2$(N-N) with HgX_2 (N-N = bpy, X = O_2CCH_3, O_2CCF_3; N-N = Ph_2Me_2phen, X = Cl, Br, I, O_2CCH_3, O_2CCF_3) gave novel platinum–mercury compounds of formula $PtMe_2X(HgX)$(N-N) according to eq 1. These compounds

$$PtMe_2(\text{N-N}) + HgX_2 \rightarrow PtMe_2X(HgX)(\text{N-N}) \qquad (1)$$

are the first reported compounds of four-valent platinum, bonded to mercury and according to ^1H NMR were formed in quantitative yield (in CH_2Cl_2 solution). The strong tendency of $PtMe_2$(N-N) compounds to undergo oxidative addition reactions with post-transition metals was shown previously with germanium, tin, and lead compounds.[6,7] The ^1H NMR data of the platinum–mercury compounds are given in Table II,



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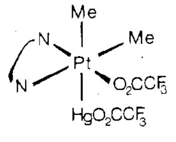

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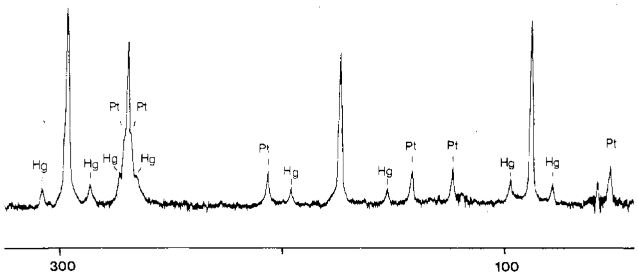

Figure 1. Proposed structures for $PtMe_2X(HgX)(N\text{-}N)$ (X = Cl, Br, I, O_2CCF_3, O_2CCH_3; N-N = bpy, Ph_2Me_2phen) and the ^1H NMR methyl region of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$.

and the following conclusions can be drawn from these data: The methyl groups of $PMe_2X(HgX)(N\text{-}N)$ have become inequivalent but remain bonded to platinum, as shown by their values of the $^2J(^{195}Pt\text{-}H)$ coupling constants of 62 to 72 Hz. The presence of a platinum–mercury bond was evidenced by the $J(^{199}Hg\text{-}H)$ coupling with both methyl groups bonded to platinum (Figure 1). Furthermore, one of the acetato groups in $PtMe_2(O_2CCH_3)(HgO_2CCH_3)(N\text{-}N)$ has a $^4J(^{195}Pt\text{-}H)$ coupling of 3 Hz, indicating that this acetato group is bonded to platinum. From these data it is concluded that the reaction of $PtMe_2(N\text{-}N)$ with HgX_2 resulted in a cis oxidative addition of HgX_2 to platinum, which is in contrast with the trans oxidative addition observed with germanium, tin, and lead compounds to formula MR_nCl_{4-n} (R = Me, Ph; n = 0, 1, 2, 3).[6,7]

Depending upon the mode of the cis addition, two structures are in principle possible for the platinum–mercury compounds and these are given in Figure 1. For several reasons structure I in which the mercury atom is in the plane of the bpy or Ph_2Me_2phen ligand is the most likely one. Comparison of the $^3J(^{199}Hg\text{-}H)$ coupling constants of the two platinum methyls shows that they differ by a factor of about 2–2.5. This difference is much smaller than the differences found for the $J(^{199}Hg\text{-}^{31}P)$ values of cis and trans PPh_3 groups (positions relative to the mercury atom) in the compounds $IrX(HgCl)(CO\text{-}DMT)(PPh_3)_2$[2] (X = Cl, I, O_2CCF_3). In this latter case the ratio is 7–10. This suggests that both methyl groups on platinum are cis bonded relative to the mercury atom (structure I). Also the methyl group above the N-N plane, which has the high-field resonance,[7] has the lowest $^3J(^{199}Hg\text{-}H)$ value. Since trans coupling most likely is larger than a cis coupling, this is against structure II. Furthermore, it has been reported that silicon and tin bonded to platinum give rise to a strong trans effect.[9,10] It is anticipated that the mercury atom will also exhibit such a strong trans effect and for structure II (Figure 1) this would mean a drastic lowering of the $J(^{195}Pt\text{-}H)$ coupling constant[11] with the trans methyl group, which is not observed. Since only structure I is consistent with the above, this structure is proposed for the platinum–mercury compounds.

The cis oxidative addition of HgX_2 to $PtMe_2(N\text{-}N)$ is also different from the observed trans oxidative addition of HgX_2 to $IrCl(CO)(PPh_3)_2$ (X = Cl, Br, I, O_2CCH_3, O_2CCF_3)[1,2] and $RhCl(CO)(PPh_3)_2$ (X = O_2CCH_3, O_2CCF_3),[2] which are also d^8 compounds. Other reactions of HgX_2 with dimethyl

Table II. ^1H NMR Data in CH_2Cl_2 (ppm relative to CH_2Cl_2)

Compd	Pt–Me[a]	HgR, Pt, RO_2CCH_3	bpy[b] or Ph_2Me_2phen[b]
Ph_2Hg		~1.95 m, 2.12 d (101 Hz)[i]	
Me_2Hg		−5.07 (102.5 Hz)[i]	
$MeHgO_2CCF_3$		−4.05 (227 Hz)[i]	
$PtMe_3(O_2CCF_3)(bpy)$	−4.09 (68 Hz), −4.87 (76.5 Hz)		3.67 (12 Hz); 2.35; 2.78; 2.93
trans-$PtMe_2Ph(O_2CCF_3)(bpy)$[c]	−3.77 (68 Hz)	1.42 (ortho: 56 Hz)[j]	3.82 (12 Hz); 2.39; 2.73; 2.81
cis-$PtMe_2Ph(O_2CCF_3)(bpy)$[c]	−3.86 (67 Hz), −4.49 (77 Hz)	1.82 mult	3.68 (13 Hz), 3.31 (13 Hz); 2.39, 2.19; . . ., ~2.94
$PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$	−3.78 (63 Hz, 26.5 Hz), −4.17 (75 Hz, 7.5 Hz)		4.27 (12 Hz), 3.49 (. . .); 2.52, 2.37; 2.86, 2.93; 3.03–3.05
$Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$	−~3.86 ($\nu_{1/2}$ ~22 Hz)		3.71 br,[d] 2.33 br; 2.82; 3.00
$Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4 \cdot CH_2Cl_2$	−4.18 ($\nu_{1/2}$ ~3.6 Hz)		3.58 br,[d] 2.17 br; ~2.78; ~2.78
$PtMe_2(O_2CCH_3)(HgO_2CCH_3)(bpy)$	−3.97 (63 Hz, 35 Hz), −4.49 (71 Hz, 17 Hz)	−3.38, −3.65 (3 Hz)[j]	4.29 (15 Hz), 3.46 (18 Hz); 2.43, 2.24; 2.82, 2.74; 3.11, 3.04
$PtMe_2(O_2CCH_3)(HgO_2CCH_3)(Ph_2Me_2phen)$	−3.59 (64 Hz, 52 Hz), −4.62 (67 Hz, 26 Hz)	−3.33, −3.46 (3 Hz)[j]	−2.08 (21 Hz),[i] −2.13 (3 Hz, ~5 Hz); 2.38, 2.35; 2.24 (Ph); 2.56[e]
$PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$	−3.39 (64 Hz, 41 Hz), −4.25 (70 Hz, 17.5 Hz)		−2.06 (22 Hz),[i] −2.13 (4 Hz, . . .); 2.44, 2.38; 2.24 (Ph); 2.59[e]
$PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$[f]	+1.74 (63.5 Hz, 43 Hz), +0.88 (70 Hz, 19 Hz)		2.59 (3 Hz, 8 Hz), 2.97 (21.5 Hz); 6.79 (6.5 Hz), 6.75 (7 Hz); not assigned
$Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$[f]	2.22 br, 1.37 br		3.03 br, 3.46 br; ~6.95; 7.16; 7.40
$PtMe_2Cl(HgCl)(Ph_2Me_2phen)$	−3.27 (66 Hz, 36 Hz), −4.57 (67 Hz, 15 Hz)		−1.95 (20 Hz),[i] −2.01 (3.5 Hz, 7 Hz); 2.43, 2.33; 2.25 (Ph); 2.61[e]
$PtMe_2Br(HgBr)(Ph_2Me_2phen)$[g]	−3.33 (65 Hz, 35 Hz), −4.46 (68 Hz, 15 Hz)		−2.00 (20 Hz),[i] −2.06 (. . .); 2.44, 2.36; 2.24 (Ph); 2.60
$PtMe_2I(HgI)(Ph_2Me_2phen)$[h]	−3.35 (64 Hz, . . .), −4.63 (66 Hz, . . .)		−2.03 br; 2.39 br; 2.23 (Ph); 2.58

[a] Coupling constants are given in parentheses: $^2J(^{195}Pt\text{-}H)$, $^3J(^{199}Hg\text{-}H)$. [b] The chemical shifts for the H, Me, and/or Ph protons are given in the sequence obtained when starting from the N atom. $J(^{195}Pt\text{-}H)$ or $J(^{195}Hg\text{-}H)$ in parentheses. [c] Cis and trans denote the mode of the Ph and O_2CCF_3 addition. [d] Chemical shift is concentration dependent; br = broadened. [e] A coupling, probably with ^{199}Hg, of ~4 Hz is observed. [f] In C_6D_6, ppm relative to Me_4Si. [g] −15 °C. [h] −40 °C; the resonances are somewhat broad. [i] $J(^{199}Hg\text{-}H)$. [j] $^4J(^{195}Pt\text{-}H)$.

compounds of platinum(II) have been reported and proceeded differently. With $PtMe_2(PPhMe_2)_2$ a methyl transfer from platinum to mercury was observed ($X = Cl, O_2CCH_3$)[4,5] leaving the platinum with an oxidation state 2. With $[PtMe_2(SEt_2)]_2$ an oxidation of platinum to the oxidation state 3 occurred and the binuclear compounds $Pt_2Me_4X_2(SEt_2)_2$ ($X = O_2CCH_3, O_2CCF_3$) were obtained.[5]

The ^1H NMR data of the Ph_2Me_2phen compounds showed a broadening of the resonances of $PtMe_2X(HgX)(Ph_2Me_2phen)$ ($X = Br, I$) at 30 °C and narrowing at lower temperatures. This indicates a dissociation according to eq 2. The rate of this dissociation is more rapid for X = I than for X = Br.

$$PtMe_2X(HgX)(Ph_2Me_2phen) \rightleftharpoons PtMe_2(Ph_2Me_2phen) + HgX_2 \qquad (2)$$

The $^4J(^{195}Pt\text{–}H)$ and $^5J(^{199}Hg\text{–}H)$ couplings with the methyl groups of the Ph_2Me_2phen ligand are noteworthy since on one methyl group only a $^5J(^{199}Hg\text{–}H)$ coupling of ~20 Hz was found, whereas, on the other methyl group, both a $^5J(^{199}Hg\text{–}H)$ coupling of ~8 Hz and a $^4J(^{195}Pt\text{–}H)$ coupling of ~3 Hz were present. The absence of a platinum coupling on one methyl group might well be due to a trans-bonded mercury atom (trans to that half of the ligand which has this methyl group), which also may account for the relatively large $^5J(^{199}Hg\text{–}H)$ coupling of ~20 Hz. The presence of a mercury coupling with the other methyl group, which also has a coupling with ^{195}Pt, might well be a through-space coupling since models show that the distance between the mercury atom and the cis methyl group of Ph_2Me_2phen is very small. It should be mentioned that a structure in which the Ph_2Me_2phen ligand bridges the platinum and mercury atom is sterically extremely unlikely due to the presence of the methyl groups on the ligand and the orientation of the lone pairs on the nitrogen atoms and therefore is excluded.

II. Compounds of Composition $[PtMe_2(N\text{-}N)]_n[Hg(O_2CCF_3)_2]$ (n = 1, 2, 4). In the previous section it was shown that reaction of equimolar amounts of HgX_2 with $PtMe_2(N\text{-}N)$ gave the first binuclear compounds of formula $PtMe_2X(HgX)(N\text{-}N)$. However, in the case of $Hg(O_2CCF_3)_2$ it was found that with large amounts of $PtMe_2(N\text{-}N)$ oligonuclear compounds of composition $[PtMe_2(N\text{-}N)]_2[Hg(O_2CCF_3)_2]$ (N-N = bpy, Ph_2Me_2phen) and $[PtMe_2(N\text{-}N)]_4[Hg(O_2CCF_3)_2]$ (N-N = bpy) were formed. With ^1H NMR a remarkable difference in behavior was found in the system $n[Hg(O_2CCF_3)_2]$ (n = 0–1) + $PtMe_2(N\text{-}N)$ for N-N = bpy or Ph_2Me_2phen. When increasing amounts of $n[Hg(O_2CCF_3)_2]$ (n = 0–0.5) were added to $PtMe_2(Ph_2Me_2phen)$ in C_6D_6, a slight broadening of the resonances of this compound and the new broad methyl resonances and rather sharp aryl resonances (Table II) of $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$ were observed. For n = 0.5 these were the only resonances present. From n = 0.5 to n = 1 the sharp resonances of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(Ph_2Me_2phen)$ were observable, and for n = 1 these were the only resonances present. With CH_2Cl_2 as a solvent the resonances of $PtMe_2(Ph_2Me_2phen)$ and $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$ merged due to chemical exchange. (Low-temperature studies were not successful due to the very low solubility of $Pt_2Me_4(O_2CCF_3)_2(Hg)(Ph_2Me_2phen)_2$ in common organic solvents.)

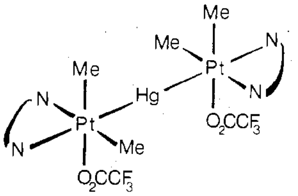

Figure 2. Proposed structure for $Pt_2Me_4(O_2CCF_3)_2(Hg)(N\text{-}N)_2$ (N-N = Ph_2Me_2phen).

Probably the latter compound was formed by successive oxidative addition of the two $Hg\text{–}O_2CCF_3$ bonds to the platinum atoms, and the proposed structure is given in Figure 2 (although a structure with the Hg atoms above the plane of the Ph_2Me_2phen ligand(s) is not excluded). The only products which could be identified by their ^1H NMR spectrum in the system $PtMe_2(bpy) + n[Hg(O_2CCF_3)_2]$ were $PtMe_2(bpy)$ for n = 0 and $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$ for n = 1. In the range n = 0–0.25 a rapid darkening of the solution occurred with increasing broadening and low-field shifts of the methyl resonances and high-field shifts of the bpy resonances. In the range n = 0.25–0.5 the solution gradually turned orange, further broadening and changes in shifts were observed (both methyl and bpy resonances to lower field), and occasionally precipitation of $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$ occurred. The ^1H NMR spectra for n = 0.25 and n = 0.5 were identical with the ^1H NMR spectra of the corresponding isolated compounds (see Experimental Section). From n = 0.5 to n = 1 the precipitate dissolved and broad methyl resonances and bpy resonances of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$ were observed. They became sharp for n = 1 and the ^{195}Pt and ^{199}Hg satellites were observed (Table II). The peculiarity of the system was displayed in the ranges n = 0–0.05 and n = 0.95–1. If small amounts of $Hg(O_2CCF_3)_2$ were added to $PtMe_2(bpy)$ (n = 0–0.05), a rapid broadening with finally disappearance of all ^{195}Pt resonances of $PtMe_2(bpy)$ was observed, whereas all its other resonances remained sharp and nearly unchanged in chemical shift (<0.02 ppm). Also addition of slight amounts of $PtMe_2(bpy)$ to $PtMe_2(O_2CCF_3)(bpy)$ or addition of slightly less than 1 equiv of $Hg(O_2CCF_3)_2$ to $PtMe_2(bpy)$ (n = 0.95–1) resulted in a broadening and disappearance of all the ^{195}Pt satellites. The ^{199}Hg satellites were then still sharp as were all other resonances, whose chemical shifts remained unchanged. This selective broadening of the ^{195}Pt satellites can be explained by a rapid formation and dissociation of intermediate oligonuclear complexes with strong $^{195}Pt\text{–}^{195}Pt$ couplings, resulting in the disappearance of the $J(^{195}Pt\text{–}H)$ couplings. This is somewhat similar to the disappearance of the $J(^{31}P\text{–}H)$ couplings in $RhCl(CO)(PPhMe_2)_2$[12] and $PdCl_2(PPh_2Me)_2$,[13] when small amounts of phosphine were added. Formation of paramagnetic intermediates (e.g., Hg radicals) might also cause disappearance of coupling constants.[13,14] However, this seems unlikely in this case since one would also expect appreciable high-field shifts and disappearance of the ^{199}Hg satellites, which were not observed.

In principle a reversible insertion of a $PtMe_2(bpy)$ molecule in the $Hg\text{–}O_2CCF_3$ or $Pt\text{–}O_2CCF_3$ bond of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(bpy)$ might occur, whereas in the case of the Ph_2Me_2phen analogues only insertion in the $Hg\text{–}O_2CCF_3$ bond is possible due to the much larger size of the Ph_2Me_2phen ligand (compared to the bpy ligand). The presence of still sharp ^{199}Hg satellites, when the ^{195}Pt satellites have broadened or disappeared (n = 0.95–1), suggests that no insertion in the $Hg\text{–}O_2CCF_3$ bond, as shown in Figure 2, took place since one would then expect a simultaneous mercury exchange on platinum. This would cause a disappearance of the ^{199}Hg satellite. Insertion in the $Pt\text{–}O_2CCF_3$ bond affords $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(bpy)_2$, a compound which is somewhat similar to the reported binuclear compounds $Pt_2Me_4(O_2CCF_3)_2(py)_2$.[5] The proposed structure is given in Figure 3 (but the structure of Figure 2 cannot be fully excluded). Further insertion of $PtMe_2(bpy)$ molecules in the newly formed $Pt\text{–}O_2CCF_3$ bond might then result in the formation of $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4$. The proposed structure is given in Figure 4.[21] The fact that this was the only platinum–mercury compound which formed extremely dark red solutions and crystals with black-brown

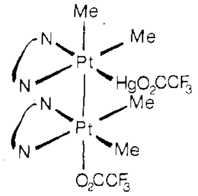

Figure 3. Proposed structure for $Pt_2Me_4(O_2CCF_3)(HgO_2CCF_3)(N\text{-}N)_2$ (N-N = bpy).

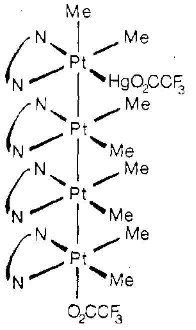

Figure 4. Proposed structure for $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(N\text{-}N)_4$ (N-N = bpy).

and "metallic golden" facets supported the proposed formation of a chain of platinum atoms, with extensive electron delocalization along the chain. In this respect the compounds showed some resemblance to certain highly conducting platinum compounds (e.g., $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$[15] and $K_{1.84}Pt(C_2O_4)_2\cdot 2H_2O$[16]) having "infinite" chains of platinum atoms and a highly metallic appearance. Other compounds with platinum chains have long been known as the "platinum blues"[17] and very recently the crystal structure of one such compound $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5$ has been reported.[18] This compound also has a chain of four platinum atoms and it was reported that, with other less bulky ligands as α-pyridone (C_5H_4ON), oligomeric mixtures with up to 15 or more platinum atoms in a chain existed.

Unfortunately, the crystals of $Pt_4Me_8(O_2CCF_3)(HgO_2CCF_3)(bpy)_4\cdot CH_2Cl_2$ were not of sufficient quality to obtain structural information[19] and reactions of $PtMe_2(bpy)$ with $Hg(ClO_4)_2$ or $Hg(NO_3)_2$, although visually very similar, afforded only extremely insoluble materials. However, the compound is of great interest, since it is the first example of an oligonuclear compound with methyl substitutents on the platinum atom. Other oxidation reactions with partial oxidation of $PtMe_2(bpy)$ are being investigated in order to obtain conducting quasi-one-dimensional compounds with "infinite" platinum chains.

III. Methyl-Transfer Reactions. In the reactions described earlier (section I) of $PtMe_2(N\text{-}N)$ with HgX_2 methyl transfer from Pt(II) to Hg(II) was never observed. However, addition of $Hg(O_2CCF_3)_2$ to a dichloromethane solution of $PtMe_2(O_2CCF_3)(HgO_2CCF_3)(N\text{-}N)$ (N-N = bpy, Ph_2Me_2phen) resulted in the formation of $MeHgO_2CCF_3$. The reaction was studied with ^1H NMR, and the following results were obtained. Addition of $Hg(O_2CCF_3)_2$ resulted in broadening of the low-field platinum methyl resonance and disappearance of the ^{199}Hg satellites, indicating a mercury exchange on platinum. After a few hours the formation of $MeHgO_2CCF_3$ was observable. The rate of this formation and the amount of $MeHgO_2CCF_3$ formed was proportional to the amount of $Hg(O_2CCF_3)_2$ added (this amount varied between 0 and 1 equiv). Only when 1 equiv was added, did all of the platinum–mercury compound react. According to integration of the ^1H NMR spectra, both methyl groups from platinum had reacted according to eq 3. The formation of $MeHgO_2CCF_3$ was identified by comparison with the ^1H NMR chemical shift

$$PtMe_2(O_2CCF_3)(HgO_2CCF_3)(N\text{-}N) + Hg(O_2CCF_3)_2 \rightarrow 2MeHgO_2CCF_3 + \text{insoluble products} \quad (3)$$

and $^2J(^{199}Hg\text{–}H)$ coupling constant of pure $MeHgO_2CCF_3$. The formation of $HgMe_2$ was never observed. The fact that methyl exchange did not occur with the two-valent platinum compounds $PtMe_2(N\text{-}N)$ but does occur with the four-valent platinum–mercury compound is remarkable. The previously reported methyl-transfer reactions of $PtMe_2(PPhMe_2)_2$ with HgX_2[4,5] (X = Cl, O_2CCH_3) might well proceed via the initial formation of an intermediate $PtMe_2X(HgX)(PPhMe_2)_2$ complex, which then reacts further with HgX_2 resulting in methyl transfer to mercury.

A different and more complicated reaction involving methyl transfer between platinum and mercury was found in the reactions of $PtMe_2(N\text{-}N)$ (N-N = bpy, Ph_2Me_2phen) and $MeHgO_2CCF_3$. When 1 equiv of $MeHgO_2CCF_3$ added to a dichloromethane solution of $PtMe_2(bpy)$, a change in color to cream was observed. ^1H NMR spectra run immediately after the addition showed a broad platinum methyl resonance at −3.98 ppm (in CH_2Cl_2, relative to CH_2Cl_2) and a sharp mercury methyl resonance at −4.29 ppm with a $^2J(^{199}Hg\text{–}H)$ coupling of 170 Hz. The resonance and/or coupling constants of the starting materials differ appreciably ($PtMe_2(bpy)$, $\delta = -4.35$ ppm, $^2J(^{195}Pt\text{–}H) = 85$ Hz); $MeHgO_2CCF_3$, $\delta = -4.05$ ppm, $^2J(^{199}Hg\text{–}H) = 227$ Hz) from these data. The shift to lower field for the platinum methyl resonance and higher field for the mercury methyl resonance with the decrease of the $^2J(^{199}Hg\text{–}H)$ value indicated the formation of a labile $PtMe_2(O_2CCF_3)(HgMe)(bpy)$ compound. Similar changes in chemical shifts and in $^2J(^{117,119}Sn\text{–}H)$ coupling constants were observed for $PtMe_2Cl(SnMe_nCl_{3-n})(bpy)$ compounds.[6,7] Besides this formation of a platinum–mercury complex, the formation of mercury, $HgMe_2$, and some $PtMe_3(O_2CCF_3)(bpy)$ was also observed. When a larger amount of $MeHgO_2CCF_3$ was added to the solution of $PtMe_2(bpy)$, the amount of Me_2Hg and mercury formed increased until 2 equiv of $MeHgO_2CCF_3$ was added. Larger amounts of $MeHgO_2CCF_3$ did not further increase this formation. Integration of the ^1H NMR spectra showed that only one methyl group of the platinum compound had reacted with $MeHgO_2CCF_3$ to form $HgMe_2$ (identified by its chemical shift in CH_2Cl_2 of −5.07 ppm relative to CH_2Cl_2 or −1.17 ppm relative to cyclohexane and a $^2J(^{199}Hg\text{–}H)$ of 102.5 Hz[20]). With time the amount of $PtMe_3(O_2CCF_3)(bpy)$ increased with a simultaneous decrease of the amount of $HgMe_2$. After 2–3 days all $PtMe_2(bpy)$ had reacted to form $PtMe_3(O_2CCF_3)(bpy)$, and no more $HgMe_2$ was present. The proposed reaction sequence is given in eq 4–6. Although $PtMe_2(O_2CCF_3)_2(N\text{-}N)$ was not observed, its formation is very likely in view of the simultaneous formation of $HgMe_2$ and Hg. The reaction with $PhHgO_2CCF_3$ is given in eq 7 and according to ^1H NMR again an intermediate platinum–mercury compound formed. However, the quantitative formation of *trans*-$PtMe_2Ph(O_2CCF_3)(bpy)$ and mercury was rapid and complete within a few minutes. Also no phenyl–mercury compounds (e.g., $HgPh_2$) were observed as was the case with $MeHgO_2CCF_3$. A slow cis ↔ trans conversion took place, reaching its equilibrium after about 3 days with a cis:trans ratio ~1:0.28 (cis and trans refer to the mode of the Ph and

$$PtMe_2(bpy) + MeHgO_2CCF_3 \rightarrow PtMe_2(O_2CCF_3)(HgMe)(bpy) \quad (4)$$

$$PtMe_2(O_2CCF_3)(HgMe)(bpy) + MeHgO_2CCF_3 \rightarrow PtMe_2(O_2CCF_3)_2(bpy) + HgMe_2 + Hg \quad (5)$$

$$PtMe_2(O_2CCF_3)_2(bpy) + HgMe_2 \rightarrow PtMe_3(O_2CCF_3)(bpy) + MeHgO_2CCF_3 \quad (6)$$

$$PtMe_2(bpy) + PhHgO_2CCF_3 \rightarrow trans\text{-}PtMe_2Ph(O_2CCF_3)(bpy) + Hg \rightleftharpoons cis\text{-}PtMe_2Ph(O_2CCF_3)(bpy) \quad (7)$$

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

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

$HgPh_2$ 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.

Acknowledgment. I express my gratitude to Dr. G. B. Street and Dr. J. Crowley for their helpful discussions and to the office of Naval Research for a partial support of this work by ONR Contract No. 318-042. I also express my gratitude to IBM for an IBM World Trade Fellowship from The Netherlands.

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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(21) Again, a structure obtained by insertion of $PtMe_2(bpy)$ in the $Pt–O_2CCF_3$ bonds of the compound given in Figure 2 cannot be excluded.

Contribution from the Department of Chemistry,
University of Victoria, Victoria, British Columbia, Canada, V8W 2Y2

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

D. MICHAEL HEINEKEY and STEPHEN R. STOBART*

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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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