

are expected to be slower, individual linkage isomers have been detected in solution at ambient temperature by ^{31}P NMR spectroscopy.^{13,14,19-21}

The results summarized in Table III clearly indicate that all three linkage isomers, 1-3, can be detected in appreciable concentrations for solutions of complexes of the type (diphosphine)Pd(CNS)₂ at low temperatures. For the dimer (dpm)₂Pd₂(CNS)₂, only two linkage isomers 4 and 5 are detectable in solution at low temperature.

There are significant solvent effects on the proportions of linkage isomers in solution. For the (diphosphine)Pd(CNS)₂ complexes, the all-sulfur-bound linkage isomer 1 is present in greater proportions in the chlorinated solvents than in the carbonyl containing solvents. Conversely the all-nitrogen-bound linkage isomer 3 is found in greater relative quantities in the carbonyl containing solvent than in the chlorinated solvents. For (dpm)₂Pd₂(CNS)₂, the effect of solvent on the proportions of linkage isomers is less marked, and in no solvent is a detectable amount of the all nitrogen bound isomer 6 present.

Notice that the solvent effects observed for the (diphosphine)Pd(CNS)₂ complexes are opposite those reported earlier for (Ph₃P)₂Pd(CNS)₂ and some other palladium(II)

thiocyanate complexes.²² From infrared spectral measurements it was noted that *N,N*-dimethylformamide (along with dimethyl sulfoxide) was one of several solvents favoring sulfur coordination while chlorocarbon solvents stabilized nitrogen coordination. On the other hand studies of *cis*-(R₃P)₂Pt(CNS)₂ have shown that the proportion of NS linkage isomer relative to NN isomer is larger in dichloromethane than in dimethyl sulfoxide.^{19,20} The linkage isomerization of the thiocyanate ligand is object to many subtle effects, and a consistent pattern of some of these has yet to emerge. It is clear from the distribution of isomers in solution and the ability to selectively crystallize certain linkage isomers by the choice of solvent system that not only are steric effects operative in altering the balance between isomers but electronic and environmental effects all contribute to the stability of the individual isomers.

Acknowledgment. We thank the National Science Foundation (Grant CHE79 24575) for financial support.

Registry No. Pd₂(dpm)₂(SCN)₂, 68079-56-1; Pd₂(dpm)(SCN)(NCS), 68447-96-1; Pd(dpm)(SCN)₂, 51320-63-9; Pd(dpm)(SCN)(NCS), 76793-83-4; Pd(dpm)(NCS)₂, 80293-85-2; Pd(dpe)(SCN)₂, 19998-22-2; Pd(dpe)(SCN)(NCS), 29893-44-5; Pd(dpe)(NCS)₂, 69237-91-8; Pd(dpv)(SCN)₂, 41278-37-9; Pd(dpv)(SCN)(NCS), 80293-86-3; Pd(dpv)(NCS)₂, 80293-87-4; Pd(dpp)(SCN)₂, 80293-88-5; Pd(dpp)(SCN)(NCS), 76793-82-3; Pd(dpp)(NCS)₂, 51886-81-8.

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Correlation between NMR Coupling Constants and Molecular Structure. Synthesis and ^{31}P NMR Measurements of [HgX₂(*cis*-Ph₂PCH=CHPh₂)] and X-ray Crystal Structures of [HgBr₂(*cis*-Ph₂PCH=CHPh₂)], [Hg(NO₃)₂(PPh₃)₂], and [Hg(CN)₂(PPh₃)₂]

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Received April 28, 1981

The complexes [HgX₂(*cis*-Ph₂PCH=CHPh₂)] (X = ac, Cl, Br, I, CN, (EtO)₂PO) have been synthesized and studied by ^{31}P NMR methods. Results of the X-ray structure analyses of [Hg(CN)₂(PPh₃)₂] (I), [Hg(NO₃)₂(PPh₃)₂] (II), and [HgBr₂(*cis*-Ph₂PCH=CHPh₂)] (III) are presented. Changes of $^1J(^{199}\text{Hg}, ^{31}\text{P})$ (2.6-5.9 kHz) in complexes of the general type [HgX₂P₂] are correlated to changes in the bond angles $\theta(\text{P}, \text{Hg}, \text{P})$ (80-150°) and $\theta(\text{X}, \text{Hg}, \text{X})$ (70-113°). A two-dimensional function $^1J(^{199}\text{Hg}, ^{31}\text{P}) = f[\theta(\text{P}, \text{Hg}, \text{P}), \theta(\text{X}, \text{Hg}, \text{X})]$ is presented, whose general form was investigated by EHMO calculations on the model compound [HgCl₂(PPh₃)₂], whereas its numerical parameters were derived from the available structural and spectroscopic data by linear regression. Chemical formula, lattice constants (esd), crystal system, space group, and Z for compounds I, II, and III are as follows: C₃₈H₃₀HgN₂P₂, 18.023 (5) Å, 18.262 (4) Å, 10.032 (3) Å, orthorhombic, *Pn*2₁a, 4; C₃₆H₃₀HgN₂O₆P₂, 13.415 (3) Å, 14.004 (4) Å, 17.874 (3) Å, 91.72 (2)°, monoclinic, *C2/c*, 4; C₂₆H₂₂Br₂HgP₂, 8.773 (5), 18.952 (2), 7.710 (2) Å, 101.77 (3)°, monoclinic, *P2*₁/*m*, 2.

Introduction

There have been a number of recent studies concerned with the effects of coordination number and anion on ^{31}P NMR parameters for the complexes [HgX₂(PR₃)₂],² [HgX₂PR₃],^{3,4}

and [HgXPR₃]⁺,⁵ where X is an anion and PR₃ stands for a tertiary phosphine. These reports have considered changes in $\delta(^{31}\text{P})$ and $^1J(^{199}\text{Hg}, ^{31}\text{P})$ primarily in terms of changes in electronic properties. Using solid-state data, we have shown for some complexes [HgX₂(PPh₃)₂] that marked deviations in molecular structure from ideal tetrahedral bond angles and standard bond distances may occur.⁶ A juxtaposition of the

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solid-state structural data and the experimental solution ^{31}P NMR data shows $^1J(^{199}\text{Hg}, ^{31}\text{P})$ values changing about 3 kHz when the Hg–P bond lengths, $d(\text{Hg}, \text{P})$, and P–Hg–P bond angles, $\theta(\text{P}, \text{Hg}, \text{P})$, change by about 0.1 Å and 20° , respectively. Large coupling constants are accompanied by small $\theta(\text{X}, \text{Hg}, \text{X})$, long $d(\text{Hg}, \text{X})$, large $\theta(\text{P}, \text{Hg}, \text{P})$ short $d(\text{Hg}, \text{P})$, and anions with poor σ -donating capability.⁶ Moreover, we interpreted our $^1J(^{199}\text{Hg}, ^{31}\text{P})$ and X-ray structural data on the basis of electronic arguments derived from extended Hückel MO calculations (EHMO), thus providing predictive value to the empirical correlation.⁶ From the calculations, the dependence of the coupling constant on bond-length changes was shown to be of lesser importance than the dependence on angular changes.

The calculations also suggested that $^1J(^{199}\text{Hg}, ^{31}\text{P})$ should change as described above even if a single structural parameter were to be varied and the others held constant. This is somewhat difficult to confirm experimentally, because in most compounds the various factors affecting the nuclear spin–spin interactions are coupled. In complexes of the type $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)]$, at least one parameter is more or less fixed: the angle $\theta(\text{P}, \text{Hg}, \text{P})$ is constrained to a value of $\sim 80^\circ$ due to the chelate nature of the phosphine. The ethylenic version of diphos was chosen in order to minimize the known tendency of chelating phosphines to form higher molecular weight complexes as a consequence of rotation about the carbon–carbon bond.⁷ We have prepared a series of hitherto unknown $\text{cis-Ph}_2\text{PCH=CHPPh}_2$ chelating complexes of Hg^{2+} and report here ^{31}P NMR data for the series $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)]$, structural results for $[\text{Hg}(\text{CN})_2(\text{PPh}_3)_2]$, $[\text{Hg}(\text{NO}_3)_2(\text{PPh}_3)_2]$, and $[\text{HgBr}_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)]$, as well as EHMO calculations on the model compound $[\text{HgCl}_2(\text{PPh}_3)_2]$. All available data are combined into the two-dimensional function $^1J(^{199}\text{Hg}, ^{31}\text{P}) = f\{\theta(\text{P}, \text{Hg}, \text{P}), \theta(\text{X}, \text{Hg}, \text{X})\}$, whose form is obtained from EHMO calculations whereas its numerical parameters are derived via multiple linear regression from the available structural and spectroscopic data.

Results

A. X-ray Structures. In all three complexes, the mercury coordination is distorted tetrahedral with four strong bonds (Table I). Similar geometries are found in $[\text{HgI}_2(\text{PPh}_3)_2]$, $[\text{Hg}(\text{SCN})_2(\text{PPh}_3)_2]$, and $[\text{Hg}(\text{CF}_3)_2(\text{PPh}_3)_2]$. We will begin with a brief discussion of the coordination geometries at both mercury and phosphorus and follow with an overview of mercury–ligand distances and angles for all compounds used later in the paper.

$[\text{Hg}(\text{CN})_2(\text{PPh}_3)_2]$. The two Hg–P bond lengths, at 2.434 (5) and 2.589 (5) Å, are significantly different (22.1σ) from each other; the larger value is close to the sum of the covalent radii of Hg and P (1.48 Å + 1.10 Å = 2.58 Å).⁸ The Hg–C bond lengths of 2.19 and 2.27 Å are also different (2.2σ), with the shorter bond length close to the sum of the covalent radii of Hg and C (1.48 Å + 0.68 Å = 2.16 Å).⁸

The deviation of bond angles at Hg from C_{2v} symmetry is significant: the short P(1)–Hg bond bends toward and the

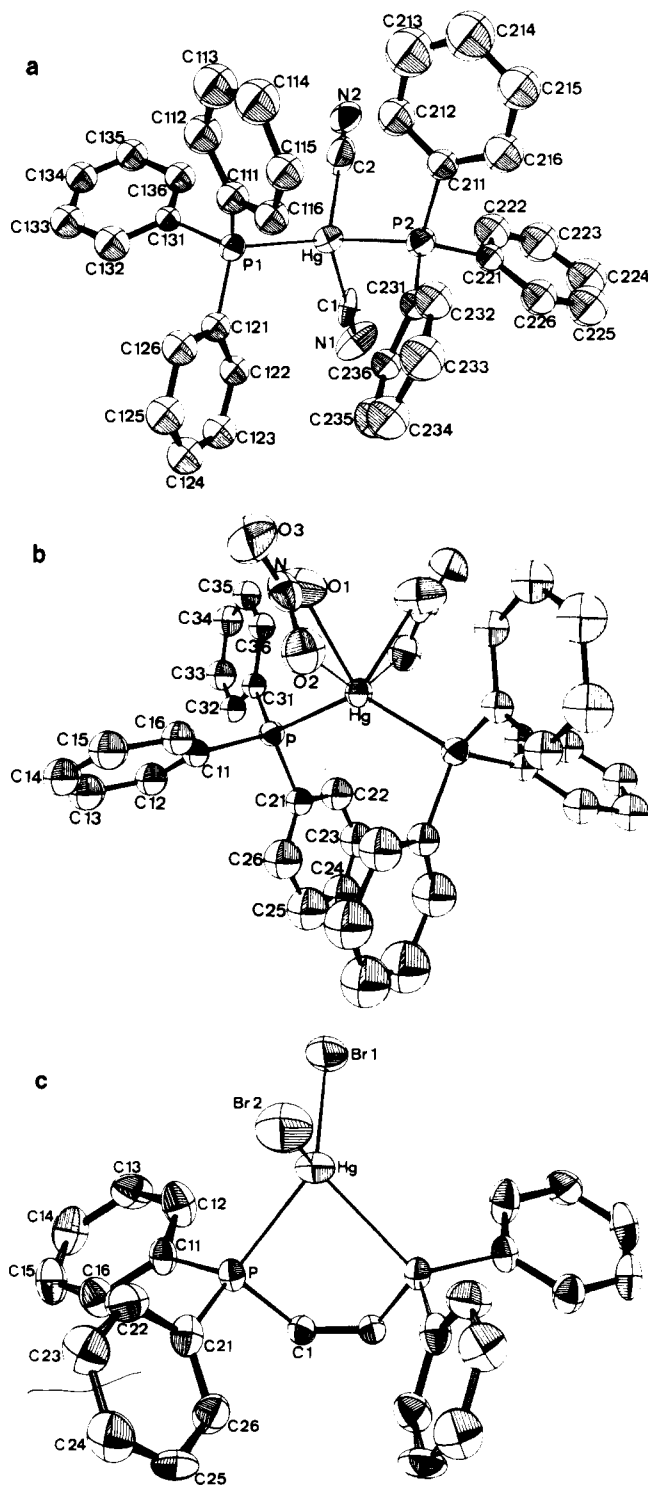


Figure 1. Molecular conformation and atom numbering for the complexes (a) $[\text{Hg}(\text{CN})_2(\text{PPh}_3)_2]$, (b) $[\text{Hg}(\text{NO}_3)_2(\text{PPh}_3)_2]$, and (c) $[\text{HgBr}_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)]$.

long P(2)–Hg bond bends away from the C(1)HgC(2) plane (rocking deformation). The result is that the angles P(1)–HgC(1) and P(1)HgC(2) (116.7 and 114.7° , respectively) are larger than the angles P(2)HgC(1) and P(2)HgC(2) (103.8 and 103.6° , respectively). The structure is thus between a tetrahedron and trigonal pyramid and may be interpreted as lying on the reaction path of the reaction $[\text{Hg}(\text{CN})_2(\text{PPh}_3)_2]$ (tetrahedral) \rightarrow $[\text{Hg}(\text{CN})_2(\text{PPh}_3)]$ (trigonal) + PPh_3 (Table Ia and Figure 1a).

$[\text{Hg}(\text{NO}_3)_2(\text{PPh}_3)_2]$ has crystallographic C_2 symmetry relating the two phosphine and two nitrate groups. The Hg–P bond length (2.451 Å) is considerably shorter than the sum

(7) We have recently determined the structure of $[\text{Hg}(\text{CN})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ and found it to be polymeric: L. Zambonelli, R. Coruso, R. W. Kunz, and P. S. Pregosin, unpublished results. See also K. Aurivillius and K. Wendel, *Acta Crystallogr., Sect. B*, **B32**, 2941 (1976).

(8) Covalent radii are from ref 9. The carbon radius in CN toward Hg has been chosen somewhat arbitrarily as 0.68 Å. This value together with the C–C single-bond covalent radius of 0.77 Å reproduces C–C single bond lengths in $\text{CH}_3\text{—C=CH}$ and $\text{CH}_3\text{—C=N}$ (see ref 10).

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Table I. Interatomic Distances (Å) and Angles (Deg)

a. $\text{Hg}(\text{PPh}_3)_2(\text{CN})_2$					
Hg-P(1)	2.434 (5)	C(121)-C(122)	1.39 (3)	C(215)-C(216)	1.40 (4)
Hg-P(2)	2.589 (5)	C(122)-C(123)	1.37 (3)	C(216)-C(211)	1.36 (3)
Hg-C(1)	2.19 (2)	C(123)-C(124)	1.38 (4)	C(221)-C(222)	1.39 (3)
Hg-C(2)	2.27 (3)	C(124)-C(125)	1.30 (3)	C(222)-C(223)	1.40 (4)
P(1)-C(111)	1.83 (2)	C(125)-C(126)	1.38 (3)	C(223)-C(224)	1.42 (5)
P(1)-C(121)	1.79 (2)	C(126)-C(121)	1.35 (3)	C(224)-C(225)	1.32 (4)
P(1)-C(131)	1.84 (2)	C(131)-C(132)	1.36 (3)	C(225)-C(226)	1.40 (4)
P(2)-C(211)	1.85 (2)	C(132)-C(133)	1.40 (4)	C(226)-C(221)	1.41 (3)
P(2)-C(221)	1.84 (2)	C(133)-C(134)	1.35 (3)	C(231)-C(232)	1.43 (3)
P(2)-C(231)	1.76 (2)	C(134)-C(135)	1.30 (3)	C(232)-C(233)	1.34 (4)
C(111)-C(112)	1.43 (3)	C(135)-C(136)	1.49 (3)	C(233)-C(234)	1.40 (4)
C(112)-C(113)	1.38 (4)	C(136)-C(131)	1.33 (3)	C(234)-C(235)	1.33 (4)
C(113)-C(114)	1.38 (4)	C(211)-C(212)	1.36 (3)	C(235)-C(236)	1.35 (3)
C(114)-C(115)	1.39 (4)	C(212)-C(213)	1.40 (4)	C(236)-C(231)	1.42 (3)
C(115)-C(116)	1.40 (3)	C(213)-C(214)	1.35 (5)	C(1)-N(1)	1.13 (3)
C(116)-C(111)	1.39 (3)	C(214)-C(215)	1.39 (4)	C(2)-N(2)	1.13 (3)
P(1)-Hg-P(2)	108.9 (2)	P(1)-C(131)-C(132)	121 (2)		
P(1)-Hg-C(1)	116.7 (10)	P(1)-C(131)-C(136)	118 (2)		
P(1)-Hg-C(2)	114.7 (6)	C(132)-C(131)-C(136)	121 (2)		
P(2)-Hg-C(1)	103.8 (5)	C(131)-C(132)-C(133)	120 (2)		
P(2)-Hg-C(2)	103.6 (7)	C(132)-C(133)-C(134)	119 (2)		
C(1)-Hg-C(2)	107.8 (12)	C(133)-C(134)-C(135)	124 (2)		
Hg-P(1)-C(111)	108.9 (7)	C(134)-C(135)-C(136)	118 (2)		
Hg-P(1)-C(121)	111.8 (7)	C(135)-C(136)-C(131)	118 (2)		
Hg-P(1)-C(131)	116.4 (6)	C(211)-P(2)-C(221)	102 (1)		
Hg-P(2)-C(211)	115.4 (7)	C(221)-P(2)-C(231)	110 (1)		
Hg-P(2)-C(221)	111.1 (6)	C(221)-P(2)-C(231)	107 (1)		
Hg-P(6)-C(231)	111.1 (7)	P(2)-C(211)-C(212)	117 (2)		
Hg-C(1)-N(1)	178 (1)	P(2)-C(211)-C(216)	121 (2)		
Hg-C(2)-N(2)	177 (2)	C(212)-C(211)-C(216)	122 (2)		
C(111)-P(1)-C(12)	107 (1)	C(211)-C(212)-C(213)	119 (2)		
C(111)-P(1)-C(131)	104 (1)	C(212)-C(213)-C(214)	121 (3)		
C(121)-P(1)-C(131)	109 (1)	C(213)-C(214)-C(215)	120 (3)		
P(1)-C(111)-C(112)	122 (2)	C(214)-C(215)-C(216)	120 (3)		
P(1)-C(111)-C(116)	118 (2)	C(215)-C(216)-C(211)	119 (2)		
C(112)-C(111)-C(116)	119 (2)	P(2)-C(221)-C(222)	118 (2)		
C(111)-C(112)-C(113)	120 (2)	P(2)-C(221)-C(226)	122 (2)		
C(112)-C(113)-C(114)	121 (3)	C(222)-C(221)-C(226)	120 (2)		
C(113)-C(114)-C(115)	120 (2)	C(221)-C(222)-C(223)	119 (3)		
C(114)-C(115)-C(116)	120 (2)	C(222)-C(223)-C(224)	120 (3)		
C(115)-C(116)-C(111)	120 (2)	C(223)-C(224)-C(225)	121 (3)		
P(1)-C(121)-C(122)	116 (2)	C(224)-C(225)-C(226)	121 (3)		
P(1)-C(121)-C(126)	125 (2)	C(225)-C(226)-C(221)	119 (2)		
C(122)-C(121)-C(126)	118 (2)	P(2)-C(231)-C(232)	125 (2)		
C(121)-C(122)-C(123)	120 (2)	P(2)-C(231)-C(236)	119 (2)		
C(122)-C(123)-C(124)	120 (2)	C(232)-C(231)-C(236)	116 (2)		
C(123)-C(124)-C(125)	119 (2)	C(231)-C(232)-C(233)	120 (2)		
C(124)-C(125)-C(126)	123 (2)	C(232)-C(233)-C(234)	122 (2)		
C(125)-C(126)-C(121)	120 (2)	C(233)-C(234)-C(235)	120 (3)		
		C(234)-C(235)-C(236)	120 (2)		
		C(235)-C(236)-C(231)	122 (2)		
b. $\text{Hg}(\text{PPh}_3)_2(\text{NO}_3)_2^a$					
Hg-P	2.451 (1)	C(14)-C(15)	1.383 (7)	C(31)-C(32)	1.383 (4)
Hg-O(1)	2.507 (4)	C(15)-C(16)	1.385 (7)	C(32)-C(33)	1.391 (7)
Hg...O(2)	2.790 (4)	C(16)-C(11)	1.396 (6)	C(33)-C(34)	1.355 (7)
P-C(11)	1.807 (4)	C(21)-C(22)	1.374 (4)	C(34)-C(35)	1.384 (7)
P-C(21)	1.815 (4)	C(22)-C(23)	1.394 (8)	C(35)-C(36)	1.392 (7)
P-C(31)	1.815 (4)	C(23)-C(24)	1.334 (9)	C(36)-C(31)	1.395 (6)
C(11)-C(12)	1.388 (6)	C(24)-C(25)	1.340 (11)	N-O(1)	1.239 (6)
C(12)-C(13)	1.387 (6)	C(25)-C(26)	1.464 (10)	N-O(2)	1.238 (6)
C(13)-C(14)	1.368 (7)	C(26)-C(21)	1.353 (8)	N-O(3)	1.231 (6)
P-Hg-P'	131.76 (3)	P-C(21)-C(22)	118.5 (3)		
P-Hg-O(1)	96.37 (12)	P-C(21)-C(26)	121.2 (4)		
P-Hg-O(1)'	123.95 (11)	C(22)-C(21)-C(26)	120.2 (5)		
O(1)-Hg-O(1)'	70.01 (14)	C(21)-C(22)-C(23)	120.5 (5)		
Hg-O(1)-N	105.5 (3)	C(22)-C(23)-C(24)	119.3 (6)		
Hg-P-C(11)	114.4 (1)	C(23)-C(24)-C(25)	123.0 (6)		
Hg-P-C(21)	106.2 (1)	C(24)-C(25)-C(26)	118.1 (6)		
Hg-P-C(31)	115.9 (1)	C(25)-C(26)-C(21)	118.7 (6)		

Table I (Continued)

C(11)-P-C(21)	106.1 (2)		P-C(31)-C(32)	121.4 (3)	
C(11)-P-C(31)	106.1 (2)		P-C(31)-C(36)	119.3 (3)	
C(21)-P-C(31)	107.6 (2)		C(32)-C(31)-C(36)	119.3 (4)	
P-C(11)-C(12)	118.8 (3)		C(31)-C(32)-C(33)	120.1 (4)	
P-C(11)-C(16)	120.7 (3)		C(32)-C(33)-C(34)	120.5 (4)	
C(12)-C(11)-C(16)	120.4 (4)		C(33)-C(34)-C(35)	120.5 (5)	
C(11)-C(12)-C(13)	119.3 (4)		C(34)-C(35)-C(36)	119.6 (4)	
C(12)-C(13)-C(14)	120.5 (4)		C(35)-C(36)-C(31)	119.9 (4)	
C(13)-C(14)-C(15)	120.4 (4)		O(1)-N-O(2)	116.6 (4)	
C(14)-C(15)-C(16)	120.3 (4)		O(1)-N-O(3)	120.7 (4)	
C(15)-C(16)-C(11)	119.1 (4)		O(2)-N-O(3)	122.7 (4)	
c. Hg(PC=CP)Br ₂ ^b					
Hg-P	2.572 (2)	C(11)-C(12)	1.38 (2)	C(21)-C(22)	1.38 (2)
Hg-Br(1)	2.545 (2)	C(12)-C(13)	1.38 (2)	C(22)-C(23)	1.38 (2)
Hg-Br(2)	2.560 (2)	C(13)-C(14)	1.42 (2)	C(23)-C(24)	1.39 (2)
P-C(1)	1.816 (9)	C(14)-C(15)	1.35 (2)	C(24)-C(25)	1.38 (2)
P-C(11)	1.822 (9)	C(15)-C(16)	1.39 (2)	C(25)-C(26)	1.41 (2)
P-C(21)	1.801 (12)	C(16)-C(11)	1.41 (1)	C(26)-C(21)	1.38 (2)
C(1)-C(1)'	1.32 (2)				
P-Hg-P'	80.5 (1)	C(12)-C(11)-C(16)	121.1 (10)		
P-Hg-Br(1)	117.4 (1)	C(11)-C(12)-C(13)	119.7 (11)		
P-Hg-Br(2)	112.6 (1)	C(12)-C(13)-C(14)	118.6 (11)		
Br(1)-Hg-Br(2)	112.7 (1)	C(13)-C(14)-C(15)	122.3 (10)		
Hg-P-C(1)	102.4 (3)	C(14)-C(15)-C(16)	119.5 (11)		
Hg-P-C(11)	122.5 (3)	C(15)-C(16)-C(11)	118.9 (11)		
Hg-P-C(21)	111.1 (3)	P-C(21)-C(22)	118.3 (9)		
C(1)-P-C(11)	104.4 (4)	P-C(21)-C(26)	121.5 (8)		
C(1)-P-C(21)	106.8 (5)	C(22)-C(21)-C(26)	120.0 (11)		
C(11)-P-C(21)	108.3 (4)	C(21)-C(22)-C(23)	120.9 (11)		
P-C(1)-C(1)'		C(22)-C(23)-C(24)	120.1 (11)		
P-C(11)-C(12)	118.2 (8)	C(23)-C(24)-C(25)	119.1 (11)		
P-C(11)-C(16)	120.7 (8)	C(24)-C(25)-C(26)	121.2 (12)		
		C(25)-C(26)-C(21)	118.8 (11)		

^a Primed atoms are related to the unprimed atoms by the transformation $-x, y, 1/2 - z$. ^b Primed atoms are related to the unprimed atoms by the transformation $x, 1/2 - y, z$.

of the covalent radii of Hg and P (2.58 Å), whereas the Hg-O bond length of 2.507 Å is 0.37 Å longer than the sum of the covalent radii of the atoms involved [1.48 Å + 0.66 Å = 2.14 Å]. The PHgP and OHgO planes form an angle of 65°, thus lowering the local symmetry at Hg from C_{2v} to C₂. A second oxygen of each nitrate group is involved in a weak contact of 2.79 Å to mercury, leading to a six-coordinated bicapped tetrahedral mercury (Table Ib and Figure 1b).

[HgBr₂(*cis*-Ph₂PCH=CHPh₂)] shows a mirror plane containing mercury and the two bromine atoms. The Hg-P and Hg-Br bond lengths (2.575 and 2.552 Å, respectively) are close to normal (2.58 and 1.48 Å + 1.11 Å = 2.59 Å, respectively). The symmetry is lowered from C_{2v} to C_s by a rocking movement of the two bromine atoms in the mirror plane, thus giving a larger PHgBr(1) angle (117.4°) than PHgBr(2) angle (112.6°), a deformation analogous to that observed for triphenylphosphine in [Hg(CN)₂(PPh₃)₂]. As expected, the P-Hg-P angle of 80° is much less than the tetrahedral angle but similar to what one expects for such a chelating structure.¹¹ We note that in [HgCl₂(Ph₂PCH₂CH₂NET₂)], which also contains a chelating five-membered ring,¹² the P-Hg-N angle is 77° and that in [Hg(SCN)₂(NH₂CH₂CH₂NH₂)], also with a chelating ring, the N-Hg-N angle is 77°.¹³

The Br-Hg-Br angle, 113°, is only slightly larger than 109°; but taken together with the somewhat short Hg-Br distance and the longish Hg-P distance, we have the impression that

the chelating phosphine does not complex the metal as well as PPh₃ and that this should be reflected in the solution ³¹P NMR data (Table Ic and Figure 1c).

The Coordination about phosphorus in all three complexes is distorted tetrahedral with approximate local C_{3v} symmetry. HgPC angles average 112.5, 112.2, and 112.0°, respectively, and CPC angles 106.5, 106.6, and 106.5°, respectively. Our mean values for the CPC angles are in agreement with those reported for [HgI₂(PPh₃)₂],¹⁴ [HgI₂(Ph₂PCH₂-CH₂SCH₂CH₂PPh₂)],¹⁵ and [Hg(SCN)₂(PPh₃)₂],¹⁶ viz., 105.5, 106.2, and 107.2°, respectively. The CPC angles are larger in metal complexes than in free triphenylphosphine (103°)¹⁷ but smaller than the ideal tetrahedral angle of 109.5°. This is in keeping with a partial phosphonium character of coordinated phosphine. The mean P-C bond lengths, (1.82 (2), 1.81 (1), and 1.81 (1) Å, respectively) and aromatic C-C bond lengths (1.38 (1), 1.38 (3), and 1.39 (2) Å, respectively) in the three complexes are in agreement with values found for the free phosphine (Table I).

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Table II. Coordination Geometry around Hg and $J(^{199}\text{Hg}, ^{31}\text{P})$ Coupling Constants in Complexes of the Type $[\text{HgX}_2(\text{PR}_3)_2]$

phosphine	anion	bond angles ^a		bond dist, Å		$J(\text{Hg,P})_{\text{obsd}}^{36\text{ b}}$	$J(\text{Hg,P})_{\text{calcd}}^{\text{b}}$	Δ^{b}	% Δ	ref
		$\theta(\text{P,Hg,P})$	$\theta(\text{X,Hg,X})$	$d(\text{Hg,P})$	Δ					
Influence of X for $\text{PR}_3 = \text{PPh}_3$										
$(\text{PPh}_3)_2$	$(\text{NO}_3)_2$	131.8	70.0	2.451	1.85	5928	5753	175	(3.1)	
$(\text{PPh}_3)_2$	$(\text{SCN})_2$	118.1	96.7	2.488	1.53	3726	4110	384	(10.3)	16
$(\text{PPh}_3)_2$	$(\text{CN})_2$	108.9	107.8	2.512	(1.54) ^d	(2617) ^d	(3338)	(721)	(27.6)	
$(\text{PPh}_3)_2$	I_2	109.0	110.4	2.566	1.47	3074	3214	140	(4.6)	14
$(\text{PPh}_3)_2$	$(\text{CF}_3)_2$	94.8	146.6	2.91	1.35					18
Influence of the Phosphine for the Same Anion										
$(\text{PET}_3)_2$	Cl_2	158.5	105.5	2.39	1.69	5117	4696	-421	(-8.2)	19
PP^{c}	Cl_2	125.6	97.0	2.497	1.53	4671	4283	-388	(-8.3)	20
$(\text{CH}_3)_2\text{PP}(\text{CH}_3)_2$	Cl_2	119.1	101.2	2.490	1.54	polymeric				21
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$	$(\text{CN})_2$	113.5	109.5	2.570	1.50	polymeric				20
$(\text{PPh}_3)_2$	$(\text{CN})_2$	108.9	107.8	2.512	(1.54) ^d	(2617) ^d	(3338)	(721)	(27.6)	
PP	I_2	145	116	2.505	1.56	3624	3846	222	(6.1)	20
$\text{Ph}_2\text{P}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{PPh}_2$	I_2	122.8	112.5	2.515	1.53	3420	3459	39	(1.1)	15
$(\text{PPh}_3)_2$	I_2	109.0	110.4	2.566	1.47	3074	3214	140	(4.6)	14
$\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2$	I_2	100.8	108.9	2.579	1.49	polymeric				22
Miscellaneous										
$(\text{P}(\text{C}_6\text{H}_{11})_3)_2$	$(\text{CH}_3\text{COO})_2$	149.8	82.6	2.440	1.77	5232	5592	360	(6.9)	34
$\text{Ph}_2\text{PCH}=\text{CHPPH}_2$	Br_2	80.5	112.7	2.575	1.44	2547	2386	-161	(-6.3)	

^a Angles given in degrees. ^b Coupling constants given in hertz. ^c PP = 2,11-bis[(diphenylphosphino)methyl]benzo[c]phenanthrene. ^d See Discussion.

Structural Results for $[\text{HgX}_2(\text{PR}_3)_2]$ Complexes. The results given here and those reported by a number of other workers are averaged to correspond to C_{2v} symmetry and are shown in Table II. A number of trends may be discerned. First, the Hg-P bond lengths in complexes of the type $[\text{HgX}_2(\text{PPh}_3)_2]$ lie in the range 2.45–2.91 Å. As noted previously,⁶ those Hg-P bond lengths that tend to be shorter than the sum of the covalent radii of mercury and phosphorus (2.58 Å) are associated with X ligands that coordinate only weakly to mercury. The bond lengths $d(\text{Hg,X})$, on the other hand, cannot be compared directly because the anions X in these complexes have different covalent radii (r_X).⁸ However, variations of the value $\Delta = d(\text{Hg,X}) - r_X$ can be taken as a measure of the variation of the Hg-X bond length and range between 1.35 and 1.85 Å in these complexes (Table II). The angles $\theta(\text{X,Hg,X})$ and $\theta(\text{P,Hg,P})$ also change considerably (70–146° and 80–158°, respectively). These differences in distances and angles follow a definite pattern: short Hg-P bond lengths occur with long Hg-X bonds and vice versa. In those structures where the P-Hg-P angle is large, the X-Hg-X angle is short and vice versa. Furthermore, short bond lengths are accompanied by large angles. This behavior has been rationalized in terms of overlap populations obtained from EHMO calculations.⁶ A second trend concerns complexes with a given anion but varying phosphine. In these cases the angle $\theta(\text{X,Hg,X})$ is the same to within ~7°, whereas the angle $\theta(\text{P,Hg,P})$ varies widely and seems to depend on the steric and electronic requirements of the phosphine ligand (Table II).

Overall, the range of structures encompassed by the compounds in Table II is remarkable: $d(\text{Hg,P})$ varies by 0.52 Å, Δ by 0.43 Å, $\theta(\text{P,Hg,P})$ by 78°, and $\theta(\text{X,Hg,X})$ by 76°.

B. ^{31}P Chemical Shift Data. The chemical shift data, $\delta(^{31}\text{P})$, show the phosphorus resonance for the chelating phosphine at higher field than the resonance for the PPh_3 complexes. Since ^{31}P chemical shifts usually appear at much lower field when the phosphorus atom is part of a five-membered ring²³ (relative to the analogous monodentate phosphine complexes), our data are somewhat unusual. Specifically, the coordination chemical shifts $\Delta\delta$ ($\delta(\text{complex}) - \delta(\text{free ligand})$), for $[\text{HgCl}_2(\text{PPh}_3)_2]$ and $[\text{HgCl}_2(\text{cis-Ph}_2\text{PCH}=\text{CHPPH}_2)]$ are 34.1

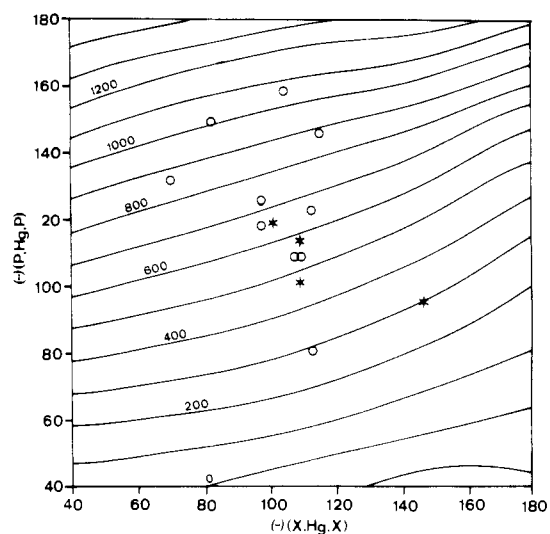


Figure 2. Contour diagram for $^1J(^{199}\text{Hg}, ^{31}\text{P})$ calculated by EHMO as a function of $\theta(\text{P,Hg,P})$ and $\theta(\text{Cl,Hg,Cl})$. Also shown are points for which experimental structural and NMR data (O) or structural data only (*) are available.

and 26.2, respectively. It is not immediately obvious whether this observation is related to some special characteristic of the phosphine or to an effect related to the distorted geometry of the mercury complexes. Coupling constants will be discussed below.

C. EHMO Calculations. On the basis of EHMO calculations we suggested that $^1J(^{199}\text{Hg}, ^{31}\text{P})$ should show a dependence on $\theta(\text{P,Hg,P})$ and $\theta(\text{X,Hg,X})$,⁶ i.e., there exists a surface in the three-dimensional space spanned by $J(\text{Hg,P})$, $\theta(\text{P,Hg,P})$, and $\theta(\text{X,Hg,X})$ describing the dependence of J on the θ 's. The dependence of $J(\text{Hg,P})$ on one or the other of these angles reported in our earlier study⁶ represents special sections through the general surface. The calculations to model the series of compounds $[\text{HgX}_2(\text{PPh}_3)_2]$, X = NO_3 , SCN , I , and CN yield a special section too, since the angles around mercury are connected by a linear relationship ($\theta(\text{P,Hg,P}) = 172.9^\circ - 0.58\theta(\text{X,Hg,X})$; correlation coefficient $r^2 = 0.98$). Here we have calculated details of the full three-dimensional surface which might provide a facile tool for determining the possible

Table III. ^{31}P NMR Parameters of the Complexes $[\text{HgX}_2(\text{PPh}_3)_2]$ and $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPH}_2)]^a$

X	PPh ₃		(cis-Ph ₂ PCH=CHPPH ₂)		$\Delta J(\text{Hg,P})$
	$J(\text{Hg,P})$	δ	$J(\text{Hg,P})$	δ	
NO ₃	5928	40.3			
ac ^c	5510	34.4	3817	7.8	1693
Cl	4682	28.3	3103	3.1	1579
Br	4227	22.2	2547	-2.0	1680
SCN	3726	31.3	2288	7.5	1438
I	3074	7.2	2170	-12.6	904
CN ^c	2617	17.9	1525	7.2	1092
(EtO) ₂ PO ₂			690 ^b	8.8 ^b	

^a Chemical shifts are in ppm (± 0.1) and coupling constants in Hz (± 3). ^b $\delta((\text{EtO})_2\text{PO}_2) = 98.9$, $^1J(^{199}\text{Hg}, ^{31}\text{P}) = 7321$ Hz. ^c $\Delta J(\text{ac}, \text{CN})$ for PPh_3 is 2893 Hz and for $\text{cis-Ph}_2\text{PCH=CHPPH}_2$ is 2292.

angle combinations ($\theta(\text{P,Hg,P})/\theta(\text{X,Hg,X})$) on the basis of the readily measured NMR parameter. We neglect as we did before the influence of $d(\text{Hg,P})$ and $d(\text{Hg,X})$, which according to our previous calculations are of lesser importance.⁶

The form of the surface $J(\text{Hg,P}) = J\theta(\text{P,Hg,P}) + \theta(\text{X,Hg,X})$ was theoretically explored by using EHMO calculations on the previously described model compound $[\text{HgCl}_2(\text{PH}_3)_2]$.⁶ The result is shown in Figure 2. To a first approximation, the surface can be regarded as a plane (slightly warped) of approximate form $J(\text{Hg,P}) = a + b\theta(\text{P,Hg,P}) + c\theta(\text{Cl,Hg,Cl})$ with b positive and c negative.

Discussion

First we compare the calculated surface with the trends observed experimentally: Starting from any point on the calculated surface, $J(\text{Hg,P})$ increases with increasing $\theta(\text{P,Hg,P})$ and decreasing $\theta(\text{Cl,Hg,Cl})$. This is the same trend as observed for the experimental values of $J(\text{Hg,P})$, $\theta(\text{P,Hg,P})$, and $\theta(\text{X,Hg,X})$ (Figure 2 and Table II). For a given value of $\theta(\text{Cl,Hg,Cl})$ we may compare $J(\text{Hg,P})$ values calculated for $\theta(\text{P,Hg,P}) \sim 80^\circ$ (representative of the complexes $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPH}_2)]$), with $J(\text{Hg,P})$ values calculated for $\theta(\text{P,Hg,P}) = 172.9 - 0.58\theta(\text{Cl,Hg,Cl})$ (representative of the complexes $[\text{HgX}_2(\text{PPh}_3)_2]$). The calculated coupling constants for the former are smaller than those for the latter, and the same trend is observed experimentally: For each X, the observed $J(\text{Hg,P})$ is smaller for $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPH}_2)]$ than for $[\text{HgX}_2(\text{PPh}_3)_2]$ (Table III; remember that $\theta(\text{X,Hg,X})$ is found to be constant to within 7° for a given anion X). Another comparison concerns the rate of change of $J(\text{Hg,P})$ along the lines $\theta(\text{P,Hg,P}) \sim 80^\circ$ and $\theta(\text{P,Hg,P}) = 172.9 - 0.58\theta(\text{Cl,Hg,Cl})$, respectively. The rate of change is calculated to be smaller in the first case than in the second, and again the result of the model calculations is borne out by experiment: The change in $J(\text{Hg,P})$ between X = ac and X = I is only ~ 1700 Hz for the complexes $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPH}_2)]$, whereas it is ~ 2400 Hz for the complexes $[\text{HgX}_2(\text{PPh}_3)_2]$, or expressed more strongly, the values of $J(\text{Hg,P})$ for $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPH}_2)]$ show an approximately linear correlation with the values of $J(\text{Hg,P})$ for $[\text{HgX}_2(\text{PPh}_3)_2]$, and the slope of the regression is less than 1 ($J(\text{Hg,P})_{\text{cis-Ph}_2\text{PCH=CHPPH}_2} = -339 \text{ Hz} + 0.73J(\text{Hg,P})_{\text{PPh}_3}$; $r^2 = 0.96$). (The case X = CN is not included and will be discussed separately later.)

Since we have just demonstrated that the observed dependence of $J(\text{Hg,P})$ on $\theta(\text{P,Hg,P})$ and $\theta(\text{X,Hg,X})$ is reproduced qualitatively by EHMO calculations, we can now expand on these ideas. The coefficients, a , b , and c of the expression $J(\text{Hg,P}) = a + b\theta(\text{P,Hg,P}) + c\theta(\text{X,Hg,X})$ can be determined from all available experimental NMR and structural data (Table II) by means of a multiple linear regression, with the result $J(\text{Hg,P}) = 5851 \text{ Hz} + 25.1\theta(\text{P,Hg,P}) \text{ Hz/deg} -$

Table IV. Comparison of the Various Contributions to the Calculated $J(\text{Hg,P})^a$ ($J_{\text{tot}} = 100\%$)

$\theta(\text{P,Hg,P})$, deg	$\theta(\text{X,Hg,X})$, deg	% of J_{tot}		
		Fermi	spin-orbit	spin-dipole
80	158	97.92	-0.14	2.23
100	125	99.82	-0.16	0.33
120	91	99.97	-0.10	0.13
140	58	100.04	-0.10	0.06
160	24	100.39	-0.43	0.05

^a Calculated according to the method of Pople and Santry.³³

$48.7\theta(\text{X,Hg,X}) \text{ Hz/deg}$ ($r^2 = 0.93$). This equation describes an empirically fitted surface analogous to the one calculated by EHMO methods for $[\text{HgCl}_2(\text{PH}_3)_2]$.

Several points are in order: As expected, the coefficients b and c obtained from the experimental data have the same sign as those applicable to the EHMO data; however, the importance of $\theta(\text{P,Hg,P})$ and $\theta(\text{X,Hg,X})$ in determining $J(\text{Hg,P})$ is reversed. For the calculated surface, $\theta(\text{P,Hg,P})$ is more important; for the experimentally fitted surface, $\theta(\text{X,Hg,X})$ is dominant. At this point it is worth remembering that all EHMO calculations have been performed on $[\text{HgCl}_2(\text{P(H}_3)_2)]$ and therefore have not taken into account the influence of varying anions. Our previous calculations⁶ have shown that a consideration of the nature of the anion has the effect of making the changes due only to $\theta(\text{X,Hg,X})$ more pronounced.

The data in Table III may serve as a test for the numerical values assigned to a , b , and c . For example, the trends outlined for the structural behavior of the $[\text{HgX}_2(\text{PR}_3)_2]$ complexes allow an estimate of the geometry of $[\text{Hg}(\text{CH}_3\text{COO})_2(\text{cis-Ph}_2\text{PCH=CHPPH}_2)]$: Estimation of $\sim 80^\circ$ for $\theta(\text{P,Hg,P})$ from the steric constraint in $\text{cis-Ph}_2\text{PCH=CHPPH}_2$ and of $\sim 80^\circ$ for $\theta(\text{O,Hg,O})$ from the fact that $\theta(\text{X,Hg,X})$ is relatively constant for a given anion but different phosphines, $J(\text{Hg,P})$ is calculated to be ~ 4000 Hz, not far from the observed value of 3817 Hz.³⁵

Several critical remarks are also necessary. We have excluded the compound $[\text{Hg}(\text{CN})_2(\text{PPh}_3)_2]$ from the linear regression for the following reasons: First, its X-ray structure shows severe deviations from C_{2v} symmetry, with mercury-phosphorus distances of 2.43 and 2.59 Å. Second, possibly related, the change of $J(\text{Hg,P})$ with temperature (dJ/dT) is still unusually large in the temperature range 210–220 K. Similar phenomena interfere with the accurate determination of data for all compounds, though less severely. Nevertheless they affect the accuracy and reliability of the empirical correlation. Thus, the agreement between observed and calculated $J(\text{Hg,P})$ cannot be expected to be better than $\sim 10\%$ (see Experimental Section and Table VII).

Another point of concern is the coordinate $\theta(\text{X,Hg,X})$ in the fitted surface $J(\text{Hg,P}) = J(\theta(\text{X,Hg,X}), \theta(\text{P,Hg,P}))$. While $\theta(\text{X,Hg,X})$ is well-defined within the calculations on $[\text{HgCl}_2(\text{PH}_3)_2]$, it is poorly defined in the series of compounds investigated experimentally, since any angular change is combined with an alteration of the nature of the anion. In reality, changing $\theta(\text{X,Hg,X})$ from 70 to 96.7° is associated with changing the coordinating atom of the anion from an oxygen to a sulfur donor. The structural evidence, however, suggests that $\theta(\text{X,Hg,X})$ changes only slightly as long as X is the same. Thus $\theta(\text{X,Hg,X})$ would seem to express the combined effects of changing the structure and the anion. Similarly, the question arises as to whether or not changing the R groups in the phosphine might change the electronic properties of the ligating atom sufficiently to complicate the nature of the coordinate $\theta(\text{P,Hg,P})$. Furthermore, the conformational flexibility and the steric demands of the phosphines might ask their tribute. In the present work, at least the anions

Table V. Microanalytical Data and Molecular Weight Determinations of Complexes $\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)^a$

X	% C	% H	% P	% N	mol wt ^b
Cl	46.79 (46.76)	3.36 (3.32)	9.11 (9.27)		681 (667.9)
Br	41.20 (41.26)	2.91 (2.93)	8.12 (8.19)		827 (756.8)
I	37.22 (36.71)	2.69 (2.61)	7.54 (7.28)		849 (850.8)
SCN ^c	47.06 (47.16)	3.28 (3.11)	9.00 (8.69)	3.90 (3.93)	727 (713.2)
CN	51.83 (51.82)	3.47 (3.42)	9.13 (9.54)	4.35 (4.32)	760 (649.1)

^a Calculated values in parentheses. ^b In CH_2Cl_2 at 30 °C. ^c S, 9.23 (8.99).

Table VI. Crystal Data and Details of Data Collection and Structure Solution

	I $\text{Hg}(\text{PPh}_3)_2(\text{CN})_2$	II $\text{Hg}(\text{PPh}_3)_2(\text{NO}_3)_2$	III $\text{Hg}(\text{cis-Ph}_2\text{PCH=CHPPh}_2)\text{Br}_2$
formula	$\text{C}_{38}\text{H}_{30}\text{HgN}_2\text{P}_2$	$\text{C}_{36}\text{H}_{30}\text{HgN}_2\text{O}_6\text{P}_2$	$\text{C}_{26}\text{H}_{22}\text{Br}_2\text{HgP}_2$
<i>a</i> , Å	18.023 (5)	13.415 (3)	8.773 (5)
<i>b</i> , Å	18.262 (4)	14.004 (4)	18.952 (2)
<i>c</i> , Å	10.032 (3)	17.874 (3)	7.710 (2)
β , deg		91.72 (2)	101.77 (3)
<i>V</i> , Å ³	3301.9	3356.4	1254.9
space group	<i>Pn</i> 2 ₁ <i>a</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>m</i>
<i>z</i>	4	4	2
<i>D</i> _{calcd} , g cm ⁻³	1.58	1.68	2.00
<i>D</i> _{obsd} , g cm ⁻³	1.56	1.69	
<i>F</i> (000)	1528	1672	716
diffractometer	Hilger and Watts Y-290	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	Mo K α^a	Mo K α^a	Mo K α^a
scan	2 θ/ω	2 θ/ω^b	2 θ/ω^b
cryst dimensions, mm ³		0.20 × 0.25 × 0.26	0.14 × 0.38 × 0.40
μ (Mo K α), cm ⁻¹	47.2	47.2	91.5
2 θ _{max} , deg	48	62	50
unique rflctns	2422	4906	2287
rflctns used	2422, all	4250, >1.5 σ (<i>I</i>)	1790, >3 σ (<i>I</i>)
$\Delta R = \Sigma \Delta F / \Sigma F_0$	0.068	0.041	0.056
$R_w = (\Sigma w \Delta F^2 / \Sigma w F_0^2)^{1/2}$	0.064	0.040	0.083

^a Graphite monochromator. ^b Variable scan speed.

are not especially sterically demanding and conformationally unconstrained. This enables them to respond to any requirements due to the phosphine; however, it is not clear whether a compound with a chelating, bidentate anion, e.g., $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)]$ with $\text{X}_2 = \text{oxalate}$, will fit our correlation.

Then, there are the well-known limitations in the EHMO method itself. Finally, we have assumed throughout that the Fermi contact term alone is sufficient to describe $^1J(^{199}\text{Hg}, ^{31}\text{P})$. This might prove incorrect, although we have some computational results (see Table IV) that support the assumption.

In spite of the potential complications outlined above, we feel that our results shed some new light on the connection between molecular structure, NMR parameters, and electronic structure in the complexes $[\text{HgX}_2(\text{PR}_3)_2]$, and we are currently investigating additional compounds to experimentally explore further parts of the surface $J(\text{Hg}, \text{P}) = a + b\theta(\text{P}, \text{Hg}, \text{P}) + c\theta(\text{X}, \text{Hg}, \text{X})$ presented here.

Experimental Section

Preparation of Substances. *cis-Ph*₂PCH=CHPPh₂ is commercially available from Strem Chemicals, Inc., and was used without further purification. For the synthesis of the halide complexes $[\text{HgX}_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)]$, ligand and mercury halide were separately dissolved in equal concentration in hot ethanol. After equal amounts of the two solutions were mixed, a white powder precipitated, which was filtered off, washed with ethanol, and dried under vacuum. The rhodanide and cyanide complexes were synthesized by mixing ligand and mercury salt in a 1:1 molar ratio in warm methylene chloride. The products precipitated on addition of ether and were filtered off and dried under vacuum. Analytical data are given in Table V.

The acetate complex could not be obtained analytically pure due to decomposition, but the analysis resembled expected values. This is in agreement with the successful isolation of $[\text{Hg}(\text{ac})_2(\text{PPh}_3)_2]$, which was found to be monomeric in solution.⁶ $[\text{Hg}(\text{EtO})_2\text{PO})_2(\text{cis-Ph}_2\text{PCH=CHPPh}_2)]$ could not be isolated as a solid. The central part of its ³¹P NMR spectrum is of the A₂M₂ type. The satellite part

is of the A₂M₂X type. No other spin systems indicating dimers were observed.

Crystal Data and Experimental Details of Data Collection. Lattice parameters were obtained from a least-squares analysis of the setting angles of 25 reflections (Table VI). Three standard reflections were monitored, with no evidence of crystal decay. Lorentz and polarization corrections were applied. *S* is the scan count, *B* is the sum of the two backgrounds, and $I = S - 2B$.

Determination and Refinement of the Structures. All structures were solved by Patterson and Fourier methods. Scattering factors of Stewart, Davidson, and Simpson²⁴ for the hydrogen atoms and those of Cromer and Mann²⁵ for the nonhydrogen atoms were used.

Bis(triphenylphosphine)mercury(II) cyanide (I) was recrystallized from ethanol and appeared as transparent, colorless, elongated blocks with well-developed faces. No absorption corrections were applied. $\sigma(I) = (S + 4B)^{1/2} + 0.03I$. A block-diagonal least-squares refinement was used (X-RAY 72).²⁶ Anisotropic thermal parameters were used for Hg, P, and cyanide C and N atoms only. Hydrogen atoms were in calculated positions with $d(\text{C}, \text{H}) = 1.0 \text{ \AA}$ and $U_{\text{iso}} = 0.07 \text{ \AA}^2$. The weighting scheme was $w = 1/(\sigma(F))^2$. The final difference Fourier synthesis showed a peak of $\sim 2 \text{ e \AA}^{-3}$ close to Hg. Final atomic coordinates and isotropic temperature factors are given in Table VIIa and molecular dimensions in Table Ia. An ORTEP view²⁷ of the molecule and a stereoscopic view of the crystal packing are shown in Figures 1a and 3a, respectively.

Bis(triphenylphosphine)mercury(II) nitrate (II) was recrystallized from ethanol and appeared as transparent, colorless, elongated blocks with well-developed faces. No absorption correction was applied. $\sigma(I) = (I + 4B + 0.0003I^2)^{1/2}$. A block-diagonal least-squares refinement was used (X-RAY 72).²⁶ Anisotropic thermal parameters were

- (24) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
 (25) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **A24**, 321 (1968).
 (26) J. M. Stewart, X-RAY 72, Technical Report TR-192, Computer Science Center, University of Maryland, College Park, MD, 1972.
 (27) C. K. Johnson, ORTEP, Technical Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

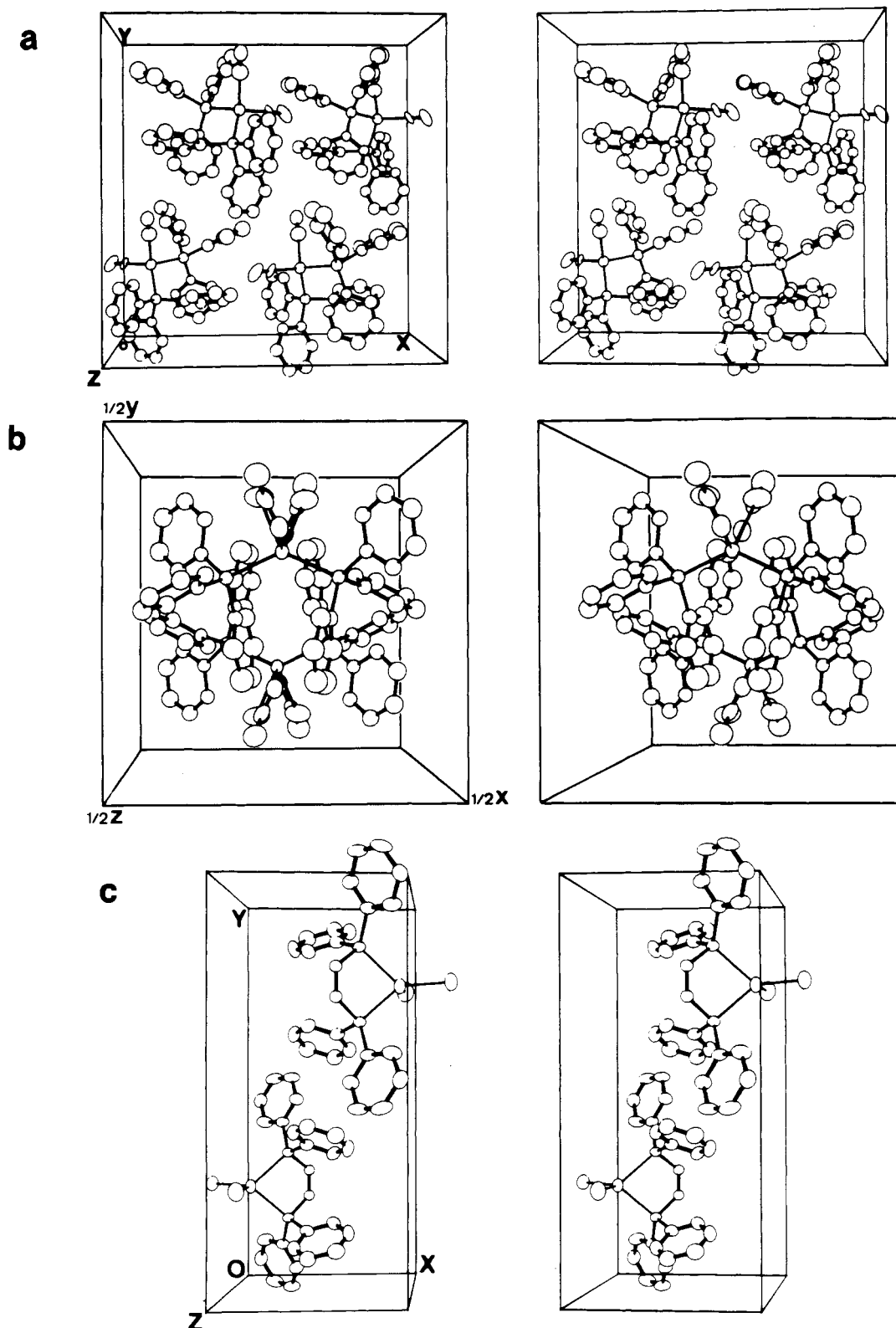


Figure 3. Molecular packing for (a) $[\text{Hg}(\text{CN})_2(\text{PPh}_3)_2]$, (b) $[\text{Hg}(\text{NO}_3)_2(\text{PPh}_3)_2]$, and (c) $[\text{HgBr}_2(\text{cis-Ph}_2\text{PCH}=\text{CHPh})_2]$.

for Hg, P, O, and N atoms only. Hydrogen atoms were in calculated positions with $d(\text{C,H}) = 1.02 \text{ \AA}$ and $U_{\text{iso}} = 0.07 \text{ \AA}^2$. The weighting scheme was $w = 1/(\sigma(F))^2$. Fractional coordinates with isotropic temperature factors and molecular dimensions are given in Tables VIIb and Ib, respectively. An ORTEP view²⁷ of the molecular structure and numbering scheme is shown Figure 1b, and a stereoview of the crystal structure is shown in Figure 3b.

cis-[1,2-Bis(diphenylphosphino)ethene]mercury(II) bromide (III) was recrystallized from a 4:1 mixture of tetrahydrofurfuryl alcohol and 1-butanol and appeared as transparent, colorless, elongated blocks with well-developed faces. Absorption corrections were applied by

using the program ORABS²⁸ (transmission coefficient 0.056–0.297). $\sigma(I) = (I + 4B + 0.0003I^2)^{1/2}$. Full-matrix least-squares refinement was used (SHELX 76).²⁹ Anisotropic thermal parameters were found for the nonhydrogen atoms. Hydrogen atoms were in calculated positions with the assumption that $d(\text{C,H}) = 0.95 \text{ \AA}$ and $U_{\text{iso}} = 0.10 \text{ \AA}^2$. The weighting scheme was $w = 1/[(\sigma(F))^2 + pF^2]$ with $p = 10^{-3}$.

(28) W. R. Busing, ORABS2, Technical Report, Oak Ridge National Laboratory, Oak Ridge, TN, 1966.

(29) G. M. Sheldrick, SHELX, A Program System for Crystal Structure Determination, University of Cambridge, England, 1976.

Table VII. Final Fractional Coordinates and Thermal Parameters^a

a. Hg(PPh ₃) ₂ (CN) ₂				
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å ²
Hg	0.09761 (4)	0.25000	0.07586 (7)	aniso
P(1)	0.1203 (3)	0.1413 (3)	0.2101 (5)	aniso
P(2)	0.2058 (3)	0.2660 (4)	-0.0913 (5)	aniso
N(1)	-0.0516 (11)	0.2466 (24)	-0.1176 (19)	aniso
N(2)	0.0944 (11)	0.4097 (11)	0.2499 (20)	aniso
C(1)	-0.0013 (9)	0.2487 (22)	-0.0507 (17)	aniso
C(2)	0.0974 (16)	0.3567 (15)	0.1915 (24)	aniso
C(111)	0.2186 (11)	0.1379 (11)	0.2540 (22)	0.047 (5)
C(112)	0.2452 (14)	0.1602 (14)	0.3816 (26)	0.063 (7)
C(113)	0.3203 (16)	0.1711 (16)	0.4010 (29)	0.078 (8)
C(114)	0.3703 (15)	0.1579 (16)	0.2998 (29)	0.075 (8)
C(115)	0.3458 (12)	0.1313 (13)	0.1773 (23)	0.053 (6)
C(116)	0.2698 (12)	0.1227 (12)	0.1539 (23)	0.049 (6)
C(121)	0.1008 (11)	0.0589 (11)	0.1197 (19)	0.040 (5)
C(122)	0.0383 (11)	0.0603 (12)	0.0381 (21)	0.044 (5)
C(123)	0.0158 (13)	-0.0023 (15)	-0.0255 (24)	0.056 (7)
C(124)	0.0556 (14)	-0.0661 (14)	-0.0111 (26)	0.060 (6)
C(125)	0.1130 (13)	-0.0662 (14)	0.0667 (26)	0.062 (6)
C(126)	0.1368 (13)	-0.0052 (13)	0.1349 (24)	0.054 (6)
C(131)	0.0730 (10)	0.1373 (10)	0.3723 (19)	0.033 (4)
C(132)	0.0520 (13)	0.0720 (14)	0.4254 (28)	0.064 (6)
C(133)	0.0156 (13)	0.0701 (14)	0.5483 (25)	0.063 (7)
C(134)	0.0028 (13)	0.1339 (13)	0.6127 (24)	0.056 (6)
C(135)	0.0203 (13)	0.1977 (13)	0.5652 (26)	0.059 (6)
C(136)	0.0558 (12)	0.2001 (12)	0.4313 (24)	0.052 (6)
C(211)	0.2905 (11)	0.3092 (11)	-0.0227 (20)	0.044 (5)
C(212)	0.2954 (13)	0.3147 (13)	0.1126 (24)	0.062 (7)
C(213)	0.3597 (19)	0.3451 (20)	0.1683 (36)	0.100 (11)
C(214)	0.4150 (18)	0.3704 (19)	0.0900 (33)	0.096 (10)
C(215)	0.4097 (15)	0.3633 (15)	-0.0474 (26)	0.072 (7)
C(216)	0.3448 (14)	0.3348 (15)	-0.1041 (25)	0.066 (7)
C(221)	0.1808 (10)	0.3302 (11)	-0.2254 (20)	0.039 (5)
C(222)	0.1385 (15)	0.3910 (15)	-0.1933 (29)	0.074 (8)
C(223)	0.1193 (17)	0.4405 (18)	-0.2934 (33)	0.089 (9)
C(224)	0.1438 (17)	0.4282 (17)	-0.4258 (34)	0.089 (9)
C(225)	0.1821 (16)	0.3691 (17)	-0.4565 (30)	0.084 (9)
C(226)	0.2024 (14)	0.3180 (14)	-0.3586 (25)	0.062 (6)
C(231)	0.2290 (11)	0.1819 (11)	-0.1672 (20)	0.039 (5)
C(232)	0.3029 (13)	0.1568 (14)	-0.1893 (24)	0.057 (6)
C(233)	0.3142 (15)	0.0901 (15)	-0.2408 (29)	0.075 (8)
C(234)	0.2555 (15)	0.0423 (15)	-0.2667 (29)	0.071 (7)
C(235)	0.1857 (14)	0.0650 (14)	-0.2517 (28)	0.068 (7)
C(236)	0.1716 (11)	0.1323 (11)	-0.2017 (21)	0.042 (5)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(112)	0.2086	0.1675	0.4567	H(212)	0.2518	0.2999	0.1702
H(113)	0.3404	0.1870	0.4891	H(213)	0.3708	0.3402	0.2649
H(114)	0.4255	0.1649	0.3144	H(214)	0.4579	0.4015	0.1278
H(115)	0.3836	0.1219	0.1030	H(215)	0.4528	0.3808	-0.1037
H(116)	0.2524	0.1033	0.0654	H(216)	0.3381	0.3332	-0.2038
H(122)	0.0086	0.1064	0.0294	H(222)	0.1192	0.3977	-0.1030
H(123)	-0.0312	-0.0021	-0.0813	H(223)	0.0918	0.4884	-0.2651
H(124)	0.0415	-0.1122	-0.0645	H(224)	0.1257	0.4620	-0.4985
H(125)	0.1396	-0.1153	0.0813	H(225)	0.1985	0.3612	-0.5503
H(126)	0.1806	-0.0073	0.1987	H(226)	0.2330	0.2738	-0.3796
H(132)	0.0639	0.0228	0.3789	H(232)	0.3468	0.1903	-0.1684
H(133)	-0.0013	0.0213	0.5869	H(233)	0.3672	0.0727	-0.2604
H(134)	-0.0258	0.1308	0.6993	H(234)	0.2676	-0.0106	-0.2968
H(135)	0.0126	0.2447	0.6186	H(235)	0.1415	0.0301	-0.2723
H(136)	0.0666	0.2493	0.3851	H(236)	0.1191	0.1485	-0.1856

b. Hg(PPh ₃) ₂ (NO ₃) ₂				
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å ²
Hg	0.00000	0.16660 (2)	0.25000	aniso
P	0.16173 (7)	0.09509 (7)	0.28433 (6)	aniso
N	0.0524 (3)	0.3021 (3)	0.1213 (2)	aniso
O(1)	0.0682 (4)	0.3133 (3)	0.1894 (2)	aniso
O(2)	0.0122 (3)	0.2262 (3)	0.1016 (2)	aniso
O(3)	0.0750 (3)	0.3647 (3)	0.0766 (3)	aniso
C(11)	0.2358 (3)	0.1638 (3)	0.3511 (2)	0.034 (1)
C(12)	0.2254 (3)	0.2624 (3)	0.3516 (2)	0.040 (1)
C(13)	0.2850 (4)	0.3163 (3)	0.4002 (3)	0.050 (1)
C(14)	0.3530 (3)	0.2729 (3)	0.4476 (3)	0.051 (1)
C(15)	0.3638 (4)	0.1747 (3)	0.4472 (3)	0.051 (1)
C(16)	0.3056 (3)	0.1192 (3)	0.3988 (2)	0.043 (1)

Table VII (Continued)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U, Å²</i>
C(21)	0.1347 (3)	-0.0173 (3)	0.3301 (2)	0.038 (1)
C(22)	0.1038 (4)	-0.0151 (4)	0.4027 (3)	0.060 (1)
C(23)	0.0811 (4)	-0.0995 (4)	0.4398 (3)	0.072 (2)
C(24)	0.0902 (5)	-0.1827 (4)	0.4043 (4)	0.081 (2)
C(25)	0.1159 (6)	-0.1893 (5)	0.3326 (4)	0.093 (2)
C(26)	0.1407 (5)	-0.1013 (5)	0.2932 (3)	0.075 (2)
C(31)	0.2427 (3)	0.0694 (3)	0.2073 (2)	0.034 (1)
C(32)	0.2195 (3)	0.1002 (3)	0.1354 (2)	0.044 (1)
C(33)	0.2866 (4)	0.0858 (4)	0.0786 (3)	0.054 (1)
C(34)	0.3752 (4)	0.0421 (3)	0.0932 (3)	0.053 (1)
C(35)	0.3984 (4)	0.0071 (4)	0.1640 (3)	0.057 (1)
C(36)	0.3324 (3)	0.0215 (3)	0.2216 (3)	0.049 (1)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(12)	0.1746	0.2950	0.3169	H(25)	0.1187	-0.2540	0.3083
H(13)	0.2780	0.3884	0.4014	H(26)	0.1578	-0.1040	0.2373
H(14)	0.3964	0.3129	0.4836	H(32)	0.1523	0.1325	0.1241
H(15)	0.4147	0.1429	0.4828	H(33)	0.2695	0.1101	0.0254
H(16)	0.3141	0.0472	0.3982	H(34)	0.4249	0.0320	0.0516
H(22)	0.0971	0.0490	0.4293	H(35)	0.4639	-0.0274	0.1744
H(23)	0.0590	-0.0960	0.4953	H(36)	0.3495	-0.0024	0.2747
H(24)	0.0774	-0.2434	0.4347				

c. Hg(PC=CP)Br₂

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Hg	0.04964 (6)	0.25000	0.17325 (8)	C(24)	0.5925 (17)	0.1079 (7)	0.6189 (16)
Br(1)	-0.2185 (2)	0.2500	-0.0296 (3)	C(25)	0.6451 (14)	0.1437 (7)	0.4875 (20)
Br(2)	0.0363 (2)	0.2500	0.5019 (3)	C(26)	0.5452 (13)	0.1594 (6)	0.3250 (15)
P	0.2521 (3)	0.1623 (1)	0.1021 (3)	H(1)	0.3975	0.1859	-0.1091
C(1)	0.3558 (11)	0.2152 (5)	-0.0327 (13)	H(12)	0.0101	0.1277	-0.1883
C(11)	0.1975 (12)	0.0827 (5)	-0.0281 (12)	H(13)	-0.0675	0.0264	-0.3567
C(12)	0.0680 (16)	0.0852 (6)	-0.1643 (15)	H(14)	0.0858	-0.0769	-0.2986
C(13)	0.0228 (14)	0.0257 (7)	-0.2646 (18)	H(15)	0.2991	-0.0819	-0.0715
C(14)	0.1144 (17)	-0.0361 (6)	-0.2279 (17)	H(16)	0.3762	0.0191	0.1015
C(15)	0.2412 (16)	-0.0393 (5)	-0.0947 (17)	H(22)	0.2318	0.0895	0.4145
C(16)	0.2868 (14)	0.0204 (5)	0.0083 (15)	H(23)	0.3990	0.0626	0.6798
C(21)	0.3911 (13)	0.1385 (5)	0.2992 (14)	H(24)	0.6612	0.0972	0.7277
C(22)	0.3380 (14)	0.1032 (6)	0.4320 (16)	H(25)	0.7510	0.1582	0.5068
C(23)	0.4368 (15)	0.0875 (7)	0.5901 (14)	H(26)	0.5830	0.1838	0.2348

^a Estimated standard deviations in parentheses are right adjusted.

The difference Fourier synthesis showed two peaks of $\sim 4 \text{ e } \text{\AA}^{-3}$ within less than 1.15 \AA of Hg, one peak of $2 \text{ e } \text{\AA}^{-3}$ within 0.1 \AA of Hg, and three peaks of $\sim 1 \text{ e } \text{\AA}^{-3}$ within 1.2 \AA of the two Br. One peak of $\sim 1 \text{ e } \text{\AA}^{-3}$ is within 2 \AA of Hg and Br(1). All other features are smaller than $1 \text{ e } \text{\AA}^{-3}$. Final coordinates are in Table VIIc and molecular dimensions are in Table Ic. ORTEP pictures²⁷ of the molecular structure and atom numbering are given in Figure 1c and of the crystal packing in Figure 3c.

NMR measurements were performed with a Bruker HX-90 spectrometer operating at 36.43 MHz for ³¹P. Samples were contained in 10-mm tubes as CDCl₃ solutions at 220 K, with the exception of the (EtO)₂PO complex, which was measured in CD₂Cl₂ at 190 K. Chemical shifts are ± 0.1 ppm (H₃PO₄); coupling constants are ± 3 Hz. *J*(Hg,P) and $\delta(^{31}\text{P})$ are subject to some uncertainty due to solvent and temperature dependence. Thus for [HgCl₂(PEt₃)₂], *J*(Hg,P) varies between 4750 and 5117 Hz and $\delta(^{31}\text{P})$ between 37.3 and 31.7, depending on the solvent;³⁶ low values of *J* are found for solvents with good coordinating ability (e.g., CD₃CN and (CD₃)₂SO) and high values of *J* are found for poorly coordinating solvents (e.g., C₆D₅CF₃ and CDCl₃). The temperature dependence may be exemplified with data for [Hg(ac)₂(PPh₃)₂]. At temperatures <240 K, $\delta(^{31}\text{P})$ changes only slightly, at a rate of ~ 0.4 Hz/K (0.01 ppm/K). At temperatures around 260 K, the rate increases to 4 Hz/K due to a chemical reaction involving dissociation of PPh₃. At temperatures >320 K, the rate decreases again. At these temperatures, *J*(Hg,P) is not observed at all. For $250 < T < 320$ K the lines are broad. Below 250 K, the lines sharpen, and the coupling constant may be measured and increases at a rate of 0.6 Hz/K with decreasing temperature (see also Table VII). Our experimental setup did not allow measurement of the limiting spectra. From line shapes we have estimated, however, some ligand dissociation rates to be 200 s⁻¹ or less at temperatures of 220 K and below. Since the ratio dissociation rate/*J*(Hg,P) is small,

Table VIII. Temperature Dependence of *J*(Hg,P) for [Hg(PPh₃)₂X₂] Complexes in CDCl₃

X	d <i>J</i> /d <i>T</i> , Hz/K	<i>T</i> range, K
ac	0.6	250-220
SCN	1.2	270-220
Cl	2.2	280-250
Br	3.3	250-220
CN	6.2	220-210

we expect the maximum uncertainty of *J*(Hg,P) to be given by (d*J*/d*T*)Δ*T* (for d*J*/d*T* values see Table VIII).

The Cl, Br, I, SCN, and CN complexes all gave satisfactory microanalytical data and solution molecular weights (osmometric) in CH₂Cl₂. The remaining complexes were characterized in solution by ³¹P NMR spectroscopy.

EHMO Calculations on [HgCl₂(PPh₃)₂]. All EHMO calculations were performed with the program WH (Wolfberg-Helmholz) written by L. Zoller. Double- ζ STO's of Clementi and Roetti³⁰ were used for the AO's of chlorine and phosphorus. The mercury functions were those of Basch et al.³¹ Hydrogen AO's were represented by a single Slater function with exponent 1.2. The main diagonal elements of the Hamiltonian matrix, *H_{ii}*, were iterated in self-consistent charge cycles (SCCC) with use of the quadratic dependence of the ionization potentials on charge as described by Basch et al.³² The charge dependence of all mercury orbitals was assumed to be linear with a slope of 5 eV/charge unit. SCCC iterations were performed on a molecule with C_{2v} symmetry and the structural parameters *d*(Hg,P)

(30) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 428 (1974).(31) H. Basch and H. B. Gray, *Theor. Chim. Acta*, **4**, 367 (1966).(32) H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).

= 2.47 Å, $d(\text{Hg}, \text{Cl}) = 2.48$ Å, $d(\text{P}, \text{H}) = 1.40$ Å, and $\theta(\text{P}, \text{Hg}, \text{P}) = \theta(\text{Cl}, \text{Hg}, \text{Cl}) = \theta(\text{H}, \text{P}, \text{H}) = 110^\circ$. All further calculations on geometrically distorted molecules ($\theta(\text{P}, \text{Hg}, \text{P})$ and $\theta(\text{Cl}, \text{Hg}, \text{Cl})$ being the only distorted structural parameters) were performed without further changes of the H_{ii} 's.

Coupling constants $J(\text{Hg}, \text{P})$ were calculated by using the formalism of Pople and Santry.³³

$$J(A, B) = \frac{32}{9} h \gamma_A \gamma_B |\Psi_{s,A}(0)|^2 |\Psi_{s,B}(0)|^2 \pi_{AB}$$

$$\pi_{AB} = +4 \sum_i^{\text{occ}} \sum_j^{\text{unocc}} ({}^3\Delta E_{ij})^{-1} C_{i,A} C_{j,A} C_{i,B} C_{j,B}$$

$|\Psi_{s,M}(0)|^2$ is the s density of the valence s orbital centered on A or B, γ is a gyromagnetic ratio, ${}^3\Delta E_{ij}$ are triplet excitation energies, and $C_{i,A}$ ($C_{j,A}$, etc.) is the coefficient of an atomic s orbital centered on A (or B) in the i th MO (j th MO). The coefficients were produced by the EHMO calculations, ${}^3\Delta E_{ij}$ was taken as the difference between

- (33) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).
 (34) E. C. Alyea, S. A. Dias, G. Ferguson, and M. A. Khan, *J. Chem. Res., Synop.*, 360 (1979); *J. Chem. Res., Miniprint*, 4101 (1979).
 (35) We are aware of the structure of $[\text{Hg}(\text{ClO}_4)_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2]$,³⁴ with $\theta(\text{P}, \text{Hg}, \text{P}) = 170.7^\circ$, $\theta(\text{O}, \text{Hg}, \text{O}) = 137.9^\circ$, a calculated $J(\text{Hg}, \text{P})$ of 3400 Hz, and an observed $J(\text{Hg}, \text{P})$ of 3755 Hz. For calculation of $J(\text{Hg}, \text{P})$ we assume that we may consider this structure a case of four-coordinate Hg^{2+} . Note, however, that the Hg-O distances are 2.93 and 3.08 Å and that there are two further perchlorate oxygens O' at 3.27 and 3.23 Å with an angle $\theta(\text{O}', \text{Hg}, \text{O}') = 141.3^\circ$ and angles $\theta(\text{O}, \text{Hg}, \text{O}') \approx 40^\circ$. Thus an alternative interpretation of this structure would be in terms of a distorted octahedron.
 (36) R. W. Kunz, Dissertation, ETH 6456, Zürich, 1979. Some of the coupling constants have been reported in the literature. Here we quote our own values, which are somewhat larger because they have been obtained at lower temperatures.

Notes

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Controlling the Number of Metal Sites to Which $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPh}_2$ Coordinates in Tungsten Carbonyls¹

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Received May 6, 1981

Polydentate phosphorus ligands have been used extensively in coordination chemistry for the past 20 years but in a narrowly focused manner that places principal emphasis on their chelating properties. A rich and relatively unexplored aspect of these ligands is their ability to bind in many arrangements other than the familiar fully chelated mode in monometallic species. This area of chemistry has been largely ignored because selective syntheses that eliminate tedious separations have not been available. In this work we have chosen to prepare complexes of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPh}_2$, triphos, to illustrate the utility of vinyl-addition reactions in controlling ligand coordination.

triphos was first synthesized in 1962.³ Interest in the ligand lagged through the 1960s because its preparation was not attractive. It became widely used, however, following the discovery of high-yield syntheses by King,⁴ Issleib,⁵ and Meek.⁶

- (1) Presented at the 1980 Biennial Inorganic Chemistry Symposium at Guelph, Canada.
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the eigenvalues E_i and E_j , and the s density at the nucleus was that of the neutral atom for phosphorus and that of $d^9s^1p^1$ mercury(I).

Multiple Linear Regression. The data in Table II were used with unit weight to determine the coefficients a' , b , and c in the expression $J(\text{Hg}, \text{P}) = a' + b[\theta(\text{P}, \text{Hg}, \text{P}) - \theta^0(\text{P}, \text{Hg}, \text{P})] + c[\theta(\text{X}, \text{Hg}, \text{X}) - \theta^0(\text{X}, \text{Hg}, \text{X})]$, where $\theta^0(\text{P}, \text{Hg}, \text{P}) = \sum \theta(\text{P}, \text{Hg}, \text{P})/N$ and $\theta^0(\text{X}, \text{Hg}, \text{X}) = \sum \theta(\text{X}, \text{Hg}, \text{X})/N$, with N the number of observations. Choosing the origin of the regression at θ^0 , the "center of mass", minimizes the trace of the variance-covariance matrix. Results are (σ in parentheses) $a' = 4149$ (117) Hz, $b = 25.1$ (5.5) Hz/deg, $c = -48.7$ (8.3) Hz/deg, $r^2 = 0.93$, and $(\sum \Delta^2/N - 3)^{1/2} = 350$ Hz (standard deviation of an observation of unit weight); $\Delta = J_{\text{obsd}} - J_{\text{calcd}}$; elements of the correlation matrix are $C(a', b) = 0$, and $C(b, c) = 0.3$. Results for $\theta^0(\text{P}, \text{Hg}, \text{P}) = \theta^0(\text{X}, \text{Hg}, \text{X}) = 109.5^\circ$ are $a'' = 3271$ (155) Hz, $C(a'', b) = -0.47$, and $C(a'', c) = 0.31$, and all others are the same as above. The values given in the Discussion are obtainable from the above results.

Acknowledgment. R.W.K. and M.P. thank the Schweizerischen Nationalfonds zur Förderung der Wissenschaftlichen Forschung for financial support and Mr. L. Zoller for computational assistance.

Registry No. I, 27902-66-5; II, 14057-00-2; III, 80063-20-3; $\text{Hg}(\text{ac})_2(\text{cis-Ph}_2\text{PCH}=\text{CHPPH}_2)$, 80063-21-4; $\text{HgCl}_2(\text{cis-Ph}_2\text{PCH}=\text{CHPPH}_2)$, 80063-22-5; $\text{Hg}(\text{SCN})_2(\text{cis-Ph}_2\text{PCH}=\text{CHPPH}_2)$, 80106-35-0; $\text{Hg}(\text{CN})_2(\text{cis-Ph}_2\text{PCH}=\text{CHPPH}_2)$, 80083-22-3; $\text{Hg}(\text{EtO})_2\text{PO}_2(\text{cis-Ph}_2\text{PCH}=\text{CHPPH}_2)$, 80083-23-4; $\text{HgI}_2(\text{cis-Ph}_2\text{PCH}=\text{CHPPH}_2)$, 80083-24-5; $\text{Hg}(\text{ac})_2(\text{PPh}_3)_2$, 66119-73-1; $\text{HgCl}_2(\text{PPh}_3)_2$, 14494-85-0; $\text{HgBr}_2(\text{PPh}_3)_2$, 14586-76-6; $\text{Hg}(\text{SCN})_2(\text{PPh}_3)_2$, 27290-69-3; $\text{HgI}_2(\text{PPh}_3)_2$, 14494-95-2.

Supplementary Material Available: Listings of structure factor amplitudes and of anisotropic thermal parameters (51 pages). Ordering information is given on any current masthead page.

At present it is routinely used in complexation studies such as those aimed at elucidating the reactions in homogeneous hydroformylation,⁷ Fischer-Tropsch synthesis,⁸ and catalytic hydrogenation.⁹

The ligating possibilities of triphos have been previously outlined, and specific examples of these species have been identified.¹⁰ In order to synthesize such complexes routinely, however, it is necessary to find a method of controlling the number of metal sites to which the polyphosphine coordinates. Substitution reactions are in general inadequate because they too often lead to mixtures of isomers or mixtures of mono- and bimetallic products that may not be easily separated. In this work we report a method of obtaining the desired products that is based upon building the complex of interest from judiciously selected coordinated fragments. The approach has been used previously in the preparation of monodentate complexes of diphos, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, such as $(\text{OC})_5\text{M}(\text{diphos})$ and $(\text{OC})_4\text{M}(\text{diphos})_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).¹¹

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