Volume 17
Number 7
July 1978

Inorganic Chemistry

Contribution from the Departments of Chemistry, The Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Guelph, Ontario, Canada N1G 2WI, and The Ohio State University, Columbus, Ohio 43210

Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Complexes of Mercury(II)[1]

ELMER C. ALYEA,*[2a] SHELTON A. DIAS,[2a] RAM G. GOEL,*[2a] WILLIAM O. OGINI,[2a] PIERRE PILON,[2a] and DEVON W. MEEK*[2b]

Received September 29, 1977

Phosphorus-31 NMR results are presented for compounds of the types $HgX_2(PR_3)_n$ where, for $n = 1$, R is *o*-tolyl, *tert*-butyl, cyclohexyl, and phenyl and, for $n = 2$, R is cyclohexyl and phenyl and where X is chloride, bromide, iodide, thiocyanate, acetate, and nitrate. The two-coordinate complex $[Hg(PCy_3)_2](ClO_4)_2$ displays the largest coordination chemical shift and a relatively low coupling constant. Phosphorus-31–mercury-199 coupling constants are in the range 3073–10 000 Hz; their correlation with the coordination chemical shift is reported. Factors (e.g., the electronegativity of the anion, the basicity and bulkiness of the phosphine, and the geometry at the mercury atom) affecting the coupling constants and chemical shifts are discussed.

Introduction

Relatively few studies of mercury-199 to phosphorus-31 nuclear spin–spin coupling in tertiary phosphine complexes of mercury(II) have been reported,[3–5] though synthetic and other physical studies of such complexes are quite extensive.[6] Grim and co-workers[3] related the $^{199}Hg–^{31}P$ coupling constants for halide complexes of the types L_2HgX_2 and $L_2Hg_2X_4$ (L = Bu_3P, Bu_2PhP, $BuPh_2P$ and, for the latter type only, Et_2PhP) to the electronegativity of the halogen, the basicity of the phosphine, the type of complex, and the coordination chemical shift. Similar correlations were reported for tri-*n*-butyl- and trioctylphosphine complexes of the above types as well as some triethyl phosphite and diethylphosphonate complexes.[4] Pidcock and co-workers[7] had earlier discussed the $^{199}Hg–^{31}P$ coupling constants in the compounds $[HgX\{(EtO)_2PO\}]$ (X = Cl, Br, I, $MeCO_2$, $(EtO)_2PO$) and the crystal structure of the chloro complex. Phosphorus-31 NMR data for a limited number of trimethylphosphine complexes of mercury(II) with different coordination numbers for the mercury are also available.[5] No ^{31}P NMR spectral data have yet been reported for triarylphosphine complexes of mercury(II).

During investigations[8] in our laboratories of the steric effects of sterically demanding phosphines such as tri-*tert*-butylphosphine, tricyclohexylphosphine, and tri-*o*-tolylphosphine we have synthesized and characterized several new 1:1 and 1:2 adducts with mercury(II) salts. Their preparation and structural elucidation via vibrational spectral studies[9] and several x-ray single-crystal determination are reported elsewhere.[10] Herein are presented ^{31}P NMR spectral data for the complexes L_nHgX_2, where, for $n = 1$, L = $t\text{-}Bu_3P$, $(o\text{-tolyl})_3P$, Cy_3P, and Ph_3P, and for $n = 2$, L = Cy_3P and Ph_3P, and where X = Cl, Br, I, SCN, OAc, and NO_3. The NMR results for the two-coordinate complex $[Hg(PCy_3)_2](ClO_4)_2$ are also discussed.

Experimental Section

The ^{31}P NMR spectra were obtained either with a Bruker HX-90 Fourier transform spectrometer at 36.43 MHz using 10-mm tubes, deuterium lock from the deuterated solvent, and external 85% H_3PO_4 as the reference or with a Bruker WP-60 FT spectrometer at 24.3 MHz using the sideband technique with 85% H_3PO_4 as reference in a concentric capillary. Chemical shifts are considered accurate to ±0.1 ppm and coupling constants to ±2 Hz. Acetone-d_6 was used as a lock in some instances. Low-temperature measurements were made on dichloromethane solutions when necessary to observe the satellite peaks due to mercury-199; several complexes undergo phosphine dissociation and rapid exchange at room temperature. Dimethylformamide and dimethyl-d_6 sulfoxide were used as solvents for some complexes, with the tri-*o*-tolylphosphine complexes having the least solubility even in these polar solvents.

Preparation of the complexes followed the general method,[6,9,11–13] which normally involves stirring the phosphine and the mercuric salt in an appropriate molar ratio (usually in ethanol). Only 1:1 adducts were isolated with tri-*tert*-butylphosphine and tri-*o*-tolylphosphine. The synthesis of one new complex $Hg(NO_3)_2(Cy_3P)_2$ is given as a representative example; satisfactory elemental analyses were obtained for all the complexes.

A mixture of $Hg(NO_3)_2$ (0.65 g, 2.0 mmol) and PCy_3 (1.12 g, 4.0 mmol) was stirred in 40 mL of dichloromethane for 5 h. The white solid obtained after filtration and concentration of the filtrate was recrystallized from dichloromethane–ether; yield 59%; mp 203–208 °C dec. Anal. Calcd for $Hg(NO_3)_2(Cy_3P)_2$: C, 48.83; H, 7.51; N, 3.16. Found: C, 48.80; H, 7.65; N, 2.94.

Discussion

Phosphorus-31 nuclear magnetic resonance data are given in Tables I–III. Plots of coordination chemical shift, $\delta_{\text{complex}} - \delta_{\text{ligand}}$ ($\Delta\delta$), against $^1J(^{199}Hg–^{31}P)$, the separation between satellite peaks, are shown in Figures 1 and 2. In those cases which showed only the relatively intense central peak at ambient temperature, the two small satellite peaks arising from those molecules containing mercury-199 (16.84% natural abundance, $I = {}^1/_2$) were observable at lower temperatures. All complexes showed positive coordination chemical shifts (downfield relative to 85% H_3PO_4 at 0.0 ppm), corresponding to a decrease in electron density upon coordination of the phosphorus atom. The data are discussed below according to the type of complex and the particular phosphine ligand.

Previous attempts[3] to observe ^{31}P signals for triphenylphosphine complexes of mercury were thwarted by solubility

0020-1669/78/1317-1697$01.00/0 © 1978 American Chemical Society

Table I. ^{31}P NMR Data for $(Ph_3P)_nHgX_2$

	X	Δδ, ppm[a]	$^1J(^{199}Hg-^{31}P)$, Hz
$n = 2$	I	13.1	3073
	SCN	37.4	3716
	Br	27.5	4178
	Cl	33.9	4740
	OAc	39.9	5024
$n = 1$	I	12.2 (24.1)[b]	4673 (4700)[b]
	SCN	43.2 (40.9)[b]	6159 (6366)[b]
	Br	(36.1)[b]	(6464)[b]
	Cl	(38.8)[b]	(7431)[b]
	OAc	35.1 (33.2)[b]	8640

[a] Δδ is the change of chemical shift on coordination in CH_2Cl_2 solution, at 243 K ($n = 1$) or at 230 K ($n = 2$); free PPh_3 has δ at −5.8 ppm with reference to 85% H_3PO_4; the ^{31}P resonance of the ligand shifts downfield on coordination to a metal. [b] In DMF solution at 243 K.

Table II. ^{31}P NMR Data for $(Cy_3P)_nHgX_2$

	X	Δδ, ppm[a]	$^1J(^{199}Hg-^{31}P)$, Hz
$n = 2$	I	19.5	3970
	SCN	49.1	4326
	Br	36.0	4561
	Cl	41.3	4815
	NO_3	56.5	4805
	OAc	46.1	5156
	ClO_4	67.8	3755
$n = 1$	I	30.4	4439
	SCN	63.0	5640
	Br	44.5	6201
	Cl	52.1	6992
	OAc	51.9	7461
	NO_3	(58.3)[b]	(8540)[b]

[a] Δδ is the change of chemical shift on coordination in CH_2Cl_2 solution. Free PCy_3 has δ at 8.6 ppm with reference to 85% H_3PO_4; the ^{31}P resonance of the ligand shifts downfield on coordination to a metal. [b] Measured in Me_2SO-d_6; Δδ at 60.0 ppm for CH_2Cl_2 solution.

Table III. ^{31}P NMR Data for $(t\text{-}Bu_3P)HgX_2$ and $[(o\text{-tolyl})_3P]HgX_2$

	X	Δδ, ppm[a]	$^1J(^{199}Hg-^{31}P)$, Hz
t-Bu_3P	I	15.8	4419
	CN	21.6	4858
	SCN	41.4	5810
	Br	30.5	5947
	Cl	37.8	6755
	OAc	36.1	7220
$(o\text{-tolyl})_3P$	I	16.6 (44.5)[b]	
	Br	(41.7)[c]	
	Cl	(42.0)[c]	
	SCN	(42.2)[c]	
	OAc	46.1 (47.8)[d]	8299 (8255)[d]
	NO_3	(48.1)[c]	(10000)[d]

[a] Change of chemical shift on coordination in CH_2Cl_2 solution; free P-t-Bu_3 at −60.9 ppm; free $P(o\text{-tolyl})_3$ at +32.2 ppm in CH_2Cl_2 solution, at +32.4 ppm in Me_2SO solution with reference to 85% H_3PO_4 at δ = 0 ppm. The ^{31}P resonance of the ligand shifts downfield on coordination to a metal. [b] In DMF solution at 218 K. [c] In Me_2SO solution. [d] In $CDCl_3$ solution.

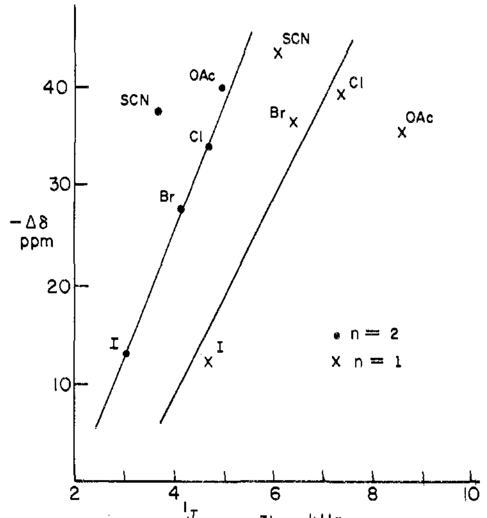

Figure 1. Phosphorus-31 NMR data for the $HgX_2(PPh_3)_n$ complexes. The lines are drawn through the halide points only, as those complexes have known structures.[9,18]

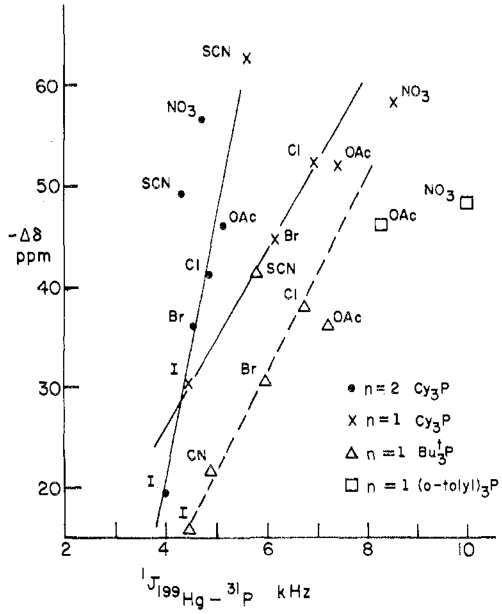

Figure 2. Phosphorus-31 NMR data for the $HgX_2(PPR_3)_n$ series of complexes. The lines are drawn through the halide points only, as those complexes have known structures.[9,18]

problems. Our Fourier transform data collection capability has allowed us to obtain spectra for dichloromethane solutions for both the $(Ph_3P)_2HgX_2$ and $[(Ph_3P)HgX_2]_2$ series of compounds (Table I, Figure 1). The former 1:2 halide and thiocyanate adducts are known to be pseudotetrahedral on the basis of vibrational spectral assignments[14-16] and the x-ray analysis of $(Ph_3P)_2Hg(SCN)_2$.[17] Similarly, vibrational data[14-16] for the 1:1 complexes are consistent with a trans-centrosymmetrical dimer, recently proved by x-ray crystallography for the chloride.[18] The structures of the $(R_3P)_2Hg(OAc)_2$ complexes are unknown, although it has been established[10d] that $(t\text{-}Bu_3P)Hg(OAc)_2$ is monomeric with unsymmetrically chelated acetato groups. Other studies indicate that $L_2Hg(OAc)_2$ complexes undergo dissociation and rapid ligand exchange in solution.[19] In the present study the temperature was lowered sufficiently to permit observance of the satellite peaks; i.e., phosphine exchange is then slow on the NMR time scale.

The various trends observed by Grim and co-workers[3] are also found for the present triphenylphosphine complexes: the magnitude of $^1J(^{199}Hg-^{31}P)$ increases in the order of the electronegativity of the halogen ligand, is larger for the 1:1 dimeric species than the corresponding 1:2 adducts, and generally increases with the coordination chemical shift. (The best straight lines in Figures 1 and 2 are drawn from the data of the halide complexes, whose similar structures are ensured by other physical methods; see text and ref 9 and 18.) These trends are consistent with the more electronegative anions and the dimeric cases leading to greater σ P–Hg interaction and larger couplings. The explanation of these observations assumes that little or no π bonding[7] occurs between mercury(II) and phosphorus and that other factors such as stereochemistry and bond angles remain constant.[20,21] Thus, while the correlation between anion electronegativity[22] and $J(^{199}\text{Hg}-^{31}\text{P})$ is extended in the present $(Ph_3P)_nHgX_2$ ($n = 1, 2$) series, it is to be noted that the coordination chemical shift does not increase in the same order, i.e., I < SCN < Br < Cl < OAc. The magnitude of the coordination chemical shift for $(Ph_3P)Hg(OAc)_2$ is substantially less than might be anticipated and is undoubtedly related to the monomeric nature of the complex, whereas the other $(Ph_3P)HgX_2$ complexes are dimeric. The coordination chemical shifts of the $(Ph_3P)_nHg(SCN)_2$ ($n = 1, 2$) complexes are considerably higher than expected on electronegativity considerations and this anomaly also occurs for $(Bu_3P)_2Hg(SCN)_2$[4] and $LHg(SCN)_2$ [L = Cy_3P, t-Bu_3P, $(o\text{-tolyl})_3P$] (vide infra). Although a change in stereochemistry as compared to that of the halide complexes[14–16,18] may be a factor for the present 1:1 complexes,[23] the $LHg(SCN)_2$ (L = t-Bu_3P, $(o\text{-tolyl})_3P$) complexes are of the same geometry as the corresponding halide adducts.[14–17] The π-bonding ability of the thiocyanato ligand[24] is not an important factor in mercury(II) complexes;[7] thus, a determination of which of the other factors[20,21] affecting chemical shift becomes dominating for the thiocyanato complexes cannot be made at the present time.

Grim[3] also observed that the mercury–phosphorus coupling constant decreases as the number of phenyl groups attached to the phosphorus atom is increased for the complexes $(Ph_nR_{3-n}P)_2HgX_2$ ($n = 0, 1, 2$). This trend, which was also reported by Mann for some cadmium[25a] and tin[25b] complexes, is the opposite of the general relationship found for metal–phosphorus coupling constants in which π interactions may be invoked.[21] The observed decrease for the mercury series of complexes was related[3] to the decreasing basicity of the tertiary phosphine (Bu_3P has pK_a of 8.43; Ph_3P, a pK_a of 2.73)[26] and cited as evidence for the dominating importance of σ-bond strength on the value of $J(^{199}\text{Hg}-^{31}\text{P})$. Our results show that both the coordination chemical shifts and the coupling constants for the $(Ph_3P)_2HgX_2$ complexes are lower, as predicted, than for $(Ph_2BuP)_2HgX_2$. The greatest decrease for both parameters occurred between the $(PhBu_2P)_2HgX_2$ and $(Ph_2BuP)_2HgX_2$ complexes. Though less marked, decreases of both coordination chemical shift and $J(^{199}\text{Hg}-^{31}\text{P})$ occur in the dimeric $[(Ph_3P)HgX_2]_2$ series relative to the alkyl-substituted phosphine series. Pidcock[7b] has suggested that dissociation and phosphine exchange may invalidate Grim's conclusions concerning the basicity–coupling constant trends. An investigation[19] of a wide range of the more soluble acetate complexes has indeed shown that L_2HgX_2 complexes may be extensively dissociated and that, as observed for the triphenylphosphine complexes in this study, ligand exchange is too fast on the NMR time scale to permit observation of coupling at ambient temperature. Nevertheless, the difference between $J(^{199}\text{Hg}-^{31}\text{P})$ in $(Ph_3P)_2HgI_2$ (3073 Hz) and $(Bu_3P)_2HgI_2$ (4100 Hz) is too great, in our estimation, to be accounted for by this phenomenon. Measurements at lower temperatures to minimize ligand exchange would probably only increase slightly the magnitude of $J(^{199}\text{Hg}-^{31}\text{P})$ in each case.[19] Our results for the triphenylphosphine complexes thus substantiate and extend Grim's conclusions.

Similar trends are observed for the $J(^{199}\text{Hg}-^{31}\text{P})$ values for the two series of tricyclohexylphosphine derivatives (Table II, Figure 2). The coupling constants increase with greater anion electronegativity, with the values for the 1:1 complexes being approximately 40% greater than for the analogous 1:2 complex. This compares with a 55% increase between the two triphenylphosphine series. The magnitude of the coordination chemical shift also generally increases in the same order as the coupling constant, though the acetate value in the 1:1 series is unexpectedly low and both thiocyanate values are unusually high. The change in structure in the 1:1 series from a trans symmetrical dimer assumed for the halides[13] to a monomer for the acetate[19] and a polymer for the thiocyanate[23] is probably a major factor contributing to the anomalous chemical shifts. As expected for the more basic tricyclohexylphosphine (pK_a of 9.70),[26] the coordination chemical shifts are substantially greater for each complex as compared to the corresponding triphenylphosphine complex. It is interesting to note that the $J(^{199}\text{Hg}-^{31}\text{P})$ values for the 1:1 tricyclohexylphosphine complexes are slightly lower than those observed for the 1:1 triphenylphosphine adducts; however, the opposite trend is found for the 1:2 series. Whereas the more basic phosphine is expected to lead to a larger coupling constant,[3] the larger steric requirements of tricyclohexylphosphine[27,28] may reduce its ability to form a strong σ bond with mercury and thus give reduced $J(^{199}\text{Hg}-^{31}\text{P})$ values. It seems unlikely that $J(^{199}\text{Hg}-^{31}\text{P})$ for the 1:1 tricyclohexylphosphine complexes could be markedly affected by slower ligand exchange (i.e., increase by several hundred hertz) and, thus, the steric effect appears to be an important factor. The bulkiness of tricyclohexylphosphine can be directly related[30] to the low chemical shift of the free phosphine (8.6 ppm in CH_2Cl_2) even though its basicity (pK_a of 9.70) is the greatest known for any tertiary phosphine. The steric effect on the magnitude of the coordination chemical shift is demonstrated by comparing the values for the $(Cy_3P)_nHgX_2$ complexes with those known for $(Bu_3P)_nHgX_2$,[3] where tributylphosphine is much less bulky[27] but of similar basicity (pK_a of 8.43);[26] those for the latter phosphine series are considerably higher.

The $J(^{199}\text{Hg}-^{31}\text{P})$ values and coordination chemical shifts again generally increase with increasing anion electronegativity for the 1:1 series of tri-*tert*-butylphosphine complexes. Since $(t\text{-}Bu_3P)Hg(SCN)_2$ is dimeric in dichloroethane solution,[9] the anomalously high $\Delta\delta$ value is inexplicable in terms of a structural change from the halides; however, the low $\Delta\delta$ value for the acetate can be explained by the change to a monomeric complex in that case.[10d] The position of the cyanide, as expected from electronegativity considerations,[22] is in agreement with earlier contentions[7,31] that π bonding is not important in mercury(II)–phosphine complexes. The similarity in $J(^{199}\text{Hg}-^{31}\text{P})$ values in the corresponding tricyclohexylphosphine and tri-*tert*-butylphosphine is as expected for two phosphines of similar basicity[26] and bulkiness.[27] However, the much lower $\Delta\delta$ values for the tri-*tert*-butylphosphine complexes reflect the fact that steric interactions are more important than in the corresponding tricyclohexylphosphine complexes. The failure to isolate any 1:2 tri-*tert*-butylphosphine complexes[9] and comparisons of x-ray crystallographic data[10] for complexes of both phosphines support this conclusion. The similarity in the slope of the plot of $\Delta\delta$ against $^1J(^{199}\text{Hg}-^{31}\text{P})$ for the three series of complexes $LHgX_2$ (L = Ph_3P, Cy_3P, *tert*-Bu_3P) supports our conclusions[9] based on vibrational spectra that the structures are the same for each anion.

The $[(o\text{-tolyl})_3P]HgX_2$ complexes are much less soluble and $\Delta\delta$ could only be measured in dichloromethane for X = I, OAc, and NO_3; although $^1J(^{199}\text{Hg}-^{31}\text{P})$ values were obtained for the latter two cases, the broadness of the central peaks signified that phosphine exchange was taking place. No coupling was observed for the iodide complex (even at 218 K in dimethylformamide) or for the other complexes in the series. Except for the acetate case, the low solubility of all of the (*o*-tolyl)$_3$P complexes, even in dimethyl sulfoxide or dimethylformamide, precluded other attempts to observe the satellite peaks. Although [(*o*-tolyl)$_3$P]Hg(NO$_3$)$_2$ may be recovered from dimethyl sulfoxide and $\Delta\delta$ is nearly unchanged for [(*o*-tolyl)$_3$P]Hg(SCN)$_2$ in dimethyl sulfoxide as compared to dichloromethane, it appears that solvation and/or solvolysis may be extensive for the [(*o*-tolyl)$_3$P]HgI$_2$ complex in dimethylformamide. The greater value of $\Delta\delta$ in the more polar solvent (44.5 ppm) is in better agreement with the presence of monomeric [(*o*-tolyl)$_3$P]HgI$_2$·DMF than the trans symmetrical dimer. Similarly, [(Ph$_3$P)HgI$_2$]$_2$ has a $\Delta\delta$ of 24.1 ppm in dimethylformamide at 243 K (12.2 ppm in dichloromethane at 243 K), the downfield shift in $\Delta\delta$ without a change in $^1J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ (4700 Hz) being consistent with solvation of the dimer to form monomeric (Ph$_3$P)HgI$_2$·DMF. It is probable that dimethyl sulfoxide also solvates the complexes [(*o*-tolyl)$_3$P]HgX$_2$ (X = Br, Cl, SCN) because $\Delta\delta$ is near 42 ppm in each case; all of these complexes are nonelectrolytes in dimethyl sulfoxide[9] so that species such as $\{[(o\text{-tolyl})_3\mathrm{P}]\mathrm{Hg}(\mathrm{Me_2SO})_x\}\mathrm{X}_2$ are not involved.

The relative position of the $\Delta\delta$ and $^1J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ values for [(*o*-tolyl)$_3$P]HgX$_2$ (X = OAc, NO$_3$) (Table III, Figure 2) is at first somewhat surprising since the basicity of (*o*-tolyl)$_3$P would be much less than that for Cy$_3$P and *t*-Bu$_3$P[26] and the bulkiness, as given by Tolman's cone angle estimates,[27] is significantly greater. However, the chemical shift for (*o*-tolyl)$_3$P is anomalously high and the effect, attributable to an interaction of the ortho methyl group with the phosphorus lone pair of electrons,[27,31] would be lost on coordination. Thus, a direct comparison of $\Delta\delta$ for the (*o*-tolyl)$_3$P compounds with the magnitude of $\Delta\delta$ for other phosphines is impossible. Nevertheless, the larger $^1J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ values correspond to smaller C–P–C bond angles,[30] implying that the steric requirements of (*o*-tolyl)$_3$P are actually less than those of *t*-Bu$_3$P. That the rings of (*o*-tolyl)$_3$P and Cy$_3$P can mesh together in a cog-like fashion has been verified by x-ray structural data for several complexes.[10] The phosphorus-31 NMR investigation of a series of (R$_3$P)$_n$Hg(OAc)$_2$ (n = 1, 2) complexes confirms that lower basicity and greater bulkiness lead to lower $\Delta\delta$ and $^1J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ values.[19]

The complex [(Cy$_3$P)$_2$Hg](ClO$_4$)$_2$ has been characterized by conductivity, infrared, and single-crystal x-ray diffraction analysis as a two-coordinate species.[19] The high $\Delta\delta$ and low $^1J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ values relative to the other (Cy$_3$P)$_2$HgX$_2$ species deserves some comment. Schmidbaur's results for $[(\mathrm{Me_3P})_n\mathrm{Hg}]^{2+}$ (n = 2, 3, 4) species led him to suggest that the greatest coupling occurs for the linear two-coordinate cation [$^1J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ = 5550 Hz], consistent with greater s character in the Hg–P bond.[5] However, the ^{31}P NMR study by Pidcock and co-workers[7] of the diethylphosphonate complexes ((EtO)$_2$PO)HgX [X = Cl, Br, I, OAc, (EtO)$_2$PO] showed that the coupling constant is considerably reduced and that $\Delta\delta$ is increased when X is the (EtO)$_2$PO moiety. The trans influence of phosphorus thus also explains the current data, with the value of $^1J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ for $[(\mathrm{Cy_3P})_2\mathrm{Hg}]^{2+}$ (3755 Hz) being lower than that reported for $[(\mathrm{Me_3P})_2\mathrm{Hg}]^{2+}$[5] due to the greater bulkiness of Cy$_3$P. Attempts to prepare other $[(\mathrm{R_3P})_2\mathrm{Hg}]^{2+}$ species[32] for phosphorus-31 NMR studies are currently in progress.

Acknowledgment. This work was supported primarily by operating grants from the National Research Council of Canada (to E.C.A. and R.G.G.). We gratefully acknowledge Professor G. Ferguson's interest in this work. We also acknowledge the NSF instrument grant that aided in the purchase of the Bruker HX-90 NMR instrument at OSU.

Registry No. (Ph$_3$P)$_2$HgI$_2$, 14494-95-2; (Ph$_3$P)$_2$Hg(SCN)$_2$, 27290-69-3; (Ph$_3$P)$_2$HgBr$_2$, 14586-76-6; (Ph$_3$P)$_2$HgCl$_2$, 14494-85-0; (Ph$_3$P)$_2$Hg(OAc)$_2$, 66119-73-1; (Ph$_3$P)HgI$_2$, 22573-17-7; (Ph$_3$P)Hg(SCN)$_2$, 29050-70-2; (Ph$_3$P)HgBr$_2$, 22573-16-6; (Ph$_3$P)HgCl$_2$, 22573-15-5; (Ph$_3$P)Hg(OAc)$_2$, 66119-74-2; (Cy$_3$P)$_2$HgI$_2$, 50725-85-4; (Cy$_3$P)$_2$Hg(SCN)$_2$, 50725-94-5; (Cy$_3$P)$_2$HgBr$_2$, 50725-84-3; (Cy$_3$P)$_2$HgCl$_2$, 50725-83-2; (Cy$_3$P)$_2$Hg(NO$_3$)$_2$, 66119-61-7; (Cy$_3$P)$_2$Hg(OAc)$_2$, 66161-25-9; (Cy$_3$P)$_2$Hg(ClO$_4$)$_2$, 66119-63-9; (Cy$_3$P)HgI$_2$, 50725-93-4; (Cy$_3$P)Hg(SCN)$_2$, 50725-74-1; (Cy$_3$P)HgBr$_2$, 50725-92-3; (Cy$_3$P)HgCl$_2$, 50725-91-2; (Cy$_3$P)Hg(OAc)$_2$, 66119-64-0; (Cy$_3$P)Hg(NO$_3$)$_2$, 66119-65-1; (*t*-Bu$_3$P)HgI$_2$, 66119-66-2; (*t*-Bu$_3$P)Hg(CN)$_2$, 66119-67-3; (*t*-Bu$_3$P)Hg(SCN)$_2$, 66119-68-4; (*t*-Bu$_3$P)HgBr$_2$, 66119-69-5; (*t*-Bu$_3$P)HgCl$_2$, 66119-70-8; (*t*-Bu$_3$P)Hg(OAc)$_2$, 66119-71-9; [(*o*-tolyl)$_3$P]HgI$_2$, 66119-55-9; [(*o*-tolyl)$_3$P]HgBr$_2$, 66119-56-0; [(*o*-tolyl)$_3$P]HgCl$_2$, 66119-57-1; [(*o*-tolyl)$_3$P]Hg(SCN)$_2$, 66119-58-2; [(*o*-tolyl)$_3$P]Hg(OAc)$_2$, 66119-59-3; [(*o*-tolyl)$_3$P]Hg(NO$_3$)$_2$, 66119-60-6.

References and Notes

(1) Presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, La., 1977; see Abstracts, No. INOR 60.
(2) (a) The Guelph-Waterloo Centre for Graduate Work in Chemistry. (b) The Ohio State University.
(3) (a) S. O. Grim, P. J. Lui, and R. L. Keiter, *Inorg. Chem.*, **13**, 342 (1974); (b) R. L. Keiter and S. O. Grim, *J. Chem. Soc., Chem. Commun.*, 521 (1968).
(4) A. Yamasaki and E. Fluck, *Z. Anorg. Allg. Chem.*, **396**, 297 (1973).
(5) H. Schmidbaur and K.-H. Räthlein, *Chem. Ber.*, **106**, 2491 (1973).
(6) K. K. Chow, W. Levason, and C. A. McAuliffe in "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands", C. A. McAuliffe, Ed., Macmillan, London, 1973, p 33, and references therein.
(7) (a) J. Bennett, A. Pidcock, C. R. Waterhouse, P. Coggon, and A. T. McPhail, *J. Chem. Soc. A*, 2094 (1970); (b) A. Pidcock in "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands", C. A. McAuliffe, Ed., Macmillan, London, 1973, p 1.
(8) (a) E. C. Alyea, A. Costin, G. Ferguson, G. T. Fey, R. G. Goel, and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1294 (1975); (b) E. C. Alyea, G. T. Fey, and R. G. Goel, *J. Coord. Chem.*, **5**, 143 (1976); (c) R. G. Goel and W. O. Ogini, *Inorg. Chem.*, **16**, 1968 (1977); (d) R. G. Goel and R. Montemayor, *ibid.* **16**, 2183 (1977).
(9) E. C. Alyea, S. A. Dias, R. G. Goel, and W. O. Ogini, *Can. J. Chem.*, **55**, 4227 (1977).
(10) (a) G. Ferguson, E. C. Alyea, R. J. Restivo, and P. J. Roberts, Paper HN8, American Crystallographic Association Spring Meeting, Asilomar, Calif., 1977; (b) E. C. Alyea, G. Ferguson, and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1845 (1977); (c) E. C. Alyea, S. A. Dias, G. Ferguson, and R. J. Restivo, *Inorg. Chem.*, **16**, 2329 (1977); (d) P. J. Roberts, G. Ferguson, R. G. Goel, W. O. Ogini, and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 253 (1978).
(11) R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940).
(12) G. B. Deacon and B. O. West, *J. Inorg. Nucl. Chem.*, **24**, 169 (1962).
(13) F. G. Moers and J. P. Langhout, *Recl. Trav. Chim. Pays-Bas*, **92**, 996 (1973).
(14) G. B. Deacon, J. H. S. Green, and D. J. Harrison, *Spectrochim. Acta, Part A*, **24a**, 1921 (1968).
(15) A. R. Davis, C. J. Murphy, and R. A. Plane, *Inorg. Chem.*, **9**, 423 (1970).
(16) S. C. Jain and R. Rivest, *Inorg. Chim. Acta*, **4**, 291 (1970).
(17) R. C. Makhija, A. L. Beauchamp, and R. Rivest, *J. Chem. Soc., Dalton Trans.*, 2447 (1973).
(18) N. A. Bell, M. Goldstein, T. Jones, and I. W. Nowell, *J. Chem. Soc., Chem. Commun.*, 1039 (1976).
(19) E. C. Alyea and S. A. Dias, unpublished results; slight increases in the value of J have been observed for the acetate complexes on changing the temperature from 303 to 183 K.
(20) L. S. Meriwether and J. R. Leto, *J. Am. Chem. Soc.*, **83**, 3192 (1961).
(21) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969).
(22) (a) J. P. Jesson and E. L. Muetterties in "Chemist's Guide", Marcel Dekker, New York, N.Y., 1969; (b) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).
(23) The crystal structure[10b] for (Cy$_3$P)Hg(SCN)$_2$ contains infinite chains of mercury atoms linked by bridging thiocyanato groups; each mercury atom has a distorted trigonal-pyramidal configuration. Vibrational spectra of other LHg(SCN)$_2$ complexes with bulky phosphine ligands are compatible with similar structures.[9]
(24) M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson, and W. A. G. Graham, *J. Am. Chem. Soc.*, **91**, 291 (1969).
(25) (a) B. E. Mann, *Inorg. Nucl. Chem. Lett.*, 7, 595 (1971); (b) J. F. Malone and B. E. Mann, *ibid.*, **8**, 819 (1972).
(26) C. A. Streuli, *Anal. Chem.*, **32**, 985 (1960).
(27) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).
(28) The C–P–C angles in Hg(NO)$_3$)$_2$(PCy$_3$)[10c] and Hg(SCN)$_2$(PCy$_3$)[10b] are near 109° as compared to C–P–C angles of 107° (average) in (Ph$_3$P)$_2$Hg(SCN)$_2$[17] and near 104° in other triphenylphosphine complexes.[29]
(29) (a) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1427 (1974); (b) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc. A*, 2970 (1968).
(30) B. E. Mann, *J. Chem. Soc., Perkin Trans. 2*, 30 (1972).
(31) S. O. Grim and A. W. Yankowsky, *J. Org. Chem.*, **42**, 1236 (1977).
(32) P. W. A. Dean and O. G. Ibbott, *Can. J. Chem.*, **54**, 177 (1976).