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Multinuclear NMR Spectroscopic and X-ray Crystallographic Studies of a Series of Mercury(II) Complexes Containing the Bidentate Phosphine Ligand $Ph_2PCH_2Si(CH_3)_2CH_2PPh_2$ (L^2)

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The bidentate phosphine ligand $Ph_2PCH_2Si(CH_3)_2CH_2PPh_2$ (L^2), an analogue of 1,3-bis(diphenylphosphino)propane (dppp), coordinates to mercury(II) salts to form complexes of the general formula $[HgX_2\cdot L^2]$ (X = Cl, Br, I, NCS). Infrared, Raman, and multinuclear (^1H, ^{13}C, ^{31}P, ^{199}Hg) NMR spectroscopic studies show that the complexes exhibit four-coordinate pseudotetrahedral metal geometry. $[HgI_2(Ph_2PCH_2Si(CH_3)_2CH_2PPh_2)]$ (**1**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.028(2)$ Å, $b = 17.402(5)$ Å, $c = 13.849(2)$ Å, $\beta = 90.635(14)°$, $V = 3139.5(11)$ Å^3, and $Z = 4$. The structure contains a tetrahedral mercury center with the phosphine ligand bound in a bidentate fashion: Hg−P 2.511(2), 2.515(2) Å; P−Hg−P 105.28(6)°. The complex $[HgCl_2]_2\cdot L^2$ has also been generated via a 2:1 metal:phosphine stoichiometry.

Introduction

Very few ditertiary phosphine complexes of mercury(II) are known. Several groups have studied the reactions of mercury halides with (diphenylphosphino)alkanes, and species of the general formulas $[Hg(dppe)X_2]$ and $[(HgX_2)_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) have been assigned on the basis of vibrational spectroscopy.[1] The crystal structure of $[Hg(CN)_2(dppe)]$ was found to consist of infinite chains in which four-coordinate mercury centers were linked by bridging dppe ligands.[2] The sole structurally-characterized mononuclear mercury(II) species containing a chelating bidentate phosphine ligand reported prior to this study was $[HgBr_2(Ph_2PCH{=}CHPPh_2)]$.[3] Mercury phosphine complexes are amenable to study by multinuclear (^{199}Hg, ^{31}P) NMR spectroscopy.[4,5] However, the inherent insolubility of $[HgX_2$((diphenylphosphino)alkane)] complexes has often precluded such investigation.

We have previously detailed our interest in the design of bidentate phosphine ligands that incorporate a dimethylsilicon component into the backbone.[6] The $Si(CH_3)_2$ unit solubilizes the ligands and also provides an excellent NMR handle. The ligand 2,2-dimethyl-1,3-bis(diphenylphosphino)-2-silapropane (L^2) is an analogue of dppp and has been complexed to a range of metals.[7] The crystal structures of $[Ni(NO_3)_2\cdot L^2]$[8] and $[CoBr_2\cdot L^2]$[9] have been reported; each featured a four-coordinate tetrahedral metal center. The improved solubility and proven mononuclear complex formation engendered by L^2 thus make the ligand highly suitable for the study of mercury(II) phosphines by NMR spectroscopic and X-ray crystallographic techniques.

Table 1. Crystallographic Data for **1**

formula	$C_{28}H_{30}I_2HgP_2Si$	V/Å^3	3139.5(11)
fw	910.94	Z	4
color	colorless	T/°C	20
space group	$P2_1/n$	λ(Mo Kα)/Å	0.709 30
a/Å	13.028(2)	ρ_{calcd}/g cm^{-3}	1.927
b/Å	17.402(5)	μ/mm^{-1}	7.024
c/Å	13.849(2)	R^a	0.0472
β/deg	90.635(14)	$R_w{}^a$	0.0727

[a] Residuals calculated for reflections with $I > 2\sigma(I)$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Experimental Section

General Comments. Ligand L^2 was prepared according to the literature method.[6] All complexes were prepared and handled under a nitrogen atmosphere using standard Schlenk techniques. The solvents used were reagent grade and were dried and distilled immediately prior to use. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. Infrared spectra were recorded between CsI plates as Nujol mulls on a Perkin-Elmer 180 double-beam spectrometer.

X-ray Crystallography. Diffraction-quality crystals of **1** were obtained by slow evaporation of a dichloromethane solution of the complex. The crystallographic data are summarized in Table 1. X-ray measurements were made on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Data were collected in the range $4° \leq 2\theta \leq 55°$ and corrected for Lorentz, polarization, and absorption effects. The structure was solved using the heavy-atom method and the NRCVAX[10] program system. Final refinement was performed with SHELXL-93[11] using all F^2 data, with all non-H atoms allowed anisotropic motion and hydrogen atoms allowed for as riding atoms. An absorption correction was applied, based on ψ-scan data.[12]

$[HgX_2\cdot L^2]$ (X = Cl, Br, I). Equimolar quantities of the mercury salt dissolved in THF and solutions of the ligand in dichloromethane were mixed and stirred for 5 h at room temperature. The slow addition of dry ether afforded the products as white precipitates, which were filtered off, washed with ethanol and dry ether, and pumped dry overnight. Yields: 75%. Anal. Calcd: for $C_{28}H_{30}HgCl_2P_2Si$: C, 46.47; H, 4.29. Found: C, 46.20; H, 4.15. Calcd for $C_{28}H_{30}HgBr_2P_2$-

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Table 2. ^{1}H NMR Data for Mercury(II) Complexes

	chem shift^a/ppm			coupling const^b/Hz	
complex	Ph_2P-	$>P-CH_2-$	$-Si(CH_3)_2-$	$^2J(^{31}P-^1H)$ + $^4J(^{31}P-^1H)$	$^3J(^{199}Hg-^1H)$
$HgCl_2 \cdot L^2$	7.82−7.43 (m)	2.02 (t)	-0.27 (s)	6.0	62.2
$HgBr_2 \cdot L^2$	7.79−7.38 (m)	2.02 (t)	-0.28 (s)	6.6	57.4
$HgI_2 \cdot L^2$ (**1**)	7.77−7.36 (m)	1.99 (t)	-0.29 (s)	6.8	41.7
$Hg(SCN)_2 \cdot L^2$	7.77−7.48 (m)	2.35 (t)	-0.31 (s)	7.1	55.1
$[HgCl_2]_2 \cdot L^2$	7.78−7.29 (m)	1.85 (t)	-0.01 (s)	6.5	not obsd

^{a} Solvent $CDCl_3$, referenced to 7.25 ppm. ^{b} Coupling constants ± 0.1 Hz; m = multiplet, t = apparent triplet, s = singlet.

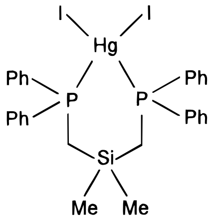
Si: C, 41.17; H, 3.70. Found: C, 40.98; H, 4.02. Calcd for $C_{28}H_{30}HgI_2P_2Si$ (**1**): C, 36.92; H, 3.32. Found: C, 37.22; H, 3.46.

$[Hg(SCN)_2 \cdot L^2]$. Equimolar amounts of a THF solution of mercury thiocyanate and a dichloromethane solution of the ligand were added together and stirred at 50 °C for 5 h. On cooling and addition of *n*-hexane, a white precipitate was deposited; this was washed with dry ether and *n*-hexane and dried *in vacuo* overnight. Yield: 73%. Anal. Calcd for $C_{30}H_{30}HgN_2P_2S_2Si$: C, 46.59; H, 3.91; N, 3.62. Found: C, 46.68; H, 4.08; N, 3.65.

$[HgCl_2]_2 \cdot L^2$. Addition of mercury chloride dissolved in acetone to a solution of the ligand in dichloromethane in a 2:1 ratio yielded a white precipitate. The mixture was stirred at 50 °C for 1 h, cooled, and filtered. The precipitate was washed with dry ether and pumped dry overnight. Yield: 76%. Anal. Calcd for $C_{28}H_{30}Hg_2Cl_4P_2Si$: C, 33.65; H, 3.03. Found: C, 33.66; H, 3.09.

Results and Discussion

The 1:1 stoichiometric addition of L^2 to HgX_2 (X = Cl, Br, I, SCN) salts produced a series of moisture-sensitive white powders whose general formula was shown to be $[HgX_2 \cdot L^2]$ from elemental analysis data. The compounds were sparingly soluble in chloroform and dichloromethane. The complexes were studied using multinuclear NMR and vibrational spectroscopic techniques. Recrystallization from dichloromethane produced diffraction-quality crystals of $HgI_2 \cdot L^2$ (**1**). Addition of 2 equiv of $HgCl_2$ to L^2 produced $[(HgCl_2)_2 \cdot L^2]$, but a corresponding attempt to generate $[Hg(L^2)_2](ClO_4)_2$ via the reaction of $Hg(ClO_4)_2$ and L^2 in a 1:2 ratio was unsuccessful.



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Multinuclear NMR Studies. The ^{1}H NMR spectra of the $[HgX_2 \cdot L^2]$ complexes are summarized in Table 2. In each example, the methylene $P-CH_2$ protons ($A_2XX'A'_2$ system) appear as a triplet, downfield from the free ligand at δ 1.50 ppm; the triplet is due to two- and four-bond coupling to the phosphorus atoms, with $^2J(^{31}P-^1H) + {}^4J(^{31}P-^1H) = 6.0-7.7$ Hz. The apparent phosphorus coupling was confirmed by performing 2-dimensional ^{1}H and ^{31}P heteronuclear correlation experiments; an example is shown in Figure 1. In addition, three-bond coupling to the mercury center is clearly shown by the presence of mercury satellites (Figure 2) ($^3J(^{199}Hg-^1H)$ = 41.7−62.2 Hz: ^{199}Hg $I = {}^1/_2$). The methyl groups attached to the silicon appear as a singlet, indicating their chemical equivalency; they are shifted upfield from the free ligand (δ 0.15 ppm).

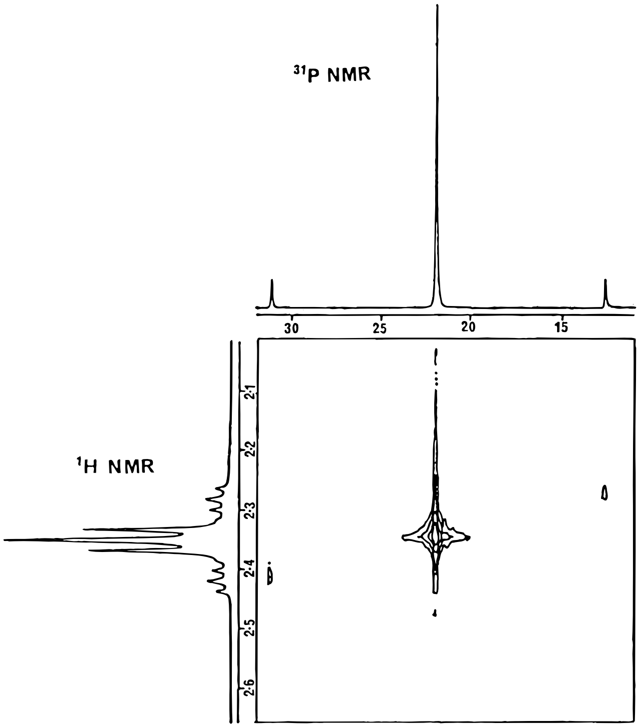

Figure 1. Two-dimensional $^{31}P-^1H$ heteronuclear correlated NMR contour plot for $Hg(NCS)_2 \cdot L^2$.

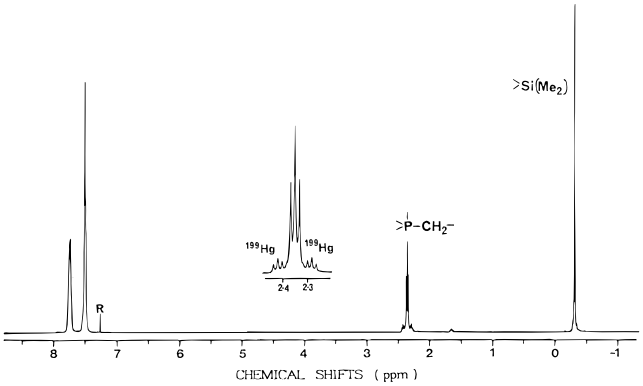

Figure 2. ^{1}H NMR spectrum of $Hg(NCS)_2 \cdot L^2$ at 298 K.

The ^{13}C NMR spectra of the complexes are all very similar. The methylene $P-CH_2$ protons in the chloride and thiocyanate appear downfield from the free ligand, at 14.54 and 15.22 ppm, respectively (free ligand 14.20 ppm); the bromide (13.78 ppm) and iodide (12.56 ppm) complexes are shifted slightly upfield. This apparent discrepancy in chemical shift values is presumably a reflection of the differing electronic properties of the ligands. An overnight (15 h) run of the thiocyanate complex produced a highly detailed ^{13}C NMR spectrum; inspection of the aromatic region showed clear $^{13}C-^{31}P$ coupling, with values of 21.5 Hz ($^1J(^{13}C-^{31}P)$) for the ipso carbon, 7.6 Hz ($^2J(^{13}C-^{31}P)$) for the

Table 3. ^{31}P NMR Data for Mercury(II) Complexes

	chem shift[a]/ppm ($^1J(^{199}Hg-^{31}P)$/Hz)[b]				
complex	298 K	273 K	243 K	213 K	183 K
$HgCl_2 \cdot L^2$	17.5 (3684)	18.1 (3743)	18.5 (3780)		
$HgBr_2 \cdot L^2$	7.6 (3199)	12.4 (3256)	13.1 (3302)	13.7 (3373)	14.7 (3454)
$HgI_2 \cdot L^2$ (**1**)	−7.5 (2355)	−2.5 (2436)	−1.6 (2517)	−1.2 (2563)	0.1 (2654)
$Hg(SCN)_2 \cdot L^2$	19.5 (3010)	19.7 (3031)	20.0 (3085)	20.4 (3127)	20.8 (3163)
$[HgCl_2]_2 \cdot L^2$	26.4 (7653)				

[a] In CH_2Cl_2, referenced to 85% H_3PO_4, $\delta \pm 0.1$ ppm. [b] $^1J \pm 5$ Hz.

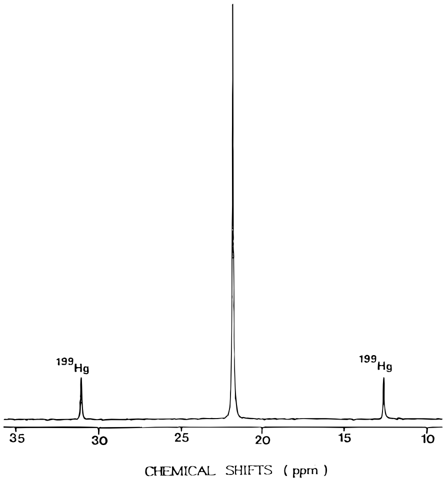

Figure 3. ^{31}P NMR spectrum of $Hg(NCS)_2 \cdot L^2$ at 298 K.

ortho, and 5.6 Hz ($^3J(^{13}C-^{31}P)$) for the meta. No coupling was observed for the para carbon in the aromatic region.

^{31}P NMR spectra of $HgX_2(PR_3)_2$ complexes have been well documented.[13] The $^1J(^{199}Hg-^{31}P)$ coupling constant has been correlated to Hg−P distance, X−Hg−X and P−Hg−P bond angles, the ionization potential of X, nucleophilicity, and the 6s(Hg)/3s(P) orbital overlap. A summary of the ^{31}P NMR data for the L^2 complexes is presented in Table 3. At room temperature, there is no evidence for phosphine/halide/thiocyanate exchange: the spectra always appear as single sharp resonances, with visible mercury satellites (Figure 3). The magnitude of the coupling constant here is comparable to values noted[3] for $[HgI_2(Ph_2PCH{=}CHPPh_2)]$ (2547 Hz) and $[HgI_2(Ph_2P(CH_2)_2S(CH_2)_2PPh_2)]$ (3420 Hz). The magnitude of $^1J(^{199}Hg-^{31}P)$ varies in the order Cl > Br > SCN > I; this correlates with the order observed for monodentate phosphine complexes.[14] Upon a decrease in temperature, the spectra broaden and the coupling constants increase as exchange becomes slower on the NMR time scale. The fact that coupling is observed at room temperature indicates that exchange is slow, while the lack of any abrupt change in J between 280 and 180 K implies that exchange is still occurring at low temperature; although a broadening of the spectra is noted, the signals are still fairly sharp even at 180 K.

Comparison of $^1J(^{199}Hg-^{31}P)$ values for $[HgCl_2 \cdot L^2]$ and $[(HgCl_2)_2 \cdot L^2]$ is noteworthy. It has been shown that the one-bond coupling in dimeric $[HgX_2.PR_3]_2$ species is greater than that in the monomeric analogues.[15] In this case, the J values are 3684 Hz $[HgCl_2 \cdot L^2]$ and 7653 Hz $[(HgCl_2)_2 \cdot L^2]$, thus indicating that a structure incorporating a bridged "$HgCl_3P$" environment is likely.

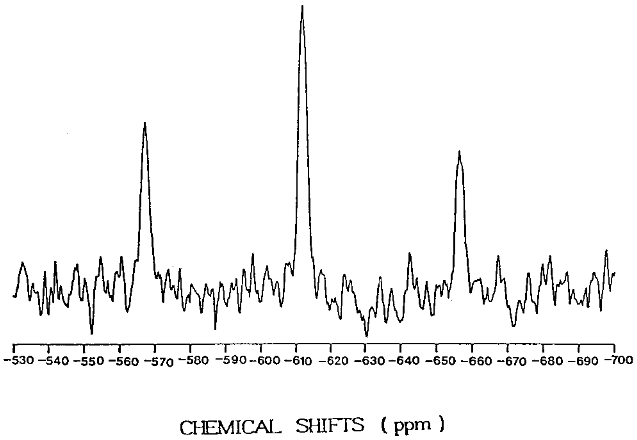

Figure 4. ^{199}Hg NMR spectrum of $HgBr_2 \cdot L^2$ at 298 K.

Due to the sparingly soluble nature of the complexes and the fast relaxation time associated with the isotope, a ^{199}Hg NMR spectrum could only be obtained for $[HgBr_2 \cdot L^2]$; this is shown in Figure 4. Prior studies[4] have shown that the metal atom geometry can be obtained by examining the metal−phosphorus coupling. When one, two, or three phosphorus atoms are bound to the mercury atom, the signal in the ^{199}Hg NMR spectrum appears as a doublet, triplet, or quadruplet, respectively. In this case, a clear 1:2:1 triplet results from bis coordination of L^2. The coupling constant ($^1J(^{199}Hg-^{31}P) = 3199$ Hz) obtained from the spectrum is identical to that observed in the ^{31}P NMR spectrum, as expected. The chemical shift value of −611 ppm, relative to $(CH_3)_2Hg$, is much greater than the value of −250 ppm noted for $[Hg(dppp)_2]^{2+}$.[16] A value of −657 ppm has been noted[4] for $[HgBr_2(pmp)_2]$ (pmp = tris(4-methoxyphenyl)-phosphine). Allman and Goel[17] showed that the ^{199}Hg chemical shift is directly related to coordination number, with 1:2 > 1:4 > 1:3. The similarity in values here implies that L^2 is coordinated via both available phosphorus donor sites to give a four-coordinate mercury center. It was also concluded that the magnitude of the Hg−P coupling constants was directly related to phosphine basicity, with J values increasing with increased basicity; the value observed for the L^2 complex here is very similar to that reported for the pmp complex, indicating that L^2 is comparable in σ-donor character and basicity to pmp.

IR and Raman Spectroscopy. Vibrational spectroscopy is well established as a tool for characterizing metal geometries in phosphine complexes of mercury halides and pseudohalides.[18,19] Mercury halide ν(Hg−X) stretching modes for X = Cl, Br, I, SCN have been assigned on the basis of far-IR and Raman studies on dppe complexes;[1] both terminal and bridging species were identified.

Notable peaks in the IR and Raman spectra of the L^2 complexes are presented in Table 4. The various modes are assigned with respect to Strommen's studies.[1] An important point to note is that the 1:1 complexes display only terminal

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Table 4. Vibrational Spectroscopic Data for Mercury(II) Complexes

complex	IR ν/cm^{-1} and assignt[a]	Raman ν/cm^{-1} and assignt[b]
$HgCl_2\cdot L^2$	280 vs, 270 vs ν_t(Hg−Cl); 165 m ν(Hg−P)	
$HgBr_2\cdot L^2$	175 vs, 155 vs ν_t(Hg−Br); 145 vs ν(Hg−P)	175 w, 158 m ν_t(Hg−Br); 135 w ν(Hg−P)
$HgI_2\cdot L^2$ (**1**)	130 vs, 112 s ν_t(Hg−I); 145 w ν(Hg−P)	
$Hg(SCN)_2\cdot L^2$	2090 s ν(CN); 840 vs, 795 vs ν(CS); 465 m δ(SCN); 215 br ν_t(Hg−SCN); 160 vw ν(Hg−P)	
$[HgCl_{2]2}\cdot L^2$	280 br s ν_t(Hg−Cl); 200 w ν_b(Hg−Cl); 160 w ν(Hg−P)	295 w, 278 w ν_t(Hg−Cl); 205 w νb(Hg−Cl); 168 m ν(Hg−P)

[a] Nujol−KBr plates (4000−400 cm^{-1}), Nujol−polyethylene plates (500−32 cm^{-1}). [b] Raman samples in capillaries (500−50 cm^{-1}). vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

Hg−X stretching bands in their IR spectra, together with lower energy Hg−P stretches: this implies the presence of discrete monomeric tetrahedral complexes. The IR spectrum of the bromide complex shows intense bands at 175 and 155 cm^{-1} (terminal Hg−Br), together with a strong band at 145 cm^{-1} (Hg−P). The Raman spectrum of the $HgBr_2$ complex shows weak bands at 175, 158, and 135 cm^{-1}, with bridging Hg−Br modes clearly absent. Strommen also predicted, and showed, that terminal ν(Hg−Br) bands appeared at frequency values roughly 0.7 times those of ν(Hg−Cl) positions. For the L^2 complexes reported here, bands for the $HgBr_2$ complex are at a value approximately 0.61 times those of the $HgCl_2$ complex (280, 270 cm^{-1} for $HgCl_2$, 175, 155 cm^{-1} for $HgBr_2$). The $[HgCl_2]_2\cdot L^2$ complex should theoretically contain bridging chlorine atoms; the bands observed at 200 cm^{-1} (IR) and 205 cm^{-1} (Raman) confirm this; this is in agreement with the prediction of "$HgCl_3P$" environments made from NMR studies.

The complex $[Hg(SCN)_2\cdot L^2]$ contains S-bonded thiocyanate: although the value of 2090 cm^{-1} for ν(CN) is quite low, there is a clear, broad ν(Hg−SCN) stretch observed at 215 cm^{-1} in the far-IR spectrum; M−NCS stretches in related N-bonded systems are noticeably shifted to higher frequency (330, 290 cm^{-1} for $[Co(NCS)_2\cdot L^2]$;[9] 325, 285 cm^{-1} for $[Ni(NCS)_2\cdot L^2]$[20]).

Crystal Structure of $[HgI_2(Ph_2PCH_2Si(CH_3)_2CH_2PPh_2)]$ (1). A view of the complex appears in Figure 5. The mercury center exhibits tetrahedral geometry, with the ligand L^2 bound in bidentate fashion; this correlates with the spectroscopic observations previously discussed. Selected bond lengths and angles for **1** appear in Table 5. The Hg−I distances are noncontroversial (Hg1−I1 2.8393(7), Hg1−I2 2.7242(8) Å). The angles around the mercury atom are in the range 95.83(5) (P2−Hg1−I1) to 121.17(4)° (P2−Hg1−I2). The phosphorus ligand acts as a bidentate chelate (Hg1−P1 2.515(2), Hg1−P2 2.511(2) Å) with a P1−Hg1−P2 bite angle of 105.28(6)°. This compares with the values of 101.54(6) and 94.81(3)° observed in $[CoBr_2\cdot L^2]$[9] and $[Ni(NO_3)_2\cdot L^2]$,[8] respectively. Each of these values is considerably enhanced over the value of 89.3(2)° noted for the analogous dppp ligand in $[Pd(NCS)_2(dppp)]$.[22] The enhancements are presumably due to the incorporation of a silicon atom into the ligand backbone. The range of values observed for the chelate bite in L^2 complexes is testament to the conformational flexibility of the ligand. As previously observed for the cobalt complex, the six-membered ring comprising Hg1, P1, C1, Si1, C2, and P2 adopts a chair conformation, with torsion angles ranging from 35.5(2)° for P2−Hg1−P1−C1 to −73.1(4)° for C1−Si1−C2−P2.

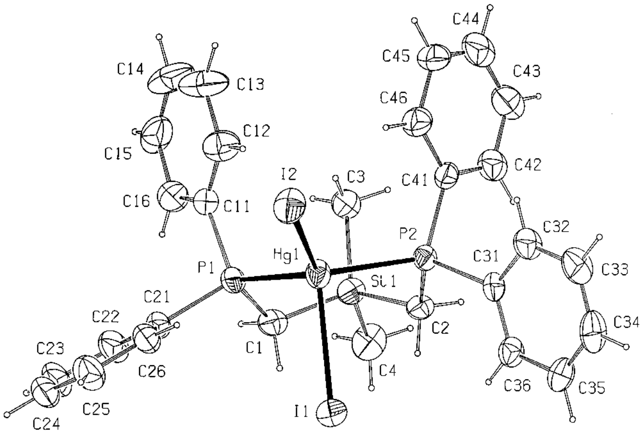

Figure 5. ORTEP[21] view of **1**. Thermal ellipsoids are drawn at the 30% probability level.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **1**

Hg1−I1	2.8393(7)	P1−C11	1.814(7)
Hg1−I2	2.7242(8)	P1−C21	1.816(7)
Hg1−P1	2.515(2)	P2−C2	1.806(6)
Hg1−P2	2.511(2)	P2−C31	1.811(6)
P1−C1	1.820(7)	P2−C41	1.812(7)

I1−Hg1−I2	114.87(2)	Hg1−P2−C2	105.9(2)
I1−Hg1−P1	96.42(4)	Hg1−P2−C31	112.4(2)
I1−Hg1−P2	95.83(5)	Hg1−P2−C41	118.0(2)
I2−Hg1−P1	118.44(5)	C1−Si1−C2	110.0(3)
I2−Hg1−P2	121.17(4)	C1−Si1−C3	111.9(3)
P1−Hg1−P2	105.28(6)	C1−Si1−C4	106.7(3)
Hg1−P1−C1	105.8(2)	C2−Si1−C3	112.2(3)
Hg1−P1−C11	115.2(2)	C2−Si1−C4	106.1(3)
Hg1−P1−C21	115.3(2)		

Conclusions

The increased solubility of L^2 over analogous (diphenylphosphino)alkane ligands makes mercury L^2 complexes amenable to multinuclear NMR studies. These NMR investigations, together with vibrational spectroscopic studies, have suggested four-coordinate metal centers in the $[HgX_2\cdot L^2]$ complexes; this was established for the mercury iodide species by X-ray crystallography. We are pursuing further research into group 12 and other transition metal phosphine complexes using L^2 and related ligands.

Acknowledgment. E.C.A. and G.F. thank the NSERC (Canada) for research grants.

Supporting Information Available: Tables of all atomic coordinates, anisotropic displacement parameters, and bond distances and angles, as well as a printout of the CIF file, for the crystal structure of **1** (16 pages). Ordering information is given on any current masthead page.

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