

One- and Two-Dimensional Solution and Solid-State NMR Studies of Di- and Trinuclear Optically Active Ferrocenylphosphine Complexes of Mercury(II)

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Received October 9, 1992

Reaction of the 1,1'-bis(diphenylphosphino)ferrocenyl ligand, **1**, containing the chirotopic side-chain (*R*)-CH(CH₃)N(CH₃)CH₂CH₂N(CH₃)₂ in the 2-position, with HgX₂ derivatives affords the cationic complexes [Hg₃X₄(**1**)₂]X₂ (X = Cl, Br, I), **2a–c**, respectively, in which the phosphorus atom, P¹, on the disubstituted Cp ring and the two tertiary nitrogens are coordinated to one metal center and the phosphorus, P², on the second Cp ring, is coordinated to a different metal center. The structural nature of these compounds is supported by multinuclear NMR including, most importantly, ¹⁹⁹Hg NMR. Low-temperature ³¹P studies, combined with 2-D ³¹P exchange spectroscopy, suggest the existence of species with one and two mercury atoms of related structure. These complexes could be recognized in solution using both ¹⁹⁹Hg and ³¹P NMR. The chemistry for the analogous CN⁻ derivative, **2d**, is also discussed. Conventional as well as two-dimensional COSY and EXSY (spin-diffusion) cross-polarization, magic-angle spinning solid-state ³¹P spectra were recorded for the complexes **2a,b,d**, as well as for the model compounds HgX₂(1,1'-bis(diphenylphosphino)ferrocene) (X = Cl, CN). The complex **2d**, X = CN, is interesting in that the solid-state phosphorus NMR results suggest a different structure than that found in solution at low temperature. The 3-D solution structures of the complexes of the three halides, with respect to the conformation of the coordinated side chain, were determined using 1- and 2-dimensional ³¹P and ¹H NMR methods and are discussed in relation to the structure of **1**.

Introduction

Chiral ferrocene derivatives containing phosphine substituents are known to be useful ligands in a variety of homogeneously catalyzed reactions.² In addition to, e.g., cross coupling^{2a} and allylic amination chemistry,^{2b,c} the reactions of aldehydes with isocyanacetates to form dihydrooxazoles are known to be catalyzed by gold(I) salts in the presence of chelating ferrocenylphosphine ligands such as **1**;^{3,4} see eq 1. The mixtures of *cis*- and



trans-dihydrooxazoles which arise from this condensation reveal moderate to very substantial enantiomeric excesses.^{3,4} The exact nature of the intermediate gold(I) complexes in the dihydrooxazole synthesis remains unknown, due in part to the limited solubility

of these materials at relatively low temperatures but also to the complex dynamic behavior of these compounds at temperatures where NMR spectra could be recorded.⁵

To obtain some general insight with respect to how polydentate chiral ligands such as **1** behave in the presence of positively charged d¹⁰ metal centers, we have studied its reactions with several simple mercury(II) salts. Specifically, we were interested in learning which, if either, of the two potential nitrogen ligands might coordinate and whether the products would be mononuclear or perhaps oligomeric. In addition, the fact that our complexes are chiral provides an additional impetus for us to extend^{6–8} our use of ¹H NOESY methods in the determination of the three-dimensional solution structures of metal complexes. In view of the known⁹ tendency of d¹⁰ centers to dissociate ligands, thereby showing dynamic behavior on the NMR time scale, we have also measured some few solid-state ³¹P spectra for our new mercury(II) complexes with a view to recognizing differences between the structures of our materials in the solution and solid phases.

Results and Discussion

Reaction of HgX₂ (X = Cl, Br, I, CN) with **1** in ethanol afforded the cationic complexes **2**, as shown in Scheme I. We are aware of cationic four-coordinate complexes of mercury(II),¹⁰ however, we know of none which are optically active and contain this type of mixed coordination sphere. The new complexes **2** were

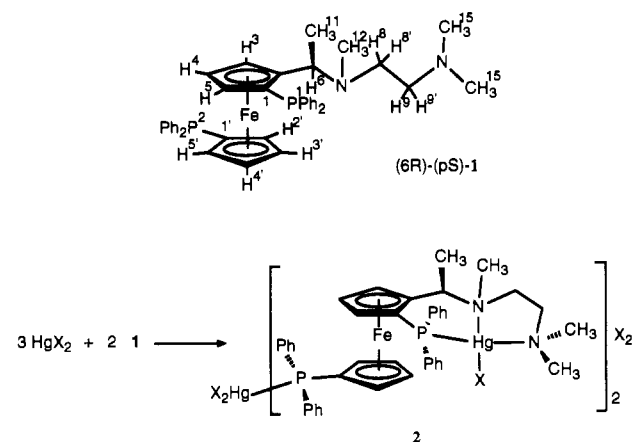
- (1) (a) ETH Zürich. (b) University of Milan. (c) Ciba-Geigy Basel. Current address: Inorg. Chem. ETH, Zürich.
- (2) (a) Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7. (b) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Haguchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (c) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301. (d) Hayashi, T.; Yamamoto, A.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1090.
- (3) (a) Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron* **1992**, *48*, 1999. (b) Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1990**, *31*, 2723. (c) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron Lett.* **1988**, *29*, 235. (d) Sawamura, M.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 2247. (e) Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 6321. (f) Ito, Y.; Sawamura, M.; Sirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron Lett.* **1988**, *44*, 5253. (g) Ito, Y.; Sawamura, M.; Kabayashi, M.; Hayashi, T. *Tetrahedron Lett.* **1988**, *29*, 239. (h) Ito, Y.; Sawamura, M.; Hayashi, T. *Tetrahedron Lett.* **1987**, *28*, 6215. (i) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405.
- (4) (a) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649. (b) Pastor, S. D.; Togni, A. *Helv. Chim. Acta* **1991**, *74*, 905. (c) Togni, A.; Pastor, S. D.; Rihs, G. *J. Organomet. Chem.* **1990**, *381*, C21. (d) Togni, A.; Pastor, S. D. *Helv. Chim. Acta* **1989**, *72*, 1038. (e) Togni, A.; Pastor, S. D. *Tetrahedron Lett.* **1989**, *30*, 1071. (f) Togni, A.; Häusel, R. *Synlett* **1990**, 633.

- (5) Togni, A.; Pregosin, P. S. Unpublished results.
- (6) Albinati, A.; Lianza, F.; Pasquali, M.; Sommovigo, M.; Leoni, P.; Pregosin, P. S.; Rügger, H. *Inorg. Chem.* **1991**, *30*, 4690.
- (7) Pregosin, P. S.; Wombacher, F. *Magn. Reson. Chem.* **1991**, *29*, 106.
- (8) (a) Rügger, H.; Kunz, R. W.; Ammann, C. J.; Pregosin, P. S. *Magn. Reson. Chem.* **1991**, *29*, 197. (b) Togni, A.; Rihs, G.; Pregosin, P. S.; Ammann, C. J. *Helv. Chim. Acta* **1990**, *73*, 723.
- (9) (a) Houlton, A.; Roberts, R. M. G.; Silver, J.; Parish, R. V. *J. Organomet. Chem.* **1991**, *418*, 269. (b) Alyea, E. C.; Dias, S. A.; Goel, R. G.; Ogini, W. O.; Pilon, P.; Meek, D. W. *Inorg. Chem.* **1978**, *17*, 1697. (c) Muettterties, E. L.; Alegrianti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.
- (10) (a) Peringer, P.; Lusser, M. *Inorg. Chim. Acta* **1986**, *117*, L25. (b) Peringer, P.; Obendorf, D. *Inorg. Chim. Acta* **1983**, *77*, L147.

Table I. One-Bond Mercury–Phosphorus Coupling Constant (Hz) and Mercury Chemical Shift (δ) Solution Data^a for the New and Model Complexes

X	2 ^a	3 ^b	[HgX ₂ (PPh ₃) ₂] ^c	[Hg ₂ X ₂ (PBU ₃) ₂] ^d	[HgCl ₃ (PBU ₃)] ^e	$\delta(^{199}\text{Hg})$ for 2
Cl	7532	4098	4682	7480, 7446	7321	-468
	4594					-736
Br	6588 ^f	3532	4227	6680, 6624	5950	-720
	4050					-993
I	5024	2488	3074	5440, 5120	4077	
	3080					
CN	4434	2366	2617			
	2784					

^a Chemical shifts: Cl, 24.6, 21.7 at 273 K; Br, 21.7, 14.7 at 273 K; I, 12.7, -0.9 at 243 K; CN, 23.2 at 213 K. All values for CD₂Cl₂ solutions. P¹ has the higher δ value. The uncoordinated ligand has P¹ and P² at -21.4 and -17.0, respectively.²² ^b Chemical shifts: Cl, 19.2; Br, 12.4; I, -1.9; CN, 12.3 at 273 K. All values are for CDCl₃ solutions. ^c Data from ref 12a. ^d Data from ref 11. ^e Data from ref 31. ^f For the second component, δ = 23.3 ppm, ¹J(Hg,P) = 6833 Hz for P¹, CD₃NO₂ solution.

Scheme I**Table II.** ¹H NMR Data for 2a–c

	2a ^a	2b ^b	2c ^c	[Hg ₂ Br ₄ (1)] ^d
H-3	4.64	4.53 ^e	5.33	4.90
H-4	5.58	5.38	5.08	5.25
H-5	3.44	3.09	4.54	3.63
H-2'	3.95	3.24	3.04	3.65 ^f
H-3'	4.92	4.94	5.28	5.02 ^f
H-4'	4.58	4.53 ^e	4.16	5.09 ^f
H-5'	3.39	3.57	2.97	4.89 ^f
H-6	4.67	4.75	4.75	4.83
H'-8	2.17	2.19	2.19 ^e	2.20
H'-8	2.87	2.86	2.89	2.88
H-9	1.97	1.91	1.76	1.95
H'-9	2.58	<i>h</i>	<i>h</i>	2.57
CH ₃ -11	0.70	0.83	0.94	0.85
CH ₃ -12	1.31	1.24	1.31	1.33
CH ₃ -15	2.40	2.30	2.16	2.36
CH ₃ -15'	2.68	2.55	2.43	2.59

^a CDCl₃, 298 K, 500 MHz. ^b CD₂Cl₂, 273 K, 400 MHz. ^c CD₂Cl₂, 243 K, 500 MHz. ^d CD₂Cl₂, 263 K, 500 MHz. ^e Signals overlap. ^f Assignments could be reversed. ^h Partially under CH₃-15.

characterized via microanalytical, conductivity, mass spectroscopic, and ¹H, ³¹P, and ¹⁹⁹Hg NMR measurements (see Tables I–III). The FAB mass spectra for 2a–d show signals due to the HgX(1)⁺ ions as well as *m/e* values which correspond to uncoordinated ligand 1. We have also obtained FAB mass spectra for the model complexes HgX₂(1,1'-bis(diphenylphosphino)ferrocene), X = Cl and CN. These spectra also show relatively intense signals which arise from [MX(1,1'-bis(diphenylphosphino)ferrocene)]⁺, i.e. loss of X⁻. Since loss of the anion X is favored in these model complexes, the observation of an [HgX(1)]⁺ ion for 2a–c may have no predictive structural value. In any case we do not see signals for complexes corresponding to 2. Conductivity measurements in nitromethane afforded values which are consistent with those expected for 1:2 electrolytes in this solvent (see Experimental Section). The gross structural details for 2a–c were deduced using phosphorus and mercury

Table III. Solid-State ³¹P Data

X	2		3	
	δ	¹ J(Hg,P) ^a	δ	¹ J(Hg,P)
Cl	22	7000	11.8	4032
	22 ^b	4500	6.6	4054
Br	24.6	6340		
	15.5	3700		
	27.0 ^c	6600 ^c		
	-21 ^c			
CN	23.5		15.3	3280
	12.2		9.2	2350
	-28		11.1	3300
	-19		8.4	2500

^a Due to broad lines the coupling constants are rather uncertain ($\sim \pm 100$ Hz). ^b Different resonances not resolved. ^c For second component, [HgBr(1)]Br.

NMR methods, whereas the more subtle molecular details followed from two-dimensional proton studies.

³¹P and ¹⁹⁹Hg NMR Spectroscopy. The room-temperature phosphorus-31 spectra for 2, X = Cl, Br, and I, in both chlorinated hydrocarbons and nitromethane show sharp to relatively sharp resonances for the phosphorus spin on the substituted Cp ring, P¹, flanked by ¹⁹⁹Hg satellites^{11–14} arising from the ca. 16.9% natural abundance of this isotope, see Figure 1, as well as broadened to very broad signals for P² (the assignments of P¹ and P² in 2 arise from 2-D phosphorus–proton correlations). For the analogous cyanide complex, which is somewhat special, both phosphorus resonances are very broad. At an appropriately reduced temperature the proton-decoupled phosphorus-31 spectra for 2a–d show two sharp signals both flanked by mercury satellites. We do not observe ²J(P,P) values, and this is important in that it suggests that the two ³¹P spins are not attached to the same metal. We show below, in connection with our solid-state results, that such ferrocenylphosphine complexes can indeed show a measurable ²J(P,P) coupling constant. Moreover, X-ray studies^{15–18} suggest that, for ligands related to 1, there are no special problems associated with coordinating both phosphorus atoms to a single metal center.

- (11) (a) Yamaski, A.; Fluck, E. Z. *Anorg. Allg. Chem.* **1973**, *396*, 297. (b) Grim, S. O.; Lui, P. J.; Keiter, R. L. *Inorg. Chem.* **1974**, *13*, 342. (c) Bond, A. M.; Colton, R.; Dakternieks, D.; Hanck, K. W. *Inorg. Chem.* **1982**, *21*, 117.
- (12) (a) Buerger, H. B.; Kunz, R. W.; Pregosin, P. S. *Inorg. Chem.* **1980**, *19*, 3707. (b) Buerger, H. B.; Fischer, E.; Kunz, R. W.; Parvez, M.; Pregosin, P. S. *Inorg. Chem.* **1982**, *21*, 1246. (c) Kunz, R. W.; Pregosin, P. S.; Camalli, M.; Caruso, F.; Zambonelli, L. *Helv. Chim. Acta* **1983**, *66*, 1661.
- (13) (a) Pregosin, P. S.; Kunz, R. W. In *NMR Basic Principles and Progress*; Springer Verlag: Heidelberg, Germany, 1979; Vol. 16. (b) Pregosin, P. S. In *Methods in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds. VCH Publishers Inc.: Deerfield Beach, FL, 1987; Vol. 8.
- (14) Garth Kidd, R.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 268.
- (15) (a) Hayashi, T.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Organomet. Chem.* **1987**, *334*, 195. (b) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

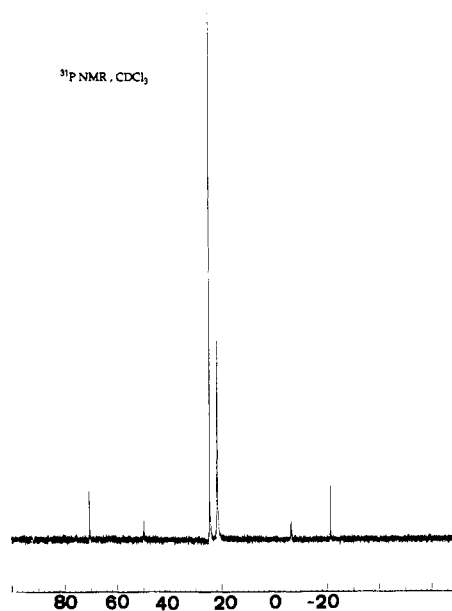


Figure 1. ^{31}P NMR spectrum of $[\text{Hg}_3(\text{Cl})_4(1)_2]\text{Cl}_2$, **2a**, in CDCl_3 solution. Note (a) that there are two very different one-bond mercury–phosphorus coupling constants and (b) that the resonance for P^2 , the PPh_2 on the Cp ring without the side chain, is broader than that for P^1 .

For $^1J(\text{Hg},\text{P})$ in the complexes **2** one finds the expected trend¹¹ with the chloride having the largest and the iodide the smallest one-bond spin–spin coupling. Somewhat surprisingly, the values $^1J(\text{Hg},\text{P})$ are very different for the two types of phosphorus within these complexes. A summary of these data along with corresponding coupling constants for various model complexes, i.e., $[\text{HgX}_2(1,1'\text{-bis}(\text{diphenylphosphino})\text{ferrocene})]$, **3**, $\text{HgX}_2(\text{PPh}_3)_2$, **4**,^{12a} and the halogen-bridged dinuclear complexes $[\text{Hg}_2\text{X}_4(\text{P}^{\text{Bu}^n})_2]$, **5**,^{11,13} are shown in Table I. The values for $^1J(\text{Hg},\text{P}^1)$ in **2** are large relative to the bisphosphine model complexes but in excellent agreement with the given values for the monophosphine compounds, whereas the $^1J(\text{Hg},\text{P}^2)$ values seem more consistent with the bisphosphine $\text{HgX}_2(\text{PPh}_3)_2$ compounds. A comparison of the coupling constants for **2** with those for **3** containing 1,1'-bis(diphenylphosphino)ferrocene, **6**, shows that the large spin–spin coupling to P^1 is presumably related to the fact that only one phosphorus ligand is coordinated in the former.

At this point, given the various electronic environments suggested by the ^{31}P data, it was likely that the complexes were not mononuclear. To determine the nuclearity we have measured several ^{199}Hg spectra in that (a) the individual Hg types and their relative intensities should be recognizable¹⁸ and (b) the phosphorus multiplicity and $^1J(\text{Hg},\text{P})$ values should help confirm our structural and spectroscopic assignments. Figure 2 shows that in **2a** there are, indeed, two different mercury absorptions in the ratio 1:2, with the former showing triplet and the latter doublet multiplicity. The observed one-bond coupling constants allow us to associate the triplet to P^2 and the doublet to P^1 . The chemical shifts for these Hg resonances, which we give in Table I, are as expected for such electronic environments.¹⁸

Since the coordination chemistry of ligand **1** has not been extensively studied, we considered it useful to prepare a model complex in order to estimate its donor properties and specifically to try to obtain an estimate of a $^2J(\text{P},\text{P})$ value in a complex of

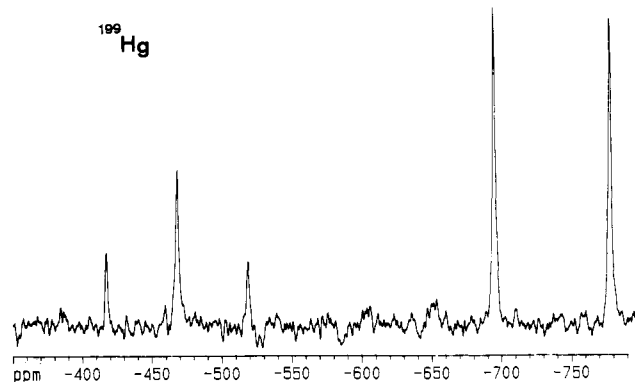


Figure 2. ^{199}Hg NMR spectrum of **2a** showing two mercury environments.

1. The model platinum(II) complex, $\text{PtCl}_2(\mathbf{1})$, **7**, was readily available (see Experimental Section), and a comparison of its $^1J(\text{Pt},\text{P})$ values, 3731 and 3836 Hz, with the extensive known literature¹³ for this spin–spin coupling revealed these values to be rather routine; however, $^2J(\text{P},\text{P})$ in **7**, at 9.6 Hz is readily measurable and normal for a cis two-bond coupling in such a square-planar complex. The value of $^1J(\text{Pt},\text{P})$ in the ferrocenylphosphine complex $\text{PtCl}_2(\mathbf{6})$, which has no side chain, is 3769 Hz⁵ and is quite similar to those found for **7**.

Returning to our mercury(II) chemistry, complex **2b** is exceptional in that at low temperature, in chlorinated hydrocarbons and nitromethane, we find significant quantities of a second component. In this molecule P^1 (with the side chain) is coordinated and P^2 uncoordinated, with the assignment following from the (a) relatively large value for $^1J(\text{Hg},\text{P}^1)$ and (b) characteristic chemical shift at ca. -17 ppm for P^2 in the free ligand. ^{31}P two-dimensional exchange spectroscopy at room temperature and at 258 K shows that the uncoordinated P^2 spin exchanges with its coordinated analog and that the two coordinated P^1 spins are also exchanging. The equilibrium shown in Scheme II is consistent with these observations. We do know that there is no intermolecular exchange involving dissociation of P^2 followed by recombination to a second mercury center since there is no exchange between the isotopomers with and without ^{199}Hg .¹⁹

In a separate preparative experiment (see Experimental Section) we isolated a second bromo complex whose structure we assign to **8** as shown in the lower part of Scheme II. This compound appears superficially related to **2b**; however, it differs in that each Hg center has only one coordinated phosphorus ligand. Support for this structure arises from the ^{199}Hg , ^1H 2-D correlation shown in Figure 3, in which each Hg resonance appears as a doublet. It is worth noting the numerous cross-peaks which arise because both ^{199}Hg spins are coupled to the Cp protons and one ^{199}Hg spin is coupled to the CH_2 and CH_3 protons. Spin–spin interactions involving a mercury(II) ion and remote Cp protons were previously unknown. Such long-range interactions may be useful in determining mercury-199 resonances, via indirect methods, in the future. A ^{31}P NMR spectrum of this dinuclear complex at 263 K shows singlet resonances at $\delta = 21.5$ and $\delta = 23.5$ with one-bond coupling constant of 6663 and 6660 Hz, respectively, thereby confirming that the lower value in **2b** is associated with the mercury-containing two phosphorus ligands.

Given that we were able to detect the bromide complex, **8**, we dissolved the chloro complex, **2a**, in methylene chloride and added an additional equivalent of HgCl_2 . This latter material slowly dissolves giving a solution whose ^{31}P NMR spectrum now contains two new resonances located at $\delta = 29.8$ and 24.4 ppm, again with no $^2J(\text{P},\text{P})$ coupling value. As with the bromo analog, above, the values $^1J(\text{Hg},\text{P})$ are now both relatively large, 7573 and 7419

(16) (a) Clemente, D. A.; Pilloni, G.; Corain, B.; Longato, B.; Tiripicchio-Camellini, M. *Inorg. Chim. Acta* **1986**, *115*, L9. (b) Casellato, U.; Ajo, D.; Valle, G.; Corain, B.; Longato, B.; Graziani, R. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 583. (c) Butler, I. R.; Cullen, W. R.; Kim, T.; Rettig, S. J.; Trotter, J. *Organometallics* **1985**, *4*, 972.
(17) (a) Powell, J. J. *Chem. Soc., Chem. Commun.* **1989**, 200. (b) Sen, A.; Chen, J. T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148. (c) Read, G.; Urgelles, M.; Galzs, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 911. (d) Howard, J.; Woodward, P. J. *Chem. Soc., Dalton Trans.* **1973**, 1840.

(18) (a) Albright, M. J.; Oliver, J. P. *J. Organomet. Chem.* **1979**, *172*, 99. (b) Breiting, D. K.; Kress, W.; Sendelbeck, P.; Ishiwada, K. *J. Organomet. Chem.* **1983**, *243*, 245.

Scheme II

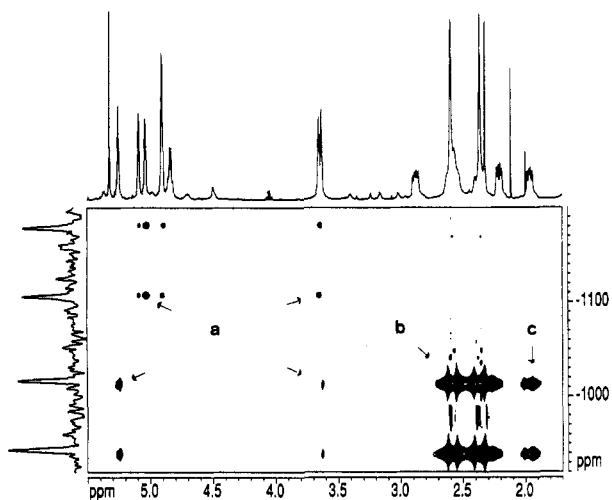
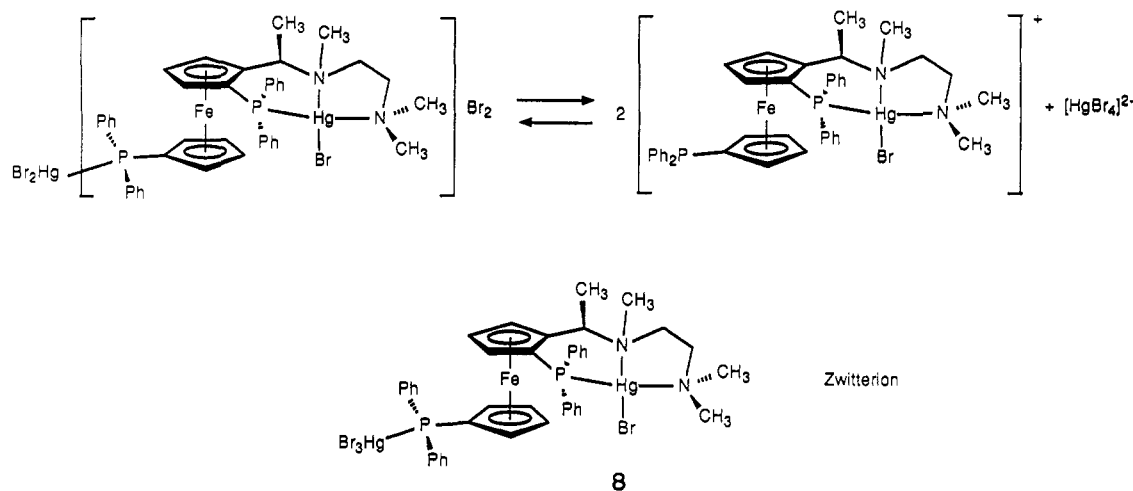


Figure 3. Section of the ^{199}Hg , ^1H correlation for the bromo complex **8** revealing not only the metal multiplicity but also spin-spin interactions between the metal and (a) some Cp protons, between 3.5 and 5.3 ppm, (b) CH_3 protons at ca. 2.3–2.6 ppm, and (c) CH_2 protons at ca. 1.9 ppm. The arrows point to selected cross-peaks.

Hz, respectively, again an indication that each Hg center has only one phosphorus attached. Thus, the bis(phosphine)mercury(II) center has given up one phosphorus spin P^2 which has now coordinated to the additional equivalent of HgCl_2 . It is obvious that the solution chemistry of **1** is not trivial and that the species isolated from the reactions of **1** with HgX_2 depend on the reaction conditions (see Experimental Section for details).

The structure for **2d**, with $\text{X} = \text{CN}$, is different from those for **2a–c** and, indeed, remains an open question. There is evidence which points toward a compound related to **2a–c**; e.g., neither of the phosphorus signals for **2d** show a $^2J(\text{P},\text{P})$ coupling. The one-bond mercury–phosphorus value for P^1 is large, 4434 Hz, relative to that for P^2 , 2784 Hz; the conductivity is that for a 1:2 electrolyte in nitromethane, and the microanalysis fits the proposed structure. However, the solution dynamics as monitored by ^{31}P NMR spectroscopy and the ^{13}C NMR are puzzling. The room-temperature ^{31}P spectrum shows two very broad features: one at ca. 18, the other at ca. 4 ppm. In CD_2Cl_2 at 223 K, the high-field signal, now at 10.8 ppm, is sharp and the low-field signal, now at 22.9 ppm, is still broad. At 193 K the low field absorption at 23.2 is sharp, but the high field resonance is now broad. Perhaps the lower temperature is responsible for the slowing of an additional process. Further, **2d** enriched with 90 atom % ^{13}C

shows the two different ^{31}P resonances as triplets at the temperatures where these resonances are sharp. Moreover, the ^{13}C spectrum of the enriched material is very complex and shows several groups of multiplets with varying multiplicities. Since the proton spectra are always broad in the temperature range 193–293 K, these data are not helpful. There are too many ambiguities to propose a structure for **2d**; but we note that both P^1 and P^2 are coordinated and this is interesting with respect to the solid-state results given below.

^1H NMR Spectroscopy. Having placed the various ^{31}P and ^{199}Hg spins relative to one another in **2a–c**, we now confront the question of the side chain. Temperature-dependent proton studies revealed a broad six-proton NMe_2 group resonance at ambient temperature which affords two nonequivalent N -methyl signals on cooling. These NMe resonances provide an immediate hint as to the nature of the complex in that they were equivalent in ligand **1**. ^{31}P , ^1H 2-D correlation spectra at the appropriate temperature for **2a–c** show a correlation of P^1 with one of the two geminal NCH_3 groups and also with $\text{CH}_3(12)$, the other NCH_3 resonance. This can only occur if both nitrogens are coordinated (i.e. there exist small $^4J(\text{P},\text{H})$ values²⁰ which are not readily resolved in the 1-D spectrum but allow us to observe cross-peaks in the 2-D spectra). For **2a**, the ^1H COSY cross-peaks are sufficiently resolved to reveal $^3J(\text{Hg},\text{CH}_2)$ values, further supporting a coordinated side chain. These mercury–proton coupling constants are not immediately recognizable in the 1-D spectra. In any case, these 2-D experiments allow us to confidently complete the coordination sphere of the mercury bound to P^1 .

With respect to the dynamics we also note that the Cp protons of the monosubstituted ring are relatively broad at ambient temperature but sharpen at about the same rate as the $\text{N}(\text{CH}_3)_2$ signals. This change in the Cp proton line width is consistent with a dynamic process connected with P^2 , as discussed above in connection with the ^{31}P studies, and may or may not be related to our observations with respect to the dynamics associated with the NMe_2 group. Perhaps we are dealing with two separate dynamic processes, i.e., one each for the P^2Ph_2 and NMe_2 ligands.

At temperatures where the proton signals are sharp, one can obtain ^1H COSY and NOESY data for **2a–c** and these have allowed us to assign many key protons and specifically those of the two cyclopentadienyl rings. With this information and selected NOE's (see Figure 4), one can define the local 3-D structure at and around the stereogenic C-6 carbon, and a partial view of the molecule is shown in Chart I. The C-6 CH_3 is directed away from the mercury(II) and lies somewhat above the plane of the upper Cp ring. The placement of this CH_3 arises from an observed

(19) Hampden-Smith, M. J.; Rügger, H. *Magn. Reson. Chem.* **1989**, *27*, 1107.

(20) Albinati, A.; Affolter, S.; Pregosin, P. S. *Organometallics* **1990**, *9*, 379. See also ref 14, 383.

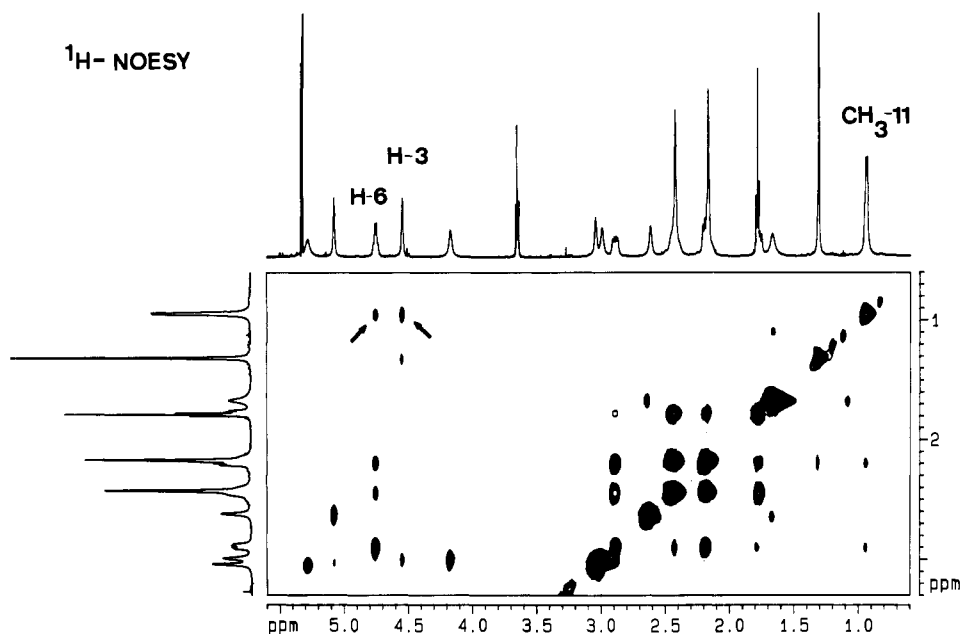
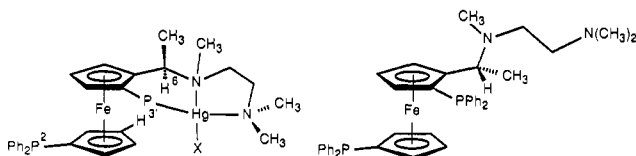
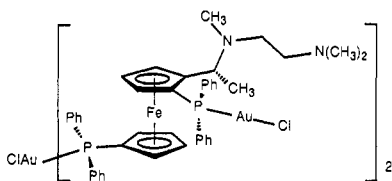


Figure 4. Section of the ^1H 2-D NOESY spectrum for the iodide complex **2c**. The cross-peaks have the same phase as that of the diagonal. Note that C(6)- CH_3 shows NOE to only one Cp proton (that *ortho* to C-6) as well as NOE to H-6 (see arrows) and no NOE's to the Cp protons of the lower ring as was found in **1**. This suggests that this CH_3 is above the Cp ring and not below it.

Chart I



Fragment of **2** showing the contact between H(6) and H(3') which results in a strong NOE. This interaction helps to define the overall 3-D structure of the molecule. In **2** the C- CH_3 is above the Cp plane, in **1**, below.



Known trinuclear complex of gold(I) with the ligand **1** (see ref. 4c)

NOE to the Cp proton H-3, *ortho* to C-6, but no NOE's from this methyl to Cp protons of the lower ring as was previously²¹ found in **1** (see Chart I). NCH_3 -12 is almost vertical to the Cp plane and is proximate to the electron cloud of one of the phosphorus phenyl groups with the result that this methyl group experiences a pronounced high-field shift. We also note a weak NOE from NCH_3 -12 to H-3. Effectively, coordination of both nitrogens results in a rotation about the C(2)-C(6) bond so that the nitrogen in **1** attached to C-6 rotates from its position almost vertical to the Cp ring (as determined previously²¹) to one in which this nitrogen is now attached to the metal.

The relative orientations of the two phosphorus spins at ca. 150 – 160° from one another, follows from *selective* inter-Cp ring NOE's (see Chart I). Specifically, H-6 shows a strong interaction to H-3' thereby placing P^2 remote from the side chain (thus indirectly supporting a chainlike structure). The four methylene protons have been tentatively assigned using NOE's arising from (a) H-6 to one of the protons on C-8 and (b) NCH_3 -12 (one side of the CH_2 - CH_2 fragment faces this NCH_3 whereas the other

^{31}P CP/MAS solid-state spectrum for $\text{HgCl}_2(\mathbf{6})$.

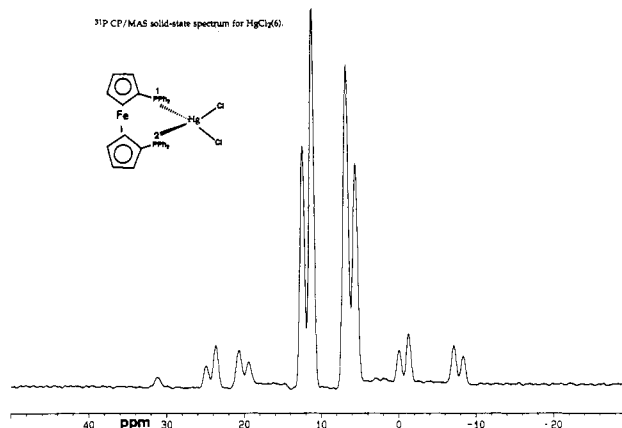


Figure 5. ^{31}P CP/MAS solid-state spectrum for $\text{HgCl}_2(\mathbf{6})$. There are two nonequivalent ^{31}P spins which spin-spin couple. The less intense resonances arise from the ^{199}Hg satellites. The spinning side bands have a negligible intensity.

side has one C-8 and C-9 proton facing "down" toward the Cp ring without the side chain). A summary of the proton NMR data for **2** is given in Table II.

Solid-State ^{31}P NMR. In view of the complicated dynamics observed in solution, we have also measured ^{31}P CP/MAS solid-state spectra for the complexes **2a,b,d** as well as two analogs with the parent ligand, **3a,d**, and summarize the data in Table III. There is an increasing literature concerned with ^{31}P solid-state measurements on metal complexes,^{22a-d} and in consideration of this we begin with the discussion of some model complexes. Figure 5 shows the phosphorus spectrum for $\text{HgCl}_2(\mathbf{6})$. In the solid, local packing effects reduce the symmetry of the complex so that nonequivalent phosphorus spins and consequently $^2J(\text{P,P})$ values are observed, and there is precedence for such solid-state effects in mercury chemistry.^{22d} The magnitudes of the observed one-bond interactions are reasonably close to what is found in solution,

(21) Togni, A.; Blumer, R. E.; Pregosin, P. S. *Helv. Chim. Acta* **1991**, *74*, 1533.

(22) (a) Rahn, J. A.; Balthuis, L.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 750. (b) Rahn, J. A.; O'Donnell, D. J.; Palmer, A. R.; Nelson, J. H. *Inorg. Chem.* **1989**, *28*, 2631. (c) Carty, A. J.; Fyfe, C. A.; Lettinga, M.; Johnson, S.; Randall, L. H. *Inorg. Chem.* **1989**, *28*, 4120. (d) Allman, T.; Lenkinski, R. E. *Inorg. Chem.* **1986**, *25*, 3202. (e) Power, W. P.; Lumsden, M. D.; Wasylshen, R. E. *Inorg. Chem.* **1991**, *30*, 2997; *J. Am. Chem. Soc.* **1991**, *113*, 8257.

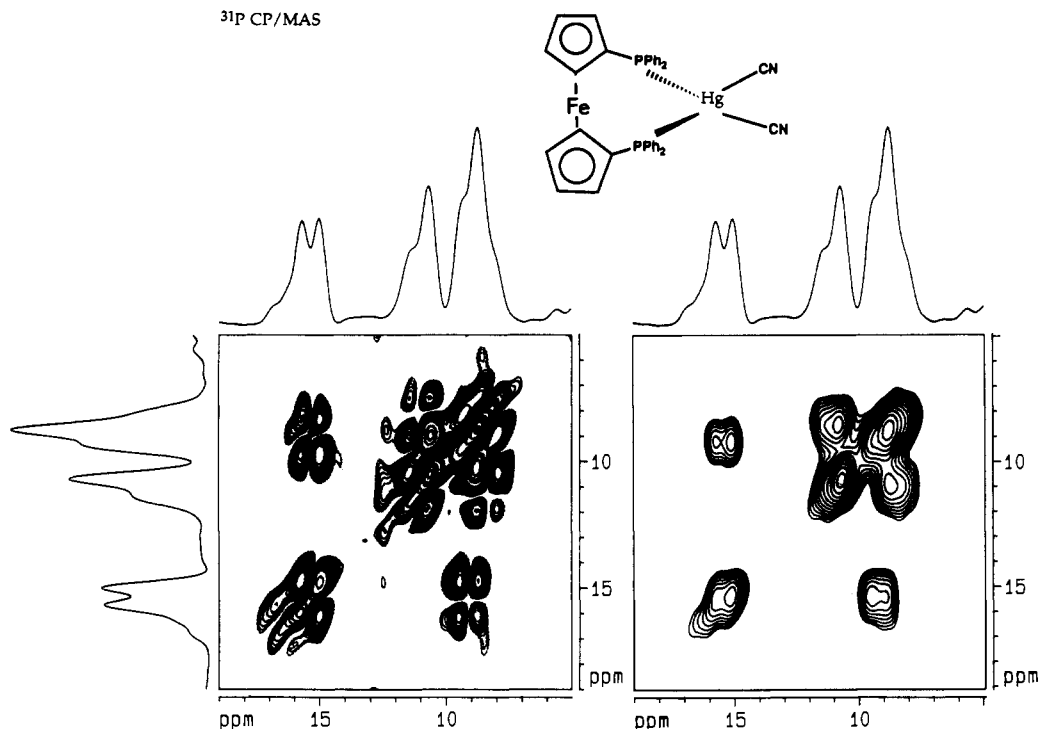


Figure 6. ^{31}P CP/MAS solid-state spectrum for $\text{Hg}(\text{CN})_2(6)$ which consists of two overlapping AB spin systems. The solid-state COSY spectrum (left) connects resonances which are coupled to one another, e.g., the two low-field groupings are *not* coupled and therefore belong to different molecules, whereas the solid-state EXSY spectrum (right) reveals spins which are relatively close in space.

and the two-bond coupling constants are in agreement with previous observations.^{22d} The corresponding spectrum for $\text{Hg}(\text{CN})_2(6)$ is more complex and can be explained assuming that there are two nonequivalent molecules in the unit cell. There may also be two different crystalline forms of the complex. This, combined with the nonequivalence of the two phosphorus spins, as above, leads to a series of overlapping lines with consequent interpretation difficulties. These can be partially overcome via the use of COSY and EXSY (spin diffusion) methods, and Figure 6 shows both types of measurement for this cyanide complex. It is obvious from both of these methodologies that there are two individual AB spin systems, A and A' at lower field and B and B', overlapping, at higher field. The observation of a 2J value in both of these model complexes suggests that one would have observed analogous splittings for the complexes **2**, in solution, and possibly also in the solid state if the two phosphorus spins were on the same metal; however, we do not observe these 2J values for **2** in solution thereby supporting the contention that these compounds have the phosphorus spins on different metal centers.

The ability to locate proximate phosphorus spins in the solid via EXSY, whether or not they are coupled, is potentially very valuable. Consider the ^{31}P solid-state spectrum for the cyanide complex **2d** (see Figure 7). The 2-D EXSY measurement (see insert in Figure 7) shows *no* cross-peaks connecting the high- and low-field signals so that one can conclude that these spins are relatively remote. In addition, on the basis of the chemical shifts of ca. 14 and 24 ppm, and ca. -20 and -29 ppm (ligand **1** in CDCl_3 solution shows signals at -16.9 and -23.5 ppm), we can suggest that, in the solid state, we are dealing with coordinated and uncoordinated phosphorus spins, respectively.

Regrettably, the lines are relatively broad due to the amorphous nature of compound **2d**; nevertheless, the chemical shifts clearly indicate that the solid-state structure of the powder is different from that found at low temperature in solution, where both P^1 and P^2 were coordinated. Just as in the solution state, the actual structure for **2d** in the solid state is not known. One can imagine a number of possibilities including a mixture with P^1 coordinated and P^2 free, and vice-versa, as well as oligomeric structures, and

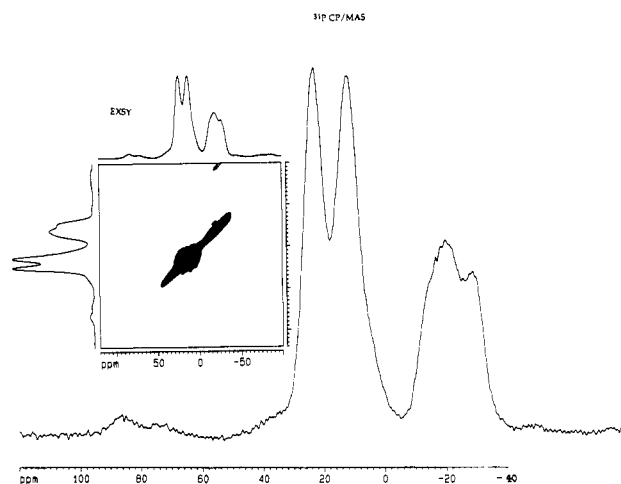


Figure 7. ^{31}P CP/MAS solid-state spectrum of **2d**, with EXSY spectrum shown as an insert. The low- and high-field regions are consistent with coordinated and uncoordinated phosphorus resonances, respectively. This is supported by the EXSY, which suggests that these spins are relatively removed from one another.

at the moment we have no way of making a definite assignment. We believe, however, that such 2-D solid-state measurements will have wide application.

NOESY and Molecular Size. Given the increase in the application of ^1H NOESY methods, we comment here with respect to the relation between molecular weight and phase of the cross-peaks.

One of the major advantages of phase-sensitive ^1H 2-D NOESY is that one can use the phases of the signals to monitor exchange at the same time that one detects structurally useful Overhauser effects.²³ This is due to the expectation that, for relatively small molecules, the exchange cross-peaks have the same sign as the diagonal whereas the NOE's have the opposite sign.²⁴ This is the

(23) (a) Ammann, C.; Pregosin, P. S.; Rügger, H.; Grassi, M.; Musco, A. *Magn. Reson. Chem.* **1989**, *27*, 355. (b) Albinati, A.; Kunz, R. W.; Ammann, C.; Pregosin, P. S. *Organometallics* **1991**, *10*, 1800.

case when the molecules in question fulfill the so-called "extreme narrowing condition",²⁴ in which the product of the molecular correlation time and the resonance frequency should be much less than unity. It is well-known that this condition is not fulfilled for many biooligomers and certainly not for proteins.²⁵ The practical consequence is that the phase (sign) of the cross-peaks changes and is now the same sign as the diagonal. Naturally, it is possible that, for a given molecular weight and consequent molecular motion, the correlation time could correspond to an NOE value which is close to zero and this problem is usually circumvented by the use of ROESY methods.²⁶

For our ligand **1** the ¹H 2-D NOESY spectrum reveals cross-peaks with signs opposite to that of the diagonal; however, complexation to afford **2** changes the situation such that there are now cross-peaks containing both phases, many of which are weaker in intensity than the corresponding cross-peaks in **1**. We assume that the complexation of **1** to Hg(II) slows certain molecular motions in the ligand. To test this we have measured ¹³C and ¹H T₁ values for **1** and **2a** and used the carbon data to estimate correlation times as these should reflect the anchoring of the ligand.²⁷ Preliminary calculations based on these T₁ data confirm the phase behavior of the cross peaks and suggest that ROESY and not NOESY measurements may be needed in the future when investigating metal complexes with a higher molecular weight.

Conclusions

Before leaving this chemistry, it is appropriate to ask what connection there might be between complexes **2** and the gold(I)-catalyzed aldol condensation described in the Introduction. While the complexes **2** do show some moderate activity in olefin oligomerization, they do *not* catalyze the aldol condensation referred to above, so that these molecules, although interesting in themselves, need not be related to this gold(I) chemistry. In a more general vein, it is obvious that future preparative chemistry with ligand **1** and its analogs may well lead to oligomeric complexes. Indeed, the only known ferrocenylphosphine/Au(I) solid-state structure^{4c} contains a trimer, of composition Au₃Cl₃(**1**)₂, with the abbreviated structure shown in Chart I. It is certainly interesting that we find a somewhat related arrangement in our mercury(II) chemistry. Further, we have shown that it is possible for this type of side chain to coordinate via both nitrogens, given a metal center with sufficient affinity for such tertiary nitrogen ligands. Finally, we consider it both useful and promising that solid-state ³¹P NMR methods provide structural results for both **2** and **3** which are not readily available from solution measurements.

Experimental Section

Platinum metals were obtained from Johnson-Matthey, and ¹³C-enriched KCN was obtained from Cambridge Isotopes Laboratories, Bern, Switzerland. Conductivity measurements in nitromethane were made using a conductivity bridge from Metrohm AG following the method of Feltham and Hayter.²⁸ Values of 126.9, 132.1, 129.8, and 137.4 Ω⁻¹ cm² mol⁻¹, respectively, were found for **2a-d**. The normal range for 1:2 electrolytes is ca. 115–250.²⁹ FAB mass spectra as well as microanalytical measurements were performed in the analytical laboratories of the ETH

Zurich and Ciba-Geigy, Basel, Switzerland. Solution NMR spectra were measured using Bruker AC-200 and AMX-500 MHz spectrometers. Referencing is to H₃PO₄ (³¹P) and TMS (¹H). Two-dimensional NMR spectra were measured as described by us previously.⁸ Solid-state NMR spectra were measured on a Bruker AMX-400 spectrometer equipped with a wide-bore magnet and a CP/MAS probehead (4 mm o.d. rotor). Cross polarization was achieved using a 2.5-ms contact time with a rotation speed of 10 kHz at the magic angle (12 kHz for the spectrum shown in Figure 7). Phase sensitive COSY and exchange spectra were measured by modified DQF-COSY and NOESY sequences, where the first 90° pulse had been replaced by the cross-polarization scheme. Mixing times in the exchange spectra were 2 s for **3d** and 1.5 s for **2d**, respectively.

Ligand **1** was prepared as described.³⁰

[HgX₂(**6**)]. These complexes were all prepared in an identical fashion with the chloride given here as a representative example. Mercury(II) chloride (0.049 g, 0.180 mmol) was suspended in 30 mL of ethanol and then warmed to 323 K. A solution of ligand **6** (0.100 g, 0.180 mmol) dissolved in 100 mL of ethanol and 10 mL of methylene chloride warmed to 323 K was then added dropwise to the HgCl₂ solution. The resulting solution was stirred for 2 h at 323 K and then cooled to room temperature. The suspension which resulted was then stirred for an additional 12 h at 243 K. Filtration of the product was followed by washing with pentane and drying in vacuo. Recrystallization from methylene chloride/ether gave the product. FAB/MS (*m/e*): 791.1, HgCl₂(**6**)⁺; 554.1, **6**⁺. FAB/MS for Hg(CN)₂(**6**)⁺: 782.1, Hg(CN)₂(**6**)⁺; 554.1, **6**⁺.

[Hg₃Cl₃(**1**)₂]Cl₂ was prepared as described above (with the exception that the ligand could be dissolved in 25 mL of ethanol at 323 K and that the HgCl₂ was suspended in the same amount of warm ethanol). The product could be recrystallized from chloroform. From HgCl₂ (0.240 g, 0.880 mmol) and **1** (0.600 g, 0.880 mmol) one obtained 419 mg (66%) of product. Anal. Calcd (found) for C₈₂H₈₈Cl₆Fe₂Hg₃N₄P₄: C, 45.09 (45.41); H, 4.03 (4.13); N, 2.56 (2.73). FAB/MS (*m/e*): 918.8, HgCl(**1**)⁺; 680.9, **1**⁺. The remaining derivatives were prepared in a similar fashion. The corresponding bromide was recrystallized from chloroform/toluene, yield 454 mg (63%). Anal. Calcd (found) for C₈₂H₈₈Br₆Fe₂Hg₃N₄P₄: C, 40.19 (40.87); H, 3.56 (2.80); N, 2.28 (2.41). FAB/MS (*m/e*): 1042.0, HgBr₂(**1**)⁺; 963.0, HgBr(**1**)⁺; 683.0, **1**⁺. The corresponding iodide was recrystallized from chloroform/THF, yield 496 mg (62%). Anal. Calcd (found) for C₈₂H₈₈Fe₂Hg₃I₆N₄P₄: C, 36.04 (37.09); H, 3.22 (3.82); N, 2.05 (1.93). FAB/MS (*m/e*): 1012.0 = HgI(**1**)⁺, 683.0 = **1**⁺. The corresponding cyanide was recrystallized from methylene chloride/pentane, yield 394 mg (63%). Anal. Calcd (found) for C₈₈H₈₈Fe₂Hg₃N₁₀P₄: C, 49.68 (50.04); H, 4.14 (4.43); N, 6.58 (6.73). FAB/MS (*m/e*): 910.3, Hg(CN)(**1**)⁺; 681.3, **1**⁺.

We have been able to grow crystals of **2c**; however, it was found that they were twinned and so not suitable for X-ray analysis.

Complex **8** (86.1 mg, 0.238 mmol) and **1** (100 mg, 0.146 mmol) were warmed in 40 mL of EtOH for 2 h. After cooling, the ethanol was removed in vacuo and the solid washed with hexane. Precipitation by slow cooling overnight at 243 K from EtOH/CH₂Cl₂ gave 156 mg of product in 76% yield. Anal. Calcd (found) for C₄₁H₄₄Br₄FeHg₂N₂P₄: C, 35.01 (35.08); H, 3.13 (3.41); N, 1.99 (2.06).

[PtCl₂(**1**)]. PtCl₂ (53 mg, 0.20 mmol) was suspended in 3 mL of degassed benzene (toluene gave poorer yields) and then treated with **1** (137 mg, 0.20 mmol) dissolved in 2 mL of the same solvent. Refluxing for 30 h (shorter reaction times afforded smaller yields of product due to presumed oligomer formation) was followed by filtration, and the brown solid which resulted was dissolved in 8 mL of methylene chloride. Addition of 2 mL of benzene induced precipitation of a small amount of brown solid, which was removed by filtration. The clear filtrate was concentrated and the solid thus obtained recrystallized from 1:5 chloroform/diethyl ether.

Acknowledgment. P.S.P. thanks the Swiss National Science Foundation and the ETH Zurich for financial support, as well as Johnson-Matthey for the loan of precious metals. We also wish to thank the University of Milan for support for F.L.

- (24) (a) Hull, W. E. In *Methods in Stereochemical Analysis*; Croasmun, W. R., Carlson, R. M. K., Eds.; VCH Publishers: New York, 1987; Vol. 9, p 153. (b) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95.
 (25) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, U.K., 1987, pp 516–538.
 (26) Davis, D. G.; Bax, A. J. *Magn. Reson.* **1985**, *64*, 533. (b) Fejzo, J.; Westler, W. M.; Macura, S.; Markley, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 2574.
 (27) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; Wiley-Interscience: New York, 1972; p 188.
 (28) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc.* **1964**, 4587.

- (29) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.
 (30) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.
 (31) Goggin, P. L.; Goodfellow, R. J.; McEwan, D. M.; Kessler, K. *Inorg. Chim. Acta* **1980**, *44*, L111.