$$|\overset{+}{(x^2-y^2)}\overset{-}{(x^2-y^2)}\overset{+}{(z^2)}\rangle$$

Only three of the seven possible one-electron transition excited states contribute to the g values. The remaining transition energies in the electronic spectra of the complexes involving dimethylaminodifluorophosphine were calculated as described previously.[4] Briefly, the coulomb and exchange integrals representing the interelectronic interaction energies involved in each of the eight (including ground state) electronic configurations are found tabulated for d orbitals in terms of Condon–Shortley parameters F_0, F_2 and F_4.[16] The values of these interaction energies for the various states and the calculated transition energies are given in Table IV. By reducing the Condon–Shortley and spin–orbit coupling constant from the free-ion values one accounts for the mixing of metal and ligand orbitals in a molecular orbital formulation. Good agreement between the observed and calculated transition energies is obtained for the states used in determining the one-electron orbital energies which are given in Table V.

Table V

Single-Electron d Orbital Energies for the CoL_3X_2 Complexes [$L = Me_2NPF_2$; $X = I, Br$][a]

Orbital	X = I	X = Br
$x^2 - y^2$	39,850	42,450
z^2	26,700	28,400
xy	19,150	21,450
xz	8,900	9,650
yz[b]	0	0

[a] Energies in cm^{-1}. [b] Assigned arbitrarily as the lowest lying orbital.

As mentioned earlier, the optical spectra of the complexes of bis(dimethylamino)fluorophosphine cannot be quantitatively handled because of the complexity of the optical spectra which arises from the presence of a substantial concentration of tetrahedral high-spin complex.

[16] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 76.

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Mercuric Halide Adducts of Ruthenocene and Ferrocene

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The reaction of ruthenocene and ferrocene with HgX_2 ($X = Cl, Br$) gives various adducts. A very recent X-ray crystal structure has shown these to be ruthenium–mercury bonded compounds. Raman and ir data are presented for these compounds and interpreted in terms of their known structures. An intense Raman band at 137 cm^{-1} (130 cm^{-1}) was assigned as the Ru–Hg stretch in the compound $Ru(C_5H_5)_2 \cdot HgX_2$ where $X = Cl(Br)$. Ferrocene reacts with HgX_2 to give $Fe(C_5H_5)_2 \cdot nHgX_2$ where $n \simeq 7$. In the case of the chloride, the initial product is a red diamagnetic material which converts (~1 day at 27°) to a blue paramagnetic ferricenium compound. Indications of an Fe–Hg interaction are seen in the infrared spectrum of the red compound.

Introduction

In a recent paper[1] we reported that the product of electrochemical oxidation of ruthenocene at a mercury anode is the mercury-bridged cation $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]^{2+}$. It was found possible to prepare salts of the same cation by direct reaction of ruthenocene with $Hg(CN)_2$ in the presence of various acids. Formation of the mercury-bridged ruthenocene cation can be viewed as an acid–base interaction between mercuric ion and ruthenocene.

In the light of the above finding and the reported[2] basicity of ruthenocene and ferrocene toward the proton, we have initiated a program to investigate the basicity of ruthenocene and ferrocene. A reaction was found between HgX_2 ($X = Cl, Br$) and ferrocene and ruthenocene. An X-ray crystal structure report[3] appeared for two of the ruthenocene–mercuric halide adducts near the completion of our physical studies. In this paper we report the results of a Raman and infrared study of these ruthenium–mercury bonded compounds.

Experimental Section

Ruthenocene (ROC/RIC) was purified by sublimation under vacuum. All other chemicals used were reagent grade unless otherwise specified. Chemical analyses were performed by the University of Illinois microanalytical laboratory.

$Ru(C_5H_5)_2 \cdot HgCl_2$.—Ruthenocene (200 mg, 0.86 mmol) was dissolved in approximately 150 ml of absolute ethanol. To this solution was added 235 mg (0.87 mmol) of $HgCl_2$ dissolved in 150 ml of absolute ethanol. On standing for several minutes, a light yellow precipitate formed. The solution was then slowly evaporated to about half its original volume. The solid material was filtered and washed with ethanol and dried under vacuum. *Anal.* Calcd for $Ru(C_5H_5)_2 \cdot HgCl_2$: C, 23.89; H, 2.00; Ru, 20.10; Hg, 39.90; Cl, 14.10. Found: C, 23.82; H, 1.85; Ru, 19.07; Hg, 39.5; Cl, 13.6.

$Ru(C_5H_5)_2 \cdot 3HgCl_2$.—Ruthenocene (200 mg) was dissolved in 150 ml of absolute ethanol and this was added to an ethanol solution saturated with 2.0 g of $HgCl_2$. A light yellow solid precipitated, and this was filtered, washed with ethanol, and vacuum dried. *Anal.* Calcd for $Ru(C_5H_5)_2 \cdot 3HgCl_2$: C, 11.49; H, 0.96; Ru, 9.66; Hg, 57.54; Cl, 20.34. Found: C, 11.63; H, 1.15; Ru, 9.95; Hg, 57.25; Cl, 20.10. It was not possible to make the $Ru(cp)_2 \cdot nHgCl_2$ compound with n greater than 3; however, compounds with $3 > n > 1$ are possible.

$Ru(C_5H_5)_2 \cdot HgBr_2$.—Ruthenocene (143 mg, 0.62 mmol) was dissolved in 150 ml of absolute ethanol and added to 223 mg of $HgBr_2$ (0.62 mmol) dissolved in 50 ml of ethanol. The solution color turned light yellow. After standing for 1.5 hr, a light yellow crystalline precipitate started to form. The volume of the solution was reduced to less than half the original and the pre-

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[1] D. N. Hendrickson, Y. S. Sohn, W. H. Morrison, Jr., and H. B. Gray, *Inorg. Chem.*, **11**, 808 (1972).

[2] J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954).

[3] A. I. Gusev and U. T. Struchkov, *Zh. Strukt. Khim.*, **6**, 1121 (1972).

cipitate was filtered and washed with ethanol. This material can be recrystallized from ethanol. *Anal.* Calcd for $Ru(C_5H_5)_2 \cdot HgBr_2$: C, 20.30; H, 1.70; Ru, 17.08; Hg, 33.90; Br, 27.01. Found: C, 20.29; H, 1.61; Ru, 16.99; Hg, 33.80; Br, 26.83. If an excess of $HgBr_2$ was used, the ratio $HgBr_2/Ru(cp)_2$ increased. The largest value obtained for this ratio was 1.8. In the case of the $Ru(cp)_2 \cdot nHgX_2$ compounds (X = Cl and Br) where $n > 1$, it is believed that the "excess" HgX_2 is in the lattice of the compound. The Results and Discussion section will comment further on this.

$Fe(C_5H_5)_2 \cdot 7HgCl_2$ (Red or Blue).—Ferrocene (2.0 g) was dissolved in 100 ml of Et_2O. To this was added a large excess (~10 g) of $HgCl_2$ dissolved in ethyl ether. The red precipitate which formed was filtered, washed with ether and dried under vacuum. *Anal.* Calcd for $Fe(C_5H_5)_2 \cdot 7HgCl_2$: C, 5.76; H, 0.48; Fe, 2.68; Hg, 67.30; Cl, 23.79. Found: C, 6.19; H, 0.43; Fe, 2.80; Hg, 66.9; Cl, 22.8. On standing, this red compound slowly turned blue (~1 day). In other solvents (CCl_4, ethanol), the red product was formed but could not be isolated as it turned blue rapidly. Variation of the relative amounts of reactants in ethyl ether did not seem to appreciably change the composition of the red compound. Thus, reaction of ferrocene with $HgCl_2$ in the ratio of 1:1 yielded a red compound with essentially the same analysis as the material from the excess $HgCl_2$ reaction.

$Fe(C_5H_5)_2 \cdot 2HgCl_2$.—The blue $Fe(cp)_2 \cdot 7HgCl_2$ was dissolved in water to form a saturated solution. This solution was placed in a stoppered vessel at room temperature and allowed to stand for several weeks. A blue crystalline material was formed; this was filtered and dried under vacuum over P_2O_5. *Anal.* Calcd for $Fe(C_5H_5)_2 \cdot 2HgCl_2$: C, 16.48; H, 1.38; Hg, 55.03. Found: C, 16.09; H, 1.18; Hg, 56.8.

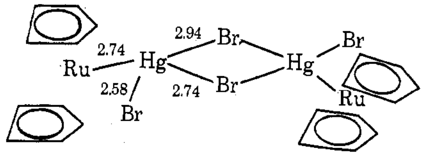
$Fe(C_5H_5)_2 \cdot 7HgBr_2$.—Ferrocene (2.0 g) was dissolved in 100 ml of either ethanol or ether and added to a flask containing 2.00 g of solid $HgBr_2$. A red coating formed on the solid $HgBr_2$, but this quickly turned blue. The mixture of $HgBr_2$ and blue compound was filtered and treated with another solution of ferrocene. This procedure was repeated until a large excess of ferrocene was used. The resulting blue solid was finally filtered, washed with solvent, and dried under vacuum. *Anal.* Calcd for $Fe(C_5H_5)_2 \cdot 7HgBr_2$: C, 4.43; H, 0.37; Fe, 2.06; Hg, 51.83; Br, 41.30. Found: C, 4.78; H, 0.39; Fe, 2.20; Hg, 51.7; Br, 39.23.

Physical Measurements.—Raman spectra were recorded on a Spex Model RS2 Ramanlab spectrometer. All spectra were run on solid samples contained in capillary tubes. The green line (19,435 cm^{-1}) of a Ne–Ar laser was used in the measurements on the light yellow ruthenocene mercuric halide compounds. Several other lines of the laser were tried, but each gave spectra of lower quality. In some instances, Raman samples were also pressed into pellets and mounted on a goniometer. The spectra secured in such a fashion were identical with those obtained for the same compounds in capillaries. No decomposition of the samples in the laser beam was noted.

Infrared spectra were obtained on Perkin-Elmer Model 457 and 521 grating spectrophotometers. Both Nujol mulls and KBr pellets were run over the 4000–250 cm^{-1} range. Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. Spectrograde acetonitrile and reagent grade THF were used. Chlorine nqr measurements were attempted on a Wilks Model NQR-IA. Room temperature magnetic susceptibilities were determined by the Faraday technique.

Results and Discussion

Ruthenocene Compounds.—Ruthenocene reacts with HgX_2 (X = Cl, Br) in ethanol to give the diamagnetic compound $Ru(cp)_2 \cdot HgX_2$ when the reactants are mixed in stoichiometric quantities. The chloride compound is an amorphous solid, while the bromide is obtained as light yellow crystals. Excess mercuric halide leads to the incorporation of additional molecules of mercuric halide in the product and in the limit we obtained $Ru(cp)_2 \cdot 3HgCl_2$ and $Ru(cp)_2 \cdot 1.8HgBr_2$. Very recently preliminary results of X-ray crystal structures were reported[3] for $Ru(cp)_2 \cdot HgBr_2$ and $Ru(cp)_2 \cdot 3HgCl_2$. Both compounds were found to possess ruthenium–mercury bonds. The structure of the mercuric bromide adduct was reported to be as follows.



The 1:1 materials are essentially simple adducts of mercuric halide and ruthenocene, complicated by the presence of halide bridging. The $Ru(cp)_2 \cdot 3HgCl_2$ structure is more complicated with the unit cell containing one ruthenocene–mercuric halide adduct (Hg–Cl bond lengths of 2.55 and 2.60 Å) and one $[(cp)_2Ru{-}Hg{-}Cl]^+$ entity (the mercury possessing one Hg–Cl bond length of 2.50 Å and four Hg–Cl bonds of 3.31, 3.34, 3.36, and 2.38 Å). The remaining $HgCl_2$ in the

TABLE I

INFRARED AND RAMAN DATA FOR VARIOUS RUTHENOCENE–MERCURIC HALIDE ADDUCTS

$Ru(cp)_2 \cdot HgCl_2$		$Ru(cp)_2 \cdot HgBr_2$		$Ru(cp)_2 \cdot 3HgCl_2$	
Ir	R	Ir	R	Ir	R
	101 (m)				105 (sh)
	137 (s)		130 (s)		140 (s)
			164 (ms)		
	194 (m)	194 (m)?	195 (mw)	204 (m)	193 (w)
	242 (m)			247 (w)	242 (w)
				271 (w)	272 (w)
		br			306 (m)
358 (m)	340 (s)	332 (vw)	338 (s)	357 (m)	348 (vs)
	386 (m)		386 (m)		392 (mw)
404 (w)	407 (w)		403 (m)		404 (sh)
420 (m)	419 (sh)	415 (ms)	418 (w)	411 (mw)	
		417 (sh)		418 (mw)	
432 (s)	437 (w)	427 (ms)	432 (w)	430 (sh)	440 (w)
450 (sh)		445 (w)		435 (m)	
			565 (sh)		
588 (w)		585 (w)	572 (w)	582 (mw)	
			579 (w)		
595 (vw)	592 (w)	594 (w)		591 (w)	
602 (vw)	600 (w)	600 (w)		598 (w)	600 (w)
811 (w)		806 (w)		809 (w)	
842 (sh)		839 (sh)		839 (sh)	
849 (s)		844 (s)	854 (w)	846 (s)	
867 (s)	879 (vw)	863 (s)		858 (s)	863 (w)
				862 (sh)	
886 (m)		882 (m)	884 (w)	884 (w)	
904 (m)		900 (m)		904 (m)	
923 (w)			920 (w)	922 (w)	
		939 (w)	932 (w)	943 (ms)	
	958 (w)				955 (vw)
973 (w)					
993 (ms)		989 (ms)	980 (vw)	990 (ms)	
1008 (sh)		1005 (sh)		1008 (sh)	
1017 (s)		1012 (s)		1012 (s)	
			1028 (vw)		
1050 (mw)		1046 (mw)	1042 (w)	1046 (mw)	
	1062 (w)		1054 (w)		1057 (w)
1066 (m)	1064 (w)	1062 (m)		1063 (m)	1060 (sh)
	1075 (w)				
1109 (ms)	1106 (ms)	1105 (ms)	1107 (ms)	1105 (ms)	1106 (ms)
1350 (w)		1348 (w)	1341 (w)	1350 (w)	
1361 (w)		1358 (w)		1358 (w)	1360 (w)
1370 (w)		1367 (w)		1367 (w)	
			1391 (w)		
			1397 (sh)		
1407 (s)		1403 (s)	1401 (w)	1404 (s)	1403 (w)
1412 (s)	1411 (w)	1407 (s)		1408 (s)	
1419 (s)	1420 (w)	1415 (s)		1417 (s)	
1425 (s)	1427 (w)	1420 (s)		1422 (s)	1422 (w)
				1614 (s)[a]	
			3036 (sh)		
			3046 (w)		
	3069 (w)		3068 (sh)	3065 (ms)	
				3071 (sh)	
3075 (ms)	3076 (w)	3065 (m)	3076 (w)	3079 (ms)	
3090 (sh)		3095 (m)	3086 (sh)	3095 (ms)	
3105 (m)	3109 (w)			3100 (sh)	
	3125 (sh)			3106 (sh)	3105 (w)
					3120 (sh)
				3518 (ms)[a]	
				3580 (ms)[a]	

[a] Due to water librations in the lattice.

$Ru(cp)_2 \cdot 3HgCl_2$ structure occupies "lattice" positions.

Raman and ir data were obtained for the various ruthenocene–mercuric halide compounds and are given in Table I. In an effort to check the sensitivity of our spectrometer and to secure relative intensity data, Raman spectra were also recorded for solid samples of $Ru(cp)_2$, $HgCl_2$, and $HgBr_2$ (see Table II). Three Raman active vibrational modes are expected for HgX_2: a symmetric Hg–X stretch ν_1, an asymmetric stretch ν_3, and a symmetric bend ν_2. In our $HgCl_2$ spectrum, the three peaks are found at $\nu_1 = 308$, $\nu_3 = 380$, and $\nu_2 = 122$ cm^{-1}. As can be seen in Table II these values agree fairly well with literature values. The $HgCl_2$ asymmetric stretch peak is weak with the ratio of intensities $\nu_1/\nu_3 \simeq 10$. In the case of $HgBr_2$ we were only able, with our spectrometer, to detect the symmetric stretch at 187 cm^{-1}; apparently the reported $\nu_3 = 251$ cm^{-1} is quite weak. A comparison of our Raman data for a solid sample of ruthenocene with that reported by Lippincott and Nelson[4] for ruthenocene in solution shows that we have detected more peaks than they reported. The recent report of Bodenheimer,[5] however, listed the same additional peaks in a single-crystal Raman study of ruthenocene. For future comparisons in this work we note that the intense band at ~335 cm^{-1} is the symmetric ring–metal–ring stretch and that the band at 114 cm^{-1} was assigned as the e_{1u} ring–metal–ring deformation. Bodenheimer reported that this band appeared at 111.5 cm^{-1} at room temperature and shifted to 130 cm^{-1} at 80°K; we will comment on this assignment later. Finally, the 400 cm^{-1} ruthenocene peak is the e_{1g} ring tilt.

TABLE II

RAMAN DATA FOR RUTHENOCENE, MERCURIC CHLORIDE, AND MERCURIC BROMIDE

Ruthenocene	Lit.[a]	$HgCl_2$	Lit.[b]	$HgBr_2$	Lit.[c,d]
			100		
114 (w)		122 (s)	120	187 (vs)	187
329 (sh)			126		251
335 (s)	330	308 (s)	310		
400 (m)	402		316		
406 (sh)			375		
604 (w)			377		
609 (sh)		380 (w)	379		
819 (w)	804				
834 (w)					
844 (w)					
994 (w)	996				
1049 (w)	1056				
1064 (m)					
1099 (s)	1104				
	1193				
1364 (w)	1360				
1411 (m)	1412				
3081 (sh)					
3089 (w)	3089				
3106 (w)	3104				
3116 (sh)					

[a] E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958), for ruthenocene in solution; data for single crystals are presented in J. Bodenheimer, *Chem. Phys. Lett.*, **6**, 519 (1970). [b] H. Poulet and J. P. Mathieu, *J. Chim. Phys. Physicochim. Biol.*, 442 (1963). [c] K. Venkateswaran, *Proc. Indian Acad. Sci., Sect. A*, **1**, 850 (1935). [d] D. M. Adams, M. Goldstein, and E. F. Mooney, *Trans. Faraday Soc.*, **59**, 2228 (1963).

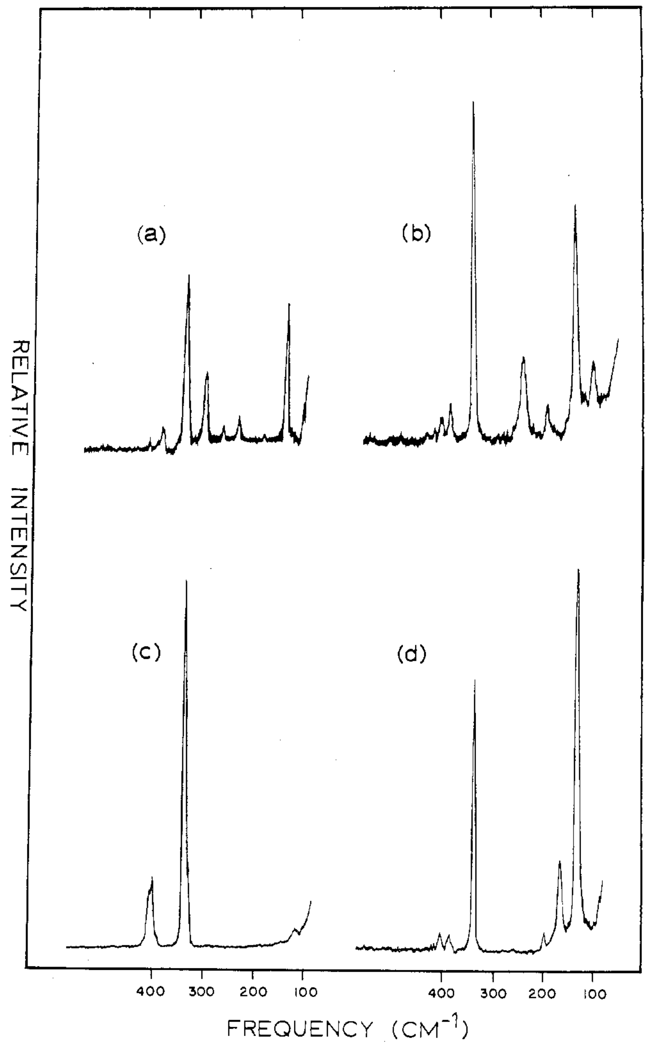


Figure 1.—Low-energy Raman bands of (a) $Ru(cp)_2 \cdot 3HgCl_2$, (b) $Ru(cp)_2 \cdot HgCl_2$, (c) $Ru(cp)_2$, and (d) $Ru(cp)_2 \cdot HgBr_2$ as solids.

The low-frequency Raman spectrum is useful in assessing the bonding characteristics of a ruthenocene mercuric halide adduct. The low-frequency regions of the Raman spectra of $Ru(cp)_2 \cdot HgCl_2$, $Ru(cp)_2 \cdot HgBr_2$, $Ru(cp)_2 \cdot 3HgCl_2$, and ruthenocene are reproduced in Figure 1. It is clear that in these $Ru(cp)_2 \cdot nHgX_2$ compounds there is a Ru–Hg bond, because for each compound we see, in addition to the intense symmetric ring–metal–ring stretch, a second intense band. This second intense low-frequency band is not associated with a dominantly Hg–X mode, because it does not move appreciably as the halide X is changed from Cl to Br.

The low-frequency Raman and ir bands (see Table I and Figure 2) for the 1:1 adducts $Ru(cp)_2 \cdot HgX_2$ can be explained in terms of the known structure. The Ru–Hg stretch is seen in the Raman at 137 cm^{-1} for the chloride and at 130 cm^{-1} for the bromide compound. The Ru-bonded HgX_2 moiety is expected to exhibit both a symmetric and an asymmetric Hg–X stretch. The symmetric Hg–X stretch occurs at 242 and 164 cm^{-1} in the Raman spectra for the chloride and bromide compounds, respectively. The symmetric stretch for the coordinated HgX_2 is less than that observed for the noncoordinated HgX_2 reflecting the acid–base interaction between the ruthenium and the mercuric

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(4) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

(5) J. Bodenheimer, *Chem. Phys. Lett.*, **6**, 519 (1970).

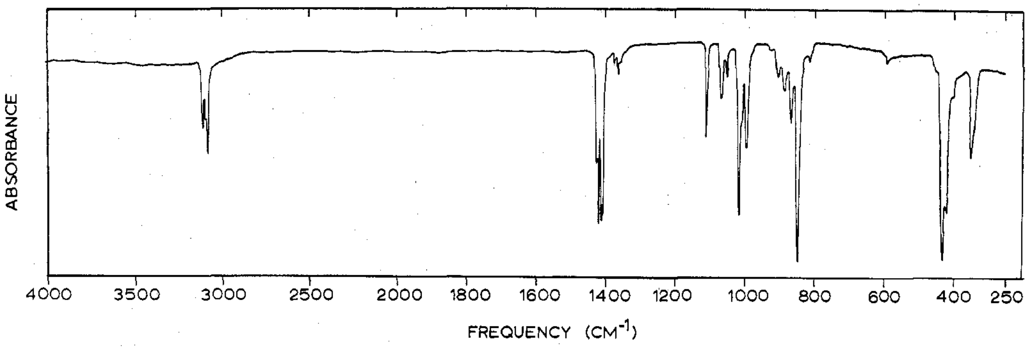

Figure 2.—Infrared spectrum of a KBr pellet of Ru(cp)$_2$$\cdot$HgCl$_2$.

atoms. It must be remembered that since the Ru–Hg stretch and the Hg–X stretch are energetically close, it is quite probable that the two modes are mixed appreciably. It is for this reason and others that it is not possible to assess whether the ruthenium–mercury bond in the two 1:1 adducts is stronger in the chloride or the bromide compound. The asymmetric Hg–X modes are unfortunately not as readily identified. The 358-cm^{-1} ir band for Ru(cp)$_2$$\cdot$HgCl$_2$ is probably the asymmetric Hg–Cl stretch and/or the symmetric ring–metal–ring stretch gaining ir activity due to lower symmetry. We were not able to identify the asymmetric Hg–Br stretch for Ru(cp)$_2$$\cdot$HgBr$_2$.

The vibrational bands associated with the Ru(cp)$_2$ moiety in these Ru(cp)$_2$$\cdot$HgX$_2$ compounds are informative. The ring–metal–ring symmetric stretch is not substantially changed (+5 and +13 cm^{-1} for X = Cl and Br, respectively) over the value in ruthenocene. This indicates that the interaction between HgX$_2$ and Ru(cp)$_2$ does not affect substantially the bonding between the rings and the ruthenium atom. Thus, the ruthenium atom (d^6) uses its essentially nonbonding d electrons for the bonding to the HgX$_2$.

The ~194-cm^{-1} band in the Raman spectra of the two Ru(cp)$_2$$\cdot$HgX$_2$ compounds is probably the ring–metal–ring deformation. Bodenheimer,[5] as we noted earlier, had assigned his very temperature-dependent 111.5-cm^{-1} ruthenocene band to this mode. The ring–metal–ring bending motion of ruthenocene, however, was calculated by Lippincott and Nelson[4] to be 185 cm^{-1} by comparison with ferrocene, where the same band is observed at 170 cm^{-1}. Perhaps the temperature-dependent 111.5-cm^{-1} ruthenocene band is the ruthenocene analog of the 70-cm^{-1} ferrocene Raman band assigned[6] to an intermolecular vibration.

It can be seen by a comparison of adduct and ruthenocene Raman and ir bands that the vibrational frequencies of the Ru(cp)$_2$ moiety are changed little upon coordination to the HgX$_2$. The splitting in the adduct bands in the 1400-cm^{-1} region, however, is indicative of the distortion of the Ru(cp)$_2$ moiety due to the HgX$_2$ interaction. The single sharp 1402-cm^{-1} band seen in ruthenocene is the antisymmetric C–C stretch of the rings. If the rings are tilted, the 1400-cm^{-1} region will be split. This is clearly seen in [(cp)$_2$Ru–I]I$_3$,[7] where each ring is tilted back by 16° resulting in two strong bands at 1402 and 1436 cm^{-1}.

The low-frequency Raman data for Ru(cp)$_2$$\cdot$3HgCl$_2$ can also be interpreted in light of the known structure. In each unit cell there are two types of adducts, Ru(cp)$_2$$\cdot$HCl$_2$ and [Ru(cp)$_2$$\cdot$HgCl]$^+$, and the appropriate amount of HgCl$_2$ in essentially lattice positions. If we compare (see Figure 1) the low-frequency Raman of Ru(cp)$\cdot$3$_2$HgCl$_2$ with that for Ru(cp)$_2$$\cdot$HgCl$_2$, we can identify the bands associated with the Ru(cp)$_2$$\cdot$HgCl$_2$ adduct in the former. These are the ring–metal–ring deformation at 193 cm^{-1}, the symmetric HgCl$_2$ stretch at 242 cm^{-1}, the Ru–Hg stretch at 140 cm^{-1}, and the symmetric ring–metal–ring stretch at 348 cm^{-1}. There are two "additional" bands in the Ru(cp)$_2$$\cdot$3HgCl$_2$ spectrum, not present in the spectrum of Ru(cp)$_2$$\cdot$HgCl$_2$. The band at 306 cm^{-1} must be the symmetric stretch of the "lattice" HgCl$_2$, whereas the band at 272 cm^{-1} is probably the Hg–Cl stretch of [Ru(cp)$_2$–HgCl]$^+$. Implicit in the above assignments are the assumptions that the symmetric ring–metal–ring stretches of the two different adducts are overlapping in the spectrum and that the same is true of the two Ru–Hg stretches. The first assumption seems quite reasonable, while the second is tenuous.

In summary, the vibrational data on these ruthenocene–mercuric halide adducts have shown us that the ruthenium is not oxidized, that the ring–metal–ring interactions in the ruthenocene are not appreciably changed, and that the rings are probably substantially tilted to accommodate the mercury atom. The very interesting feature that is surfacing from the studies of ruthenocene–mercuric complexes is the fact that all three varieties of complexes are possible. With the mercuric halides we see the 1:1 adducts Ru(cp)$_2$$\cdot$HgX$_2$ and the partially dissociated adduct [Ru(cp)$_2$–HgCl]$^+$. And finally, in our previous report[1] we showed how the reaction of mercuric cyanide with ruthenocene in the presence of acid gives the totally dissociated [(cp)$_2$Ru–Hg–Ru(cp)$_2$]$^{2+}$.

Ferrocene Compounds.—When ferrocene in ether or ethanol is mixed with a HgX$_2$ (X = Cl, Br) solution in ether or ethanol, a red precipitate is formed. On standing, this changes into a blue solid. The red compound that forms with HgBr$_2$ could not be isolated. This reaction was mentioned briefly by Spilners,[8] but he gave no indication of the structure of the compound. The empirical formula of the product is Fe(cp)$_2$$\cdot$7HgX$_2$. In the case of HgCl$_2$, it was found that the same product resulted irrespective of the initial ratio of HgCl$_2$ to Fe(cp)$_2$. In light of the proposed simple

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[6] J. Bodenheimer, E. Loewenthal, and W. Low, *Chem. Phys. Lett.*, **3**, 715 (1969).

[7] Y. S. Sohn, A. W. Schlueter, D. N. Hendrickson, and H. B. Gray, *Inorg. Chem.*, submitted for publication.

[8] I. J. Spilners, *J. Organometal. Chem.*, **11**, 381 (1968).

adduct structure for the ruthenocene–mercuric halide compounds, this complicated interaction with ferrocene is difficult to understand. The Raman spectra of these compounds could not be obtained due to strong electronic absorption across the entire visible region for the blue salts and the rapid decomposition of the red material in the laser beam. Also, no far-ir equipment was available to look for a metal–metal stretch at low energy. Thus there was no method available to us to obtain direct evidence for a metal–metal interaction.

Correlations can be drawn between the ir data for the ferrocene and ruthenocene systems (see Tables I and III). The band in the 301–305-cm^{-1} region of the ferrocene compounds is assigned to the symmetric ring–metal–ring stretch which has gained ir activity. This is similar to the ruthenocene compounds which also exhibited ir activity in the symmetric stretch. The band at ~355 cm^{-1} in Fe(cp)$_2$·7HgCl$_2$ is assigned to the "lattice" mercuric chloride. This is confirmed by the fact that no band is observed in this region for the mercuric bromide compound. These ferrocene compounds also show a splitting of the antisymmetric C–C stretching ~1400-cm^{-1} band similar to that observed for the ruthenocene compounds, which again indicates a distortion of the rings. It is interesting to note that the red Fe(cp)$_2$·7HgCl$_2$ compound shows larger splittings in the 1400-cm^{-1} region than the corresponding blue Fe(cp)$_2$·7HgCl$_2$ compound. The blue 7:1 mercuric chloride and bromide compounds show similar splittings in this region.

TABLE III

INFRARED DATA FOR FERROCENE–MERCURIC HALIDE ADDUCTS

Fe(cp)$_2$·2HgCl$_2$ (blue)	Fe(cp)$_2$·7HgCl$_2$ (blue)	Fe(cp)$_2$·7HgCl$_2$ (red)	Fe(cp)$_2$·7HgBr$_2$ (blue)
301 (m)	302 (w)	305 (s)	302 (m, br)
340 (s)	355 (m)	354 (s)	
	414 (sh)	414 (sh)	418 (sh)
	454 (s)[a]	454 (s)[a]	455 (s)[a]
484 (sh)			
499 (w)			
605 (mw)			
		766 (w)	
815 (sh)	815 (sh)	820 (s)	792 (sh)
849 (s)	846 (s)	855 (s, br)	848 (s)
864 (sh)			881 (sh)
875 (sh)			
909 (m)		911 (w)	
1007 (ms)	995 (m)	991 (s)	998 (m)
1033 (m)			
1060 (w)			
1110 (w)	1109 (w)	1108 (s)	1109 (w)
1154 (w)			
1200 (w)			
1265 (vw)			
1310 (mw)			
1345 (vw)			
1390 (ms)		1390 (sh)	
	1402 (sh)	1400 (s)	
	1410 (s)	1414 (m)	1410 (m)
1422 (s)	1417 (sh)	1418 (m)	1417 (sh)
	1600 (s)[a]	1600 (s)[a]	1602 (s)[a]
	1610 (s)[a]	1609 (s)[a]	1611 (s)[a]
3099 (s)	3093 (m)	3108 (m)	3098 (m)
3110 (sh)			
	3520 (m)[a]	3530 (m)[a]	3528 (m)[a]
	3580 (m)[a]	3585 (m)[a]	3580 (m)[a]

[a] Due to water librations in the lattice.

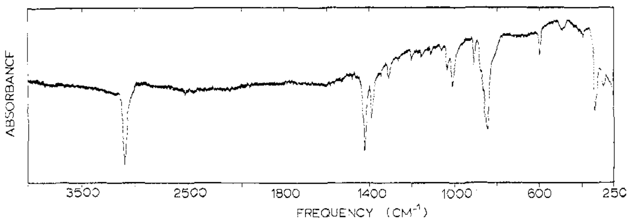

Figure 3.—Infrared spectrum of a KBr pellet of Fe(cp)$_2$·2HgCl$_2$.

The structural features of the ferrocene system are much harder to elucidate. The overall reaction between ferrocene and mercuric halide involves an oxidation, while no oxidation is apparent in the formation of the ruthenocene adducts. An understanding of the structural changes which accompany the conversion of the red Fe(C$_5$H$_5$)$_2$·7HgCl$_2$ to the blue compound is very desirable and as such an infrared study of the red to blue conversion was carried out. A KBr pellet of the fresh red material was made and ir spectra were taken over a period of several hours. After heating for 10 min at 60°, the multiplet structure in the 1400-cm^{-1} region is almost collapsed. The doublet structure in the 800-cm^{-1} band region also collapses. This latter change is much slower, and occurs only after heating for 17 hr at 60°. The bands in the 800-cm^{-1} region are associated with a C–H bending mode and the band in the 1400-cm^{-1} region is associated with the antisymmetric C–C stretching. Both of these splittings are indications of ring distortions or ring tilting. The collapse of the splittings in going from the red to the blue compound could be explained by postulating that the red compound is an adduct of HgX$_2$ with ferrocene which comes out of solution with excess lattice HgX$_2$ and that this is followed by a slow oxidation with an accompanying rupture of the iron–mercury bond. We propose that the red compound contains a mercury–iron bond and that the blue compound is a simple ferricenium ion with a complicated anion. Room temperature magnetic susceptibility measurements showed that the red Fe(cp)$_2$·7HgCl$_2$ compound is diamagnetic and that the blue Fe(cp)$_2$·7HgCl$_2$ compound is paramagnetic with a room temperature moment of 2.36 BM. This room temperature moment is within the range reported[9] (2.34–2.62 BM) for ferricenium salts and is in fact on the low end of the range. The conversion of red Fe(cp)$_2$·7HgCl$_2$ to blue compound goes at the same rate under vacuum and it thus seems that the mercurous ion produced must have dimerized to Hg$_2^{2+}$. If this were not the case, the μ_{eff} measured for the blue Fe(cp)$_2$·7HgCl$_2$ should have been greater.

In an effort to gain further insight into the structure of these ferrocene–mercuric halide compounds, a chlorine nqr study was attempted on the blue Fe(cp)$_2$·7HgCl$_2$ compound. No resonance was observed at room temperature. This blue compound was the only compound obtained in large enough quantities to do the nqr. Nmr and conductance measurements were not tried because as with the ruthenocene compounds, these ferrocene compounds apparently dissociate in solution.

The blue Fe(cp)$_2$·7HgCl$_2$ compound can be dis-

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[9] D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, *Inorg. Chem.*, **10**, 1559 (1971).

solved in water and, on standing for several weeks, a blue crystalline solid precipitates with the composition $Fe(cp)_2 \cdot 2HgCl_2$. The ir spectrum of this material shows a large splitting in the ~1400-cm^{-1} band (see Figure 3 and Table III) this splitting is larger than that observed for either the red or the blue $Fe(cp)_2 \cdot 7HgCl_2$ compound. Addition of aqueous NH_4PF_6 solution to aqueous solutions of either the blue 1:7 or blue 1:2 ferrocene–mercuric chloride compounds gives $[Fe(cp)_2]PF_6$. Thus in solution the interaction between ferrocene and mercury halide is not stable.

In summary, it seems that ruthenocene forms simple 1:1 adducts with mercuric chloride and bromide, whereas the interaction of ferrocene with mercuric halides is complicated. It is reasonable to formulate the red $Fe(cp)_2 \cdot 7HgCl_2$ compound as a 1:1 iron–mercury bonded adduct with a large excess of "lattice" $HgCl_2$; however, conclusive evidence to support this formulation has not been found. Futher work on substituted ferrocenes and other metallocenes is in progress.

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Tricarbonyl-1,2-bis(dimethylphosphinoethane)iron(0). Synthesis and Nuclear Magnetic Resonance Study of a Stereochemically Nonrigid Molecule

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The new compound $Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2](CO)_3$ (I) has been synthesized from $Fe(CO)_5$ and $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (II). Its infrared spectrum is consistent with a trigonal-bipyramidal structure with a phosphorus atom at an axial and equatorial site. The ^{13}C nmr spectrum of the carbonyl groups in I is consistent with this molecule having a nonrigid structure down to −80° on the nmr time scale due to rapid intramolecular exchange. The temperature dependence of the second-order ^1H nmr spectra of I and II between +90 and −50° have been interpreted in terms of solvent effects. The ^{13}C spectra of the methyl and methylene groups of both I and II form the X part of typical ABX spectra. The ^{31}P nmr spectra of I and II are both complex. Values of chemical shifts, ^{13}C coupling constants with phosphorus, and a P–P coupling constant found for I and II are reported.

During recent years considerable interest has been shown in the study of stereochemically nonrigid molecules.[2-6] One important class of potentially stereochemically nonrigid molecules is those which may be considered as derivatives of $Fe(CO)_5$. Carbon-13 nmr studies of iron pentacarbonyl are consistent with a stereochemically nonrigid structure at temperatures down to −63°.[7] More recently ^{13}C nmr studies on $Fe[P(C_2H_5)_n(C_6H_5)_{3-n}](CO)_4$ (n = 1–3) have indicated that these molecules are also stereochemically nonrigid on the nmr time scale and undergo intramolecular carbonyl exchange at room temperature.[8] Infrared studies on $Fe(PF_3)(CO)_4$ and $Fe(PF_3)_2(CO)_3$ and other members of the $Fe(PF_3)_{5-x}(CO)_x$ series show that each compound consists of more than one isomer and that they are stereochemically nonrigid.[9] The ^1H nmr spectrum of the related compound $Fe[P(N(CH_3)_2)_3]_2(CO)_3$ has been reported to be temperature dependent.[10] Its infrared spectrum indicated that it consisted of only the trans isomer and it was therefore postulated that the temperature dependence of its ^1H nmr spectrum could not be due to cis–trans isomerization. This implied the molecule might be stereochemically rigid. It was suggested that the temperature dependence might have been related to hindered internal rotation of the phosphorus substituents in the ligand.

The infrared spectrum of $Fe[P(C_6H_5)_3](CO)_4$ is consistent with a trigonal-bipyramidal molecule with the $P(C_6H_5)_3$ group in an axial position; similarly the infrared spectrum of $Fe[P(C_6H_5)_3]_2(CO)_3$ suggests that this molecule has a trigonal-bipyramidal configuration with the triphenylphosphine ligands occupying axial positions.[11] Infrared studies on $Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2](CO)_3$ show three CO stretching bands.[12] This has been interpreted in terms of a trigonal-bipyramidal molecule with the phosphorus atoms occupying equatorial positions.[13]

The present study was undertaken in order to gain further information concerning the stereochemical behavior of substituted iron pentacarbonyl species. It

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