those of the isolated anion and cation complexes. The orbitals of the anion and cation complexes which would be expected to have the largest overlap in forming a pair complex of the type in I are those which are largely metal orbitals which are perpendicular to the molecular planes, *viz.*, d_{z^2} and p_z. Overlap of other orbitals is expected to be significantly smaller. An energy level diagram showing the interaction of the d_{z^2} and p_z metal orbitals and the spectroscopically important π^* combination of the cyanide and isocyanide ligands is given in Figure 4. The symmetry of I will be C_{4v} if the rotameric conformation is eclipsed or staggered; otherwise it will be C_4 as long as the molecular planes of the anion and cation complexes are parallel. The levels of Figure 4 are labeled according to C_{4v}, but those of C_4 would be equivalent. Since the combinations of the d_{z^2} orbitals and those of the p_z orbitals have the same symmetry, significant mixing of these levels may be visualized, and this mixing can impart stability to the anion-cation complex by lowering the energy of the occupied orbitals. The 30-kK band is interpreted as the transition $2a_1(d_{z^2}) \rightarrow 3a_1(\pi^*)$ $[^1A_1 \rightarrow {}^1A_1]$; this transition would be dipole allowed and polarized in the direction of the Pt-Pt axis in the associated complex.

It is interesting that the *tert*-butyl complex association constant is greater than for the ethyl compound. This may be an indication that the steric requirement for the alkyl group plays a minor role in affecting the stability of the anion-cation complex and that other factors such as inductive effects of the alkyl group or solvation differences may be more important.

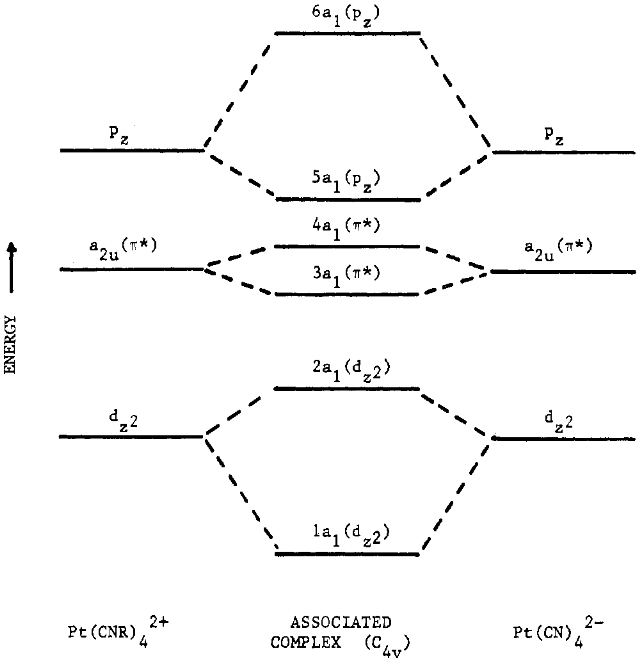

Figure 4. Energy levels of the anion-cation associated complex. Only the levels resulting from the interaction of d_{z^2} and p_z orbitals are shown along with the spectroscopically important π^* combinations from the cyanide and alkyl isocyanide ligands.

Registry No. $[Pt(CNC_2H_5)_4][Pt(CN)_4]$, 50600-85-6; $[Pt(CNCH_3)_4][Pt(CN)_4]$, 50600-86-7; $[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]$, 50600-88-9.

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Reaction of 1,1′-Bis(diphenylphosphino)ferrocene with Mercuric Halides, Mercuric Cyanide, and Other Lewis Acids

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The reaction of 1,1′-$Fe(cpPPh_2)_2$ with HgX_2 (X = Cl, Br, I, SCN) gives $Fe(cpPPh_2)_2 \cdot nHgX_2$ (n = 1, 2). Infrared, electronic absorption, polarographic, and ^{57}Fe Mossbauer spectroscopic data are presented to show that in every case it is the phosphorus not the iron atom that is bonded to the mercury. The reaction of 1,1′-$Fe(cpPPh_2)_2$ with $Hg(CN)_2$ in the presence of acid gives $[(Fe(cpPPh_2)_2)_2Hg](X)_2$ ($X^- = BF_4^-, PF_6^-$) where physical data show that the dication has a P-Hg interaction. Ruthenocene reacts with SnX_4 (X = Cl, Br) to give compounds with Ru-Sn bonds. The products of the reaction of 1,1′-$Fe(cpPPh_2)_2$ and SnX_4 are described.

Introduction

The mercury-bridged cation $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$ is the product of electrochemical oxidation of ruthenocene at a mercury anode.[1] The reaction of mercuric halides with ruthenocene also gives compounds with mercury-ruthenium bonds.[2,3] In the case of ferrocene a red diamagnetic material with the composition $Fe(cp)_2 \cdot 7HgCl_2$ can be isolated.[2] Indications of an Fe-Hg interaction were seen in the infrared spectrum of this red compound.

In this paper we report the results of a study of the interaction of various 1,1′-disubstituted ferrocenes with HgX_2 (X = Cl, Br, I, CN, SCN). Of particular interest is the case where the 1,1′-disubstituted ferrocene is 1,1′-bis(diphenylphosphino)ferrocene, $Fe(cpPPh_2)_2$. This ferrocene was recently prepared by Davison, *et al.*,[4] as a potential bidentate ligand and two very recent reports have shown that it does coordinate to platinum[5] to give $Pt[Fe(cpPPh_2)_2](n\text{-}Bu)_2$ and $Pt[Fe(cpPPh_2)_2]Cl_2$ and to molybdenum[6] to give $Mo(N_2)_2$-

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Table I. Analytical Data

Compd	% C		% H		% Fe		% X[a]		% Hg		% Sn	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Fe(cpPPh_2)_2$	73.66	73.73	5.09	5.10	10.07	10.08						
$Fe(cpPPh_2)\cdot HgCl_2$	49.45	49.48	3.42	3.61	6.76	6.67	8.59	8.88	25.59	24.29		
$Fe(cpPPh_2)_2\cdot 2HgCl_2$	37.21	36.71	2.57	2.36	5.09	4.85	12.42	12.20				
$Fe(cpPPh_2)_2\cdot HgBr_2$	44.64	44.18	3.09	2.98	6.11	6.21	17.47	16.78				
$Fe(cpPPh_2)\cdot 2HgBr_2$	32.02	31.97	2.21	2.14	4.38	4.35						
$Fe(cpPPh_2)_2\cdot HgI_2$	40.48	40.26	2.80	2.76	5.54	5.46						
$Fe(cpPPh_2)_2\cdot 2HgI_2$	27.91	28.41	1.93	1.99	3.82	3.50						
$Fe(cpPPh_2)_2\cdot Hg(SCN)_2$[b]	49.64	49.50	3.24	3.39	6.41	6.36						
$[(Fe(cpPPh_2)_2)_2Hg](BF_4)_2$	55.07	54.31	3.81	3.53	7.53	7.79			13.53	13.42		
$[(Fe(cpPPh_2)_2)_2Hg](PF_6)_2$	51.07	50.69	3.53	3.56	6.98	7.03						
$[(Ru(cp)_2)_2SnCl_2](SnCl_5)_2$	19.31	19.01	1.62	1.65			34.20	34.26			28.62	28.91
$[(Ru(cp)_2)_2SnBr_2](SnBr_5)_2$	13.51	13.96	1.13	1.20							20.03	21.58
$[Ru(cp)_2Cl](SbCl_6)$	19.98	19.04	1.68	1.79			41.28	40.33				
$Fe(cpCH_3)_2\cdot 6HgCl_2$	7.82	7.60	0.77	0.80			23.08	22.3				
$Fe(cp\text{-}n\text{-}Bu)_2\cdot 6HgCl_2$	11.22	11.96	1.36	1.53	2.90	2.76						
$Fe(cpPh)(cp)\cdot 7HgCl_2$	8.89	8.38	0.65	0.67			22.95	22.1	64.93	63.0		
$[(Fe(cpPPh_2)_2)_2SnCl_2](SnCl_5)_2$	43.21	43.42	2.99	3.58	5.91	6.62	22.51	23.46				
$Fe(cpPPh_2)_2\cdot 2SnCl_2$	37.97	37.61	2.62	2.92	5.19	5.13	26.37	27.94				
$[(Fe(cpPPh_2)_2SnBr_2](SnBr_5)_2$	33.70	32.78	2.33	2.60	4.61	4.36						
$Fe(cpPPh_2)_2\cdot 2SnBr_4$	28.54	28.65	1.97	2.36	3.90	3.58	44.67	43.46				
$Fe(cpPPh_2)_2\cdot 1.5SbCl_5$	40.72	39.98	2.81	2.79	5.57	4.71						
$Fe(cpPPh_2)_2\cdot 3SbCl_5$	28.14	28.05	1.94	2.21	3.85	3.41	36.64	36.88				

[a] X is the halogen. [b] Nitrogen analysis: calcd, 3.22%; found, 3.24%.

(diphos)[$Fe(cpPPh_2)_2$]. Only in the case of the platinum compounds is $Fe(cpPPh_2)_2$ acting as a bidentate ligand. In this work we have prepared with this ferrocene two types of compounds: $Fe(cpPPh_2)_2\cdot nHgX_2$ ($n = 1, 2$; X = Cl, Br, I, SCN) and $[(Fe(cpPPh_2)_2)_2Hg](anion)_2$ where anion = PF_6^- or BF_4^-; they are characterized in the present paper. We have also had the occasion to study the interaction of $Fe(cpPPh_2)_2$ and ruthenocene with the Lewis acids $SnCl_4$, $SnBr_4$, and $SbCl_5$ and will report on this.

Experimental Section

Ruthenocene (ROC/RIC and Strem) was purified by sublimation under vacuum. Ferrocene and the substituted ferrocenes were purchased from ROC/RIC and used without further purification. 1,1'-Bis(diphenylphosphino)ferrocene was synthesized according to Bishop, *et al.*[4] Analyses were performed by the University of Illinois microanalytical laboratory; analytical data for all of the compounds in this study are given in Table I.

$Fe(cpPPh_2)_2\cdot nHgX_2$ (n = 1, 2; X = Cl, Br, I, SCN). The mercuric halide adducts of 1,1'-(diphenylphosphino)ferrocene were formed either using stoichiometric amounts of the reactants for $n = 1$ or an excess of mercuric halide for $n = 2$. The preparation of $Fe(cpPPh_2)_2\cdot HgCl_2$ is typical. $Fe(cpPPh_2)_2$ (0.0973 g, 0.176 mmol) and $HgCl_2$ (0.0479 g, 0.176 mmol) were dissolved in ~150 ml of boiling absolute ethanol. The resulting yellow solution was reduced to a volume of about 50 ml and filtered hot. When the solution was cooled in an ice bath, yellow air- and moisture-stable crystals were obtained. The analytical results are given in Table I.

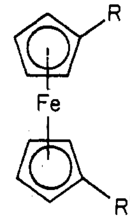
$[(Fe(cpPPh_2)_2)_2Hg](X)_2$ ($X^- = BF_4^-, PF_6^-$). $Fe(cpPPh_2)_2$ (0.111 g, 0.200 mmol) and $Hg(CN)_2$ (0.0253 g, 0.100 mmol) were dissolved in ~150 ml of boiling absolute ethanol. Excess HBF_4(aq) was added cautiously (*hood!*) and the solution volume was reduced 50% and then cooled. The yellow air- and moisture-stable BF_4^- crystals were then dried *in vacuo* over P_2O_5. The hexafluorophosphate salt of the $[Fe(cpPPh_2)_2]_2Hg^{2+}$ cation was obtained by dissolving the BF_4^- salt in hot 95% ethanol and adding a hot 95% ethanol solution of NH_4PF_6.

$SnCl_4$, $SnBr_4$, and $SbCl_5$ Adducts. The reactions of ruthenocene and 1,1'-bis(diphenylphosphino)ferrocene with these Lewis acids were performed in a nitrogen-filled glove bag equilibrated with P_2O_5. The Lewis acid and substituted ferrocene or ruthenocene were dissolved in CCl_4 under a nitrogen atmosphere and the solutions were added together to give yellow, air-stable powders analyzing as indicated in Table I.

Physical Measurements. Infrared and electronic absorption spectra were run on Perkin-Elmer Model 457 and Cary Model 14 spectrophotometers, respectively. Electrochemical measurements were carried out at 25° with a PAR Model 174 polarograph employing acetonitrile solutions with 0.1 M $LiClO_4$ electrolyte. All potentials are referenced to a saturated calomel electrode (sce). Molecular weights (in acetonitrile) were measured using a Mechrolab Model 301 A vapor pressure osmometer.

Results and Discussion

Mercuric Halides and Substituted Ferrocenes. Absolute ethanol or ether solutions of the ten substituted ferrocenes Ia-j were allowed to react either with solutions of HgX_2 (X = Cl, Br, I, SCN) or with solutions of $Hg(CN)_2$ with HBF_4 added. Solid products were obtained in the case of only four of the ten substituted ferrocenes. For the other six substituted ferrocenes there was a discernible enhancement in the solubility of HgX_2 (X = Cl, Br, I, SCN), possibly indicating some interaction between the ferrocene and the mercuric species; however, in each case the electronic absorption spectrum was that expected for a superposition of ferrocene and HgX_2 spectra. Of the four ferrocenes giving solid products upon reaction with HgX_2, three (Ib, Ic, and If) gave blue ferricenium products. The stoichiometry of these three blue ferricenium compounds (see Table I where only data for the chlorides are presented) is very similar to that of the final blue product formed between ferrocene and HgX_2, *i.e.*, $Fe(cp)_2\cdot nHgX_2$, where $n \simeq 7$. As argued before,[2] these blue salts are probably salts of ferricenium ions with mercuric anions and "lattice" HgX_2. The substituted ferrocenes which give blue ferricenium compounds are those that have



Ia, R = R' = PPh_2
b, R = R' = CH_3
c, R = R' = n-Bu
d, R = R' = COOH
e, R = R' = $COCH_3$
f, R = Ph, R' = H
g, R = $COCH_3$, R' = H
h, R = COOH, R' = H
i, R = CHO, R' = H
j, R = $C(OH)CH_3$, R' = H

oxidation potentials less than or comparable to that of ferrocene. Unfortunately, it was not possible to isolate a *red* HgX_2 adduct for any of the substituted ferrocenes.

The most interesting results of this study come from the reaction of 1,1′-bis(diphenylphosphino)ferrocene (Ia) with HgX_2 and $Hg(CN)_2$, to which we now turn. Yellow crystalline solids of the composition $Fe(cpPPh_2)_2 \cdot HgX_2$ result from the reaction of ferrocene (Ia) with HgX_2 (X = Cl, Br, I, SCN) when the two reactants are present in a 1:1 stoichiometry or when the ferrocene is in excess. Analytical data are given in Table I for these compounds. When excess HgX_2 is used, the composition of the product is $Fe(cpPPh_2)_2 \cdot 2HgX_2$. Again the material is yellow and as such it is evident that the ferrocene is *not* oxidized. This is very reminiscent of the situation[2] with ruthenocene, where reaction with HgX_2 yields either $Ru(cp)_2 \cdot HgX_2$ or $Ru(cp)_2 \cdot 2HgX_2$. Because of this apparent similarity, we were led to try the reaction of $Fe(cpPPh_2)_2$ with $Hg(CN)_2$ in the presence of some acid such as HBF_4. In the case of ruthenocene this leads to the formation[1] of the mercury-bridged cation $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$. In the case of $Fe(cpPPh_2)_2$ the apparent analogy with ruthenocene again held true and the reaction with $Hg(CN)_2$ and acid gave the cation $[Fe(cpPPh_2)_2]Hg^{2+}$, which was isolated as either the BF_4^- or the PF_6^- salt (see Table I for analyses). We have collected considerable physical data on all of these $Fe(cpPPh_2)_2$ systems and in the following it will be shown that the analogy with ruthenocene is *not* valid and that these ferrocene compounds do *not* have Fe-Hg bonds analogous to the Ru-Hg bonds present in the ruthenocene systems. There are two different types of formulations for the above compounds, one wherein there is an Fe-Hg bond and the other where the mercury interacts with the phosphorus sites on the ferrocene.

Molecular weight determinations were made on the BF_4^- and PF_6^- salts of $[Fe(cpPPh_2)_2]_2Hg^{2+}$ in acetonitrile. The effective molecular weight found for a sample of the BF_4^- salt is 414, which is in moderate agreement (−16.2%) with a 494 value calculated for dissolution of the salt to give a dication and two BF_4^- ions. For the PF_6^- salt the MW_{eff} found is 462 compared (−13.3%) with that calculated (533) for a 1:2 electrolyte. In both cases the low MW_{eff} found could indicate some dissociation of the cation $[Fe(cpPPh_2)_2]_2Hg^{2+}$, but the fair agreement with the MW_{eff} calculated is substantiation for the presence in these materials of the $[Fe(cpPPh_2)_2]_2Hg^{2+}$ unit. The solubility of the HgX_2 adducts was found to be insufficient for molecular weight measurements.

The ir spectra of all of the 1,1′-bis(diphenylphosphino)ferrocene compounds are very similar to each other and to the parent compound (excluding the obvious counterion, etc., peaks). In Figure 1 are reproduced the ir spectra (KBr pellets) of $Fe(cpPPh_2)_2$, $Fe(cpPPh_2)_2 \cdot HgCl_2$, and $[(Fe(cpPPh_2)_2)_2Hg](PF_6)_2$. The PF_6^- bands are marked with crosses in the last spectrum. The compound $Fe(cpPPh_2)_2 \cdot Hg(SCN)_2$ has a SCN band at 2111 cm^{-1}. Asymmetric C-C cyclopentadienyl ring stretching modes are seen at 1432, 1438, and 1436 cm^{-1}, respectively, for the three compounds in Figure 1. Ferrocene has a 1411-cm^{-1} asymmetric C-C stretch.[7] In the spectra reproduced in Figure 1 it is also possible to identify for the three compounds the asymmetric C-C stretch of the phosphorus-bound benzene as bands at 1477, 1481, and 1479 cm^{-1}, respectively. However, the important observation to make in respect to the ~1435-cm^{-1} region is that there is no detectable splitting in the asymmetric C-C cyclopentadienyl stretch for either the $HgCl_2$ adduct or the PF_6^- salt. Splitting in this band has been taken to indicate[1,2] appreciable ring distortion due to a metal-mercury interaction in $Ru(cp)_2 \cdot HgX_2$, red $Fe(cp)_2 \cdot 7HgX_2$, and $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$. There is also a broadening and intensity alteration of the bands in the region between 1000 and 1400 cm^{-1} in going from the parent ferrocene to the Hg-containing compounds. Many of the bands in this region have been assigned to C-P stretching and bending and ring modes in the phosphorus phenyl group.[8,9] Broadening and intensity changes such as these are seen in other phosphines upon coordination to a metal.[8,9] There are no bands in these spectra assignable to Hg-P stretches because they fall outside the range of the instrument.[10] Unsuccessful attempts were made to secure Raman spectra for these $Fe(cpPPh_2)_2$ compounds using both the red (15,454 cm^{-1}) and the green (19,435 cm^{-1}) lines of a Kr-Ar laser (Spex Model RS2 Ramalab).

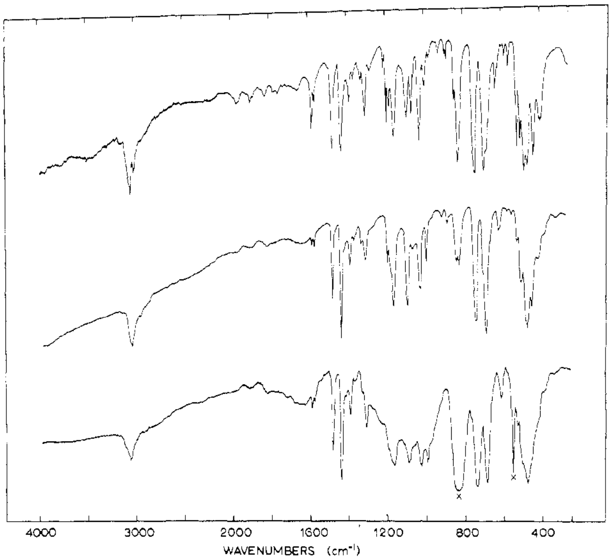


Figure 1. Infrared spectra of KBr pellets of 1,1′-$Fe(cpPPh_2)_2$ (top), $Fe(cpPPh_2)_2 \cdot HgCl_2$ (middle), and $[(Fe(cpPPh_2)_2)_2Hg](PF_6)_2$ (bottom).

Electronic absorption spectra were determined for acetonitrile solutions of the $Fe(cpPPh_2)_2$ compounds; the results are given in Table II. Analogous to the infrared data, there is little change in the electronic absorption spectrum in going from the parent compound to the Hg-containing materials. The molecule $Fe(cpPPh_2)_2$ has three features in its spectrum (441, 249, and a band at ~210 mμ). The first band system is undoubtedly an overlapping of the two lowest energy spin-allowed d-d transitions ($a^1E_{1g} \leftarrow {}^1A_{1g}$ and ${}^1E_{2g} \leftarrow {}^1A_{1g}$) as assigned in ferrocene.[11] The band system at 249 mμ is assignable to phenyl group transitions; benzene has a ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition at 254 mμ, which is variable in band position and intensity, dependent on substitution.[12,13] The two compounds $[(Fe(cpPPh_2)_2)_2Hg]X_2$ (X = PF_6, BF_4) also exhibit electronic spectra with three features which are very comparable to those for $Fe(cpPPh_2)_2$ in position and intensity per Fe-

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Table II. Electronic Spectral Data[a] for the Ferrocene-1,1′-Bis(diphenylphosphine) Complexes

	hν		
Compd	mμ	cm^{-1}	ϵ, cm^{-1} M^{-1}
$[(Fe(cpPPh_2)_2)_2Hg](X)_2$			
$X^- = BF_4^-$	423 sh	23,600	608
	241 sh	41,500	50,700
	<210	>48,000	
$X^- = PF_6^-$	425 sh	23,500	610
	239 sh	41,800	54,600
	<210	>48,000	
$Fe(cpPPh_2)_2 \cdot xHgCl_2$			
$x = 1$	442	22,600	188
	249 sh	40,200	27,500
	<210	>48,000	
$x = 2$	*b*	*b*	*b*
	226	44,200	36,800
	<210	>48,000	
$Fe(cpPPh_2)_2 \cdot xHgBr_2$			
$x = 1$	442	22,600	211
	249 sh	40,200	30,600
	<210	>48,000	
$x = 2$	*b*	*b*	*b*
	256	39,100	42,200
	<210	>48,000	
$Fe(cpPPh_2)_2$	441	22,700	204
	249	40,200	24,200
	<210	>48,000	

[a] In acetonitrile at room temperature. [b] Not soluble enough to determine these values accurately.

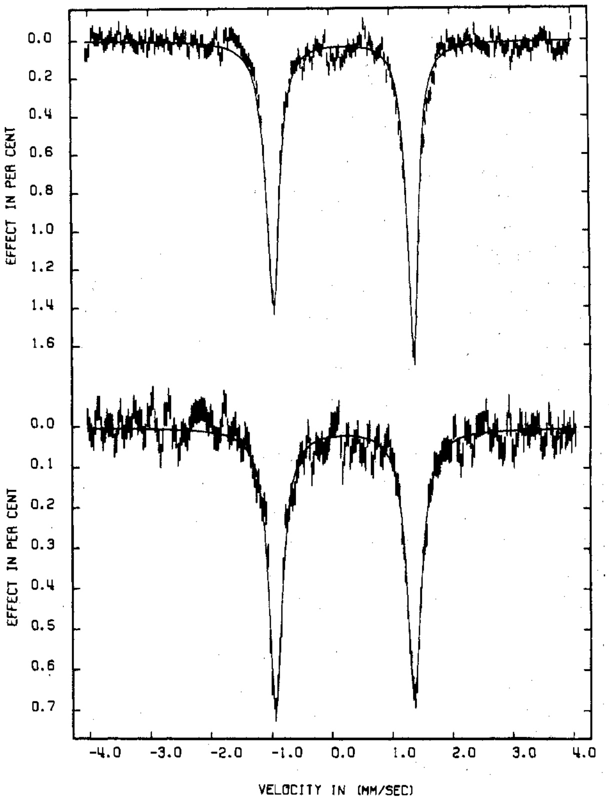
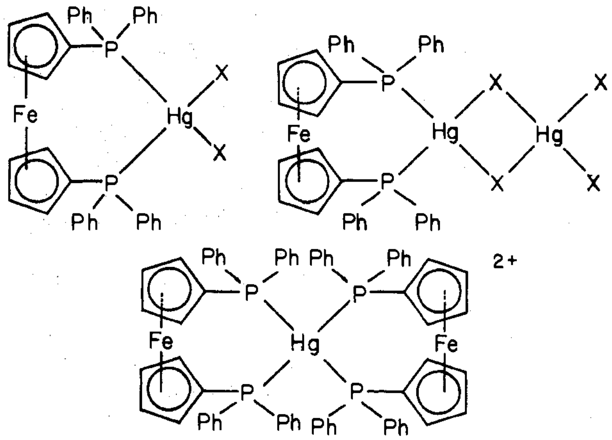


Figure 2. Iron-57 Mossbauer spectra for 1,1′-$Fe(cpPPh_2)_2$ (top) and $[(Fe(cpPPh_2)_2)_2Hg](BF_4)_2$ (bottom). Velocity scale is referenced to Co in Cu source.

$(cpPPh_2)_2$ moiety. Since we know from molecular weight measurements that $[Fe(cpPPh_2)_2]_2Hg^{2+}$ is not appreciably dissociated in acetonitrile, it is germane to note that there is no feature in the solution electronic spectrum attributable to a $\sigma \rightarrow \sigma^*$ transition expected for a Fe-Hg bond. In the solution spectra of the cation[1] $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$ and other metal-metal bonded species[14] there is an intense $\sigma \rightarrow \sigma^*$ transition. There is also no evidence in the spectra of the $Fe(cpPPh_2)_2 \cdot nHgX_2$ species for an Fe-Hg $\sigma \rightarrow \sigma^*$ transition. These HgX_2 adducts are not appreciably dissociated as per electrochemical measurements *vide infra.*

^{57}Fe Mossbauer spectra (300°K) were obtained for $Fe(cpPPh_2)_2$ and $[(Fe(cpPPh_2)_2)_2Hg](BF_4)_2$; reproductions of the spectra are given in Figure 2. It is apparent from Figure 2 that the Mossbauer spectra and therefore the iron environments are little changed in going from $Fe(cpPPh_2)_2$ to $[(Fe(cpPPh_2)_2)_2Hg](BF_4)_2$. Least-squares fit lorenztian curves (solid lines in Figure 2) were obtained for the two spectra. The parent compound has a quadrupole splitting of $\Delta E_q = 2.286$ (3) mm/sec and isomer shift of $\delta = 0.437$ (3) mm/sec relative to iron foil, while the Hg-containing compound has $\Delta E_q = 2.264$ (5) mm/sec and $\delta = 0.436$ (5) mm/sec. The relatively small change in Mossbauer parameters is good evidence to indicate that the mercury is *not* bonded to the iron. A change in ΔE_q of the order of 0.02 mm/sec is much less than that seen for most cyclopentadienyl ring substitutions on ferrocene.[15]

In summary, the above physical data point to the following structures for the $Fe(cpPPh_2)_2$ compounds



In every case it is the phosphorus *not* the iron atom that is bonded to the mercury. A few mercuric halide-phosphine compounds are known[16] which contain both bridging and nonbridging halide ions.

Dc polarograms (see Table III) of the various compounds show that the iron oxidation half-wave potential is displaced to appreciably more positive potentials upon interaction with the mercuric species. For example, in the case of $Fe(cpPPh_2) \cdot HgCl_2$ there is a shift of 0.34 V to more positive potential. The shifting to greater oxidation potentials is merely a reflection of a through-space electrostatic interaction with the partial positive charge on the mercury center. In agreement with this proposal is the observation that the $E_{1/2}$ value for $Fe(cpPPh_2)_2 \cdot HgX_2$ increases as the electronegativity of X increases. Polarographic work[17] on the Ru-Hg bonded systems has shown that extensive decomposition occurs upon oxidation, probably due to the fact that in these systems the electron being oxidized is from the metal-metal bond. In the $Fe(cpPPh_2)_2$ adducts there is no evidence for oxidative decomposition in the polarography of these systems. The various half-waves (one for each compound) are apparently

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Table III. Electrochemical Data[a] for the Ferrocene-1,1′-Bis(diphenylphosphine) Complexes

Compd	$E_{1/2}$, V	n[b]	Slope of E vs. log (i/($i_d - i$)) curve, mV
$Fe(cpPPh_2)_2$	+0.57	1	32
$Fe(cpPPh_2)_2 \cdot HgCl_2$	+0.91	1	36
$Fe(cpPPh_2) \cdot HgBr_2$	+0.89	1	35
$Fe(cpPPh_2) \cdot HgI_2$	+0.74	1	57
$Fe(cpPPh_2)_2 \cdot Hg(SCN)_2$	+1.00[c]	1	
$[(Fe(cpPPh_2)_2)_2Hg](BF_4)_2$	+1.07	2	67

[a] Run at 25° in acetonitrile with 0.1 M $NaClO_4$ as the supporting electrolyte. Corrections were made for background ir drops. The potentials were measured at a rotating platinum electrode and are *vs.* the sce. [b] This value determined by comparing i_a for equivalent concentrations of ferrocene and of the $[(Ru(cp)_2)_2Hg]^{2+}$ cation. [c] Determined from differential pulse measurements at a stationary platinum electrode instead of normal dc polarography because of high degree of irreversibility.

reversible. The most positive (+1.07 V) potential is found for the dication $[Fe(cpPPh_2)_2Hg]^{2+}$; this wave is attributable, as expected, to two electrons per dication.

Reactions with $SnCl_4$, $SnBr_4$, and $SbCl_5$. Ruthenocene reacts with a stoichiometric amount of SnX_4 (X = Cl, Br) (CCl_4 solution) under a nitrogen atmosphere to give yellow products analyzing as $Ru(cp)_2 \cdot 1.5SnX_4$. Analytical results are presented in Table I. If the SnX_4 reactant is in excess, the product composition approaches $Ru(cp)_2 \cdot 2SnX_4 \cdot H_2O$. The "excess" SnX_4 and H_2O in this compound can be washed from the sample with CCl_4 to give $Ru(cp)_2 \cdot 1.5SnX_4$. Because these complexes are yellow, it is clear that the ruthenocene is *not* oxidized. All of the ruthenocene-tin halide compounds are very hygroscopic and decompose in solution, precluding molecular weight studies.

In an effort to observe Ru-Sn vibrations, Raman studies of the compounds were undertaken, but it was found that the compounds decompose in the laser beam. However, it was possible to run an ir spectrum; the spectrum for $Ru(cp)_2 \cdot 1.5SnCl_4$ is reproduced in Figure 3. There are two Sn-Cl bands at 290 and 336 cm^{-1}, bands which move to much lower (<270 cm^{-1}) energy in the $SnBr_4$ analog. A moderately intense band is seen at 411 cm^{-1}. In an ir spectrum of ruthenocene there is only *one* strong band at 446 cm^{-1} in this region. This band has been assigned to the asymmetric ring-metal stretch. If, as seems reasonable, this is the same strong band in $Ru(cp)_2 \cdot 1.5SnCl_4$, then a shift of ~35 cm^{-1} has occurred. Such a large shift to lower energy can be taken as evidence that the bond between the ring and the ruthenium atom has been weakened substantially. It is our contention that this results from a Ru-Sn interaction which because of steric considerations forces the rings to tilt and perhaps lengthens the ring-metal distance slightly. All in all, there is a weakening of the Ru-ring interaction. Additional conclusive evidence for ring tilting (*i.e.*, lowering of symmetry) is found in the splitting of the stong 1411-cm^{-1} ruthenocene asymmetric C-C stretch into two bands at 1406 and 1431 cm^{-1}. A similar type of splitting has been noted for $[(cp)_2RuI]I_3$[18] and Ru-Hg bonded $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2](PF_6)_2$. In the former compound an X-ray crystal structure[18] has shown that the rings are tilted to accommodate the iodide ion. For comparison purposes, an ir tracing of $[(cp)_2RuI]I_3$ is also given in Figure 3. Many similarities are evident between the spectra of this iodide material and $Ru(cp)_2 \cdot 1.5SnCl_4$.

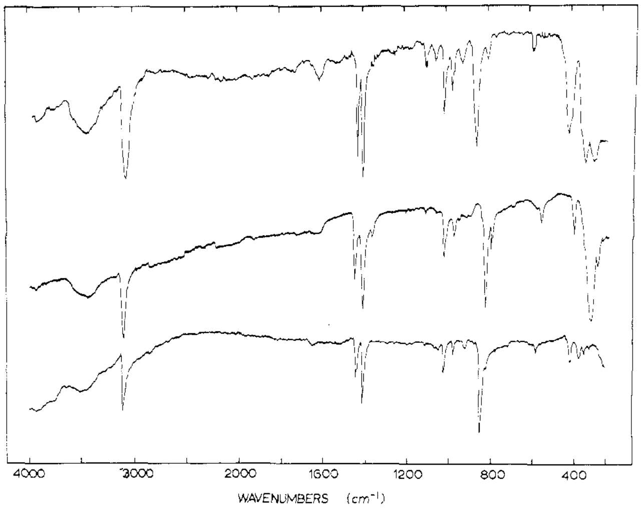
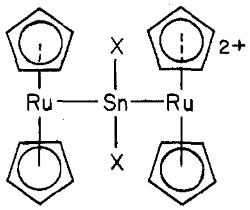


Figure 3. Infrared spectra of KBr pellets of $[(Ru(cp)_2)_2SnCl_2](SnCl_5)_2$ (top), $[Ru(cp)_2Cl](SbCl_6)$ (middle), and $[Ru(cp)_2I](I_3)$ (bottom).

If the proposal of an Ru-Sn interaction is accepted, the most probable formulation for the yellow compounds formed between ruthenocene and SnX_4 is



$\cdot 2(SnX_5^-)$ X = Cl, Br

The proposed structure of the above dication is analogous to that for $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$. X-Ray structural work has been reported for some $M\text{-}SnCl_2\text{-}M$ systems. Most notably, $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2SnCl_2$ has been shown to have the above structure wherein the bonding about the Sn is distorted from a regular tetrahedral arrangement.[19] In fact, the series $[Fe(h^5\text{-}C_5H_5)(CO)_2]_nSnCl_{4-n}$ (n = 1-3) can be prepared.[20,21] There is a successive substitution of chloride by the $Fe(h^5\text{-}C_5H_5)(CO)_2$ moiety on the Sn atom. This brings us back to the compound that we isolated of composition $Ru(cp)_2 \cdot 2SnX_4$. It is possible that this should be formulated as $[(cp)_2RuSnX_3^+](SnX_5^-)$; however, it is curious that the "excess" SnX_4 can be washed out of this compound to give $Ru(cp)_2 \cdot 1.5SnX_4$. The reactions of ruthenocene with SnX_4 are apparently reactions involving the displacement of X^- by $Ru(cp)_2$; only two or less $Ru(cp)_2$ groups can crowd around the Sn atom.

The yellow $Ru(cp)_2 \cdot 1.5SnX_4$ compounds decompose over a period of many months to red-brown solids; the coloration change is indicative of an oxidation of the ruthenocene from Ru(II) to Ru(IV). In agreement with this observation is the time dependence of the ir spectrum of the yellow $Ru(cp)_2 \cdot 1.5SnX_4$ compound. The ir spectrum slowly changes (over a period of hours) from the spectrum reproduced in Figure 3 to one more closely approximating that for $[(cp)_2RuI]I_3$ (also given in Figure 3). The splitting in the ~1400-cm^{-1} region increases and the strong band at ~411 cm^{-1} moves to higher energy (~440 cm^{-1}).

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There has been considerable work on tin halide–transition metal complexes but until recently very little on antimony halide–transition metal complexes. Recent crystal structures[22] have shown that various antimony halide–transition metal complexes have structures analogous to the tin halide complexes. For example, three $Fe(h^5\text{-}C_5H_5)(CO)_2$ moieties will displace[23] chlorides on antimony chloride to give $\{[Fe(h^5\text{-}C_5H_5)(CO)_2]_3SbCl\}^+$. We have found that ruthenocene reacts with $SbCl_5$ in the absence of oxygen to give a red-brown solid. This solid is fairly air sensitive, decomposing to a greenish yellow solid after a few minutes' exposure to air. As indicated above, it is our experience that the dark coloration (red-brown) of the reaction product is good testimony to the fact that the ruthenocene has been oxidized. The analytical data (see Table I) and ir spectrum of this red-brown compound (see Figure 3) indicate that the best formulation for this compound is $[(cp)_2RuCl](SbCl_6)$. The similarity with the ir spectrum of $[(cp)_2RuI](I_3)$ is striking, the exception being the Sb–Cl bands seen in the $\sim 290\text{-cm}^{-1}$ region. In addition, the instability of the complex is not surprising in light of the known[18] relative stabilities of the $[Ru(cp)X]^+$ cation (*i.e.*, I > Br > Cl).

The complex $Fe(cpPPh_2)_2$ also reacts with SnX_4 (X = Cl, Br) to give compounds with compositions analogous (*i.e.*, 1:1 and 1:2 "adducts") to those found for ruthenocene (see Table I). The composition of the product formed with $SbCl_5$ is different. Molecular weight and electrochemical measurements on these compounds show that dissolution of either $Fe(cpPPh_2)_2 \cdot nSnX_4$ (n = 1.5 or 2) or $Fe(cpPPh_2)_2 \cdot nSbCl_5$ (n = 1.5 or 3) leads to dissociation.

Infrared data for the $Fe(cpPPh_2)_2 \cdot nSnX_4$ compounds, as argued above for the HgX_2 compounds of this ferrocene, point to the presence of a P–Sn interaction. In contrast to the compound that we formulated as $[(Ru(cp)_2)_2SnCl_2](SnCl_5)_2$, the ir spectrum of $Fe(cpPPh_2)_2 \cdot 1.5SnCl_4$ only shows one broad Sn–Cl band with shoulders. The most probable formulation for $Fe(cpPPh_2)_2 \cdot 1.5SnX_4$ is $[(Fe(cpPPh_2)_2)_2SnX_2](SnX_5)_2$. The SnX_2 bridging moiety in this system is bonded to the phosphorus atoms. Tin Mossbauer data are needed to check this formulation. Infrared data were inclonclusive as to the molecular structures of the $Fe(cpPPh_2)_2 \cdot 1.5SbCl_5$ stoichiometric compound and the compound formed with excess $SbCl_5$, $Fe(cpPPh_2)_2 \cdot 3SbCl_5$.

Registry No. $Fe(cpPPh_2)_2$, 12150-46-8; $Fe(cpPPh_2)_2 \cdot HgCl_2$, 50803-62-8; $Fe(cpPPh_2)_2 \cdot 2HgCl_2$, 50803-63-9; $Fe(cpPPh_2)_2 \cdot HgBr_2$, 50803-59-3; $Fe(cpPPh_2) \cdot 2HgBr_2$, 50803-60-6; $Fe(cpPPh_2)_2 \cdot HgI_2$, 50803-65-1; $Fe(cpPPh_2)_2 \cdot 2HgI_2$, 50803-66-2; $Fe(cpPPh_2)_2 \cdot Hg(SCN)_2$, 50803-69-5; $[(Fe(cpPPh_2)_2)_2Hg](BF_4)_2$, 50803-76-4; $[(Fe(cpPPh_2)_2)_2Hg](PF_6)_2$, 50803-77-5; $[(Ru(cp)_2)_2SnCl_2](SnCl_5)_2$, 50803-54-8; $[(Ru(cp)_2)_2SnBr_2](SnBr_5)_2$, 50803-53-7; $[Ru(cp)_2Cl](SbCl_6)$, 50803-39-9; $Fe(cpCH_3)_2 \cdot 6HgCl_2$, 50803-42-4; $[Fe(cp\text{-}n\text{-}Bu)_2 \cdot 6HgCl_2$, 50803-52-6; $Fe(cpPh)(cp) \cdot 7HgCl_2$, 50803-50-4; $[(Fe(cpPPh_2)_2)_2SnCl_2](SnCl_5)_2$, 50803-75-3; $Fe(cpPPh_2)_2 \cdot 2SnCl_2$, 50803-64-0; $[(Fe(cpPPh_2)_2)_2SnBr_2](SnBr_5)_2$, 50803-74-2; $Fe(cpPPh_2)_2 \cdot 2SnBr_4$, 50803-61-7; $Fe(cpPPh_2)_2 \cdot 1.5SbCl_5$, 50803-67-3; $Fe(cpPPh_2)_2 \cdot 3SbCl_5$, 50803-68-4; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; $Hg(SCN)_2$, 592-85-8; $SnCl_4$, 7646-78-8; $SnBr_4$, 7789-67-5; $SbCl_5$, 7647-18-9; ruthenocene, 1287-13-4; $Fe(cpCH_3)_2$, 1291-47-0; $Fe(cp\text{-}n\text{-}Bu)_2$, 1274-08-4; $Fe(cpPh)(cp)$, 1287-25-8.

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Crystal and Molecular Structure and 5°K Electronic Spectrum of Bis(tetraphenyldithioimidodiphosphinato)manganese(II)

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The crystal and molecular structure of bis(tetraphenyldithioimidodiphosphinato)manganese(II) has been determined by single-crystal X-ray diffraction methods. The pink crystals, which form as rectangular prisms, belong to space group $P1$ with $a = 13.550\ (4)$ Å, $b = 14.334\ (4)$ Å, $c = 13.824\ (3)$ Å, $\alpha = 82.17\ (2)^\circ$, $\beta = 110.50\ (2)^\circ$, $\gamma = 114.11\ (2)^\circ$, and $Z = 2$ for the Dirichlet reduced cell. Full-matrix least-squares refinement on 8526 nonzero reflections produced a converged solution with $R_F = 5.8\%$. The complex is monomeric and consists of four sulfur atoms in an approximately tetrahedral arrangement about the manganese atom. The two MnS_2P_2N chelate rings have twisted boat conformations with sulfur and phosphorus atoms at the apices. The single-crystal electronic absorption spectra at 77 and 5°K of the tetrahedral $Mn^{II}S_4$ complex have been measured between 13,000 and 30,000 cm^{-1}. Transitions from the ${}^6A_1$ ground state to quartet excited states derived from the ${}^4G$, ${}^4D$, and ${}^4P$ Mn^{2+} levels are observed. The experimental transition energies are in excellent agreement with those calculated assuming $10Dq = -4685.6$, $B = 559.2$, and $C = 3118.7\ cm^{-1}$. Vibrational progressions in quanta of the a_1 Mn–S stretch (average spacing 254 cm^{-1}; ground state 242 cm^{-1}) are built on four electronic origins in the ${}^6A_1 \rightarrow {}^4E, {}^4A_1({}^4G)$ system. The lowest three origins (21,139; 21,186.5; 21,272.5 cm^{-1}) are assigned to transitions to the spin–orbit components of ${}^4E({}^4G)$, whereas the origin at 21,346 cm^{-1} is attributed to ${}^6A_1 \rightarrow {}^4A_1({}^4G)$.

Four-coordinate complexes of the type $M(SPR_2NPR_2S)_2$, where R = Me or Ph and M = Fe(II), Co(II), Ni(II), or Zn(II), have been reported[1] recently. Crystal structure studies have established tetrahedral MS_4 coordination for both the Ni(II)[2] and Fe(II)[3] chelates with R = Me. We have extended the synthetic and structural investigation of this series to include $Mn(SPPh_2NPPh_2S)_2$. In addition to a single-crystal X-ray structure analysis, we have measured and interpreted the 5°K single-crystal electronic absorption spectrum of this tetrahedral $Mn^{II}S_4$ complex. A preliminary

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