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Characterization of the Electrochemical Oxidation Product of Ruthenocene at a Mercury Anode

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Received August 4, 1971

Electrochemical oxidation of ruthenocene employing a mercury anode yields the Ru–Hg bonded compound $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2](ClO_4)_2$. This compound and the PF_6^- and BF_4^- salts have also been prepared by homogeneous reactions. Analytical, molecular weight, infrared, Raman, proton nmr, and electronic absorption spectral data have been utilized in assignng the molecular structure. A Raman band at 110 cm^{-1} has been assigned to the symmetrical Ru–Hg–Ru stretching mode.

Introduction

We have made a number of unsuccessful attempts to synthesize $Ru(cp)_2^+$ salts by Wilkinson's procedures[3,4] in the course of our magnetic susceptibility[5] and electronic absorption spectrosopic[6] studies on paramagnetic metallocenes. Halogen oxidation of ruthenocene results in $[Ru(cp)_2X]X_3$ (X = Br, I),[7] whereas electrochemical oxidation of ruthenocene at a mercury anode with perchlorate as supporting electrolyte yields a diamagnetic yellow salt containing an appreciable amount of chemically bound mercury. In this paper we report the characterization of the yellow product of the electrochemical oxidation of ruthenocene.

Experimental Section

Ruthenocene (Orgmet and ROC/RIC) was purified by recrystallization from ethanol and sublimation under vacuum. All other chemicals used were reagent grade unless specified. Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory and by the microanalytical laboratory at the University of Illinois.

Electrochemical oxidation of ruthenocene was carried out following Wilkinson's method.[4] A 0.10-g (0.43-mmol) sample of ruthenocene was dissolved in ~200 ml of a supporting electrolyte consisting of 90% ethanol, 0.1 *M* sodium perchlorate, and 0.01 *M* perchloric acid and then oxidized at a mercury anode by a controlled potential of +0.4 V *vs.* sce using a potentiostat (Electronische Potentiostat Nach Wenking). The initial current reading was 27 mA and the reaction was terminated at 3.8 mA after approximately 50 min. The quantity of electricity consumed during this process was 39 C in reasonable agreement with the theoretical value of 42 C calculated assuming a one-electron oxidation of $Ru(cp)_2$. This result is in accord with the previous report.[4] A yellow perchlorate salt precipitated during the electrolysis. *Caution! This perchlorate salt is highly explosive when shocked in the dry state. Scratching the glass filter proved dangerous.* Although the analytical data for this yellow product do not fit any reasonable empirical formula (*Anal.* Found: Ru, 14.83; Hg, 14.53; Cl, 8.30, C, 26.8; H, 2.88.), the compound has been found to be spectroscopically (uv–vis, ir, and Raman) the same as pure $[Ru(cp)_2]_2Hg(ClO_4)_2$ prepared by the following homogeneous reaction.

$[Ru(C_5H_5)_2]_2Hg(ClO_4)_2$.—A 1-mmol sample of ruthenocene dissolved in 150 ml absolute ethanol was mixed with an ethanol solution (50 ml) of 0.5 mmol of $Hg(CN)_2$. No color change developed until perchloric acid (~10 drops) was added. The solution color turned yellow and a yellow crystalline material started to precipitate. The solution was condensed to ~50 ml by slow evaporation. The yellow solid was filtered, washed with absolute ethanol, and dried under vacuum. The yield was 0.150 g at this stage, but more compound could be recovered by further condensation. *Anal.* Calcd for $[Ru(C_5H_5)_2]_2Hg(ClO_4)_2$: C, 27.85; H, 2.34; Ru, 23.48; Hg, 23.30; Cl, 8.24. Found: C, 27.96; H, 2.25; Ru, 23.68; Hg, 23.40; Cl, 7.95. Only the one product was obtained with different mole ratios of the reactants. This yellow material was not found to be as explosive as the electrochemical product. *Caution is still desirable.*

$[Ru(C_5H_5)_2]_2Hg(PF_6)_2$.—The perchlorate salt obtained from the homogeneous reaction was quantitatively converted to the hexafluorophosphate by dissolution in water followed by precipitation with a saturated aqueous solution of excess NH_4PF_6. Crystals can be grown in nitromethane. *Anal.* Calcd for $[Ru(C_5H_5)_2]_2Hg(PF_6)_2$: C, 25.17; H, 2.10; Ru, 21.32; Hg, 21.02. Found: C, 24.65; H, 1.99; Ru, 21.76; Hg, 20.75. The anion was identified by its infrared absorptions. This compound has also been shown to be spectroscopically the same as the hexafluorophosphate obtained by anion exchange from the electrochemical oxidation product.

$[Ru(C_5H_5)_2]_2Hg(BF_4)_2$.—Ruthenocene (0.63 mmol) and $Hg(CN)_2$ (0.32 mmol), each in 100 ml of absolute ethanol, were mixed. To this mixture approximately 8 drops of 50% aqueous tetrafluoroboric acid was added. Evaporation of the solution gave a yellow solid. This was dissolved in water and filtered to remove the unreacted ruthenocene. Water was stripped from the filtrate under vacuum to give the desired product, which was washed with ethyl ether. *Anal.* Calcd for $[Ru(C_5H_5)_2]_2Hg(BF_4)_2$: C, 28.67; H, 2.39; Hg, 23.94. Found: C, 28.19; H, 2.23; Hg, 23.64. The anion was identified by its characteristic infrared absorptions.

Physical Measurements.—The electronic absorption spectra of the various compounds were measured on a Cary Model 14 CMRI spectrophotometer. A Cary Model 14 was employed for spectral measurements near 2000 Å. An aqueous $HClO_4$ solution (0.01 *M*) was used in the room-temperature absorption measurements. Low-temperature (77°K) absorption spectra were determined using a quartz dewar and a solvent mixture of propionitrile, ethanol, and ethyl ether (1:1:3). Bubbling of the coolant (liquid nitrogen) was eliminated by operating under reduced pressures.

Infrared spectra were obtained with Perkin-Elmer Model 225 and Model 625 grating spectrophotometers; Nujol mulls were used for the 200–450-cm^{-1} region and both KBr pellets and Nujol mulls were used for the 450–4000-cm^{-1} region. Raman spectra were measured on a Cary Model 81 using both solid and acetonitrile solution samples. Room-temperature magnetic susceptibilities were determined by the Faraday technique using solid samples. Proton nmr spectra were obtained for $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2](ClO_4)_2$ dissolved in nitromethane and acetonitrile using a Varian A-60 spectrometer operating at ambient temperatures. The molecular weight of $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2](PF_6)_2$ was determined using a Mechrolab Model 301 A vapor pressure osmometer. The hexafluorophosphate salt was dissolved in nitromethane (8.8 mg/1.00 ml) and the effective molarity was determined.

Results and Discussion

The yellow electrochemical oxidation product of ruthenocene at a mercury anode has the same electronic

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(1) University of Illinois.

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(3) G. Wilkinson, *J. Amer. Chem. Soc.*, **74**, 6146 (1952).

(4) G. Wilkinson, *ibid.*, **74**, 6149 (1952).

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

(6) Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3603 (1971).

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

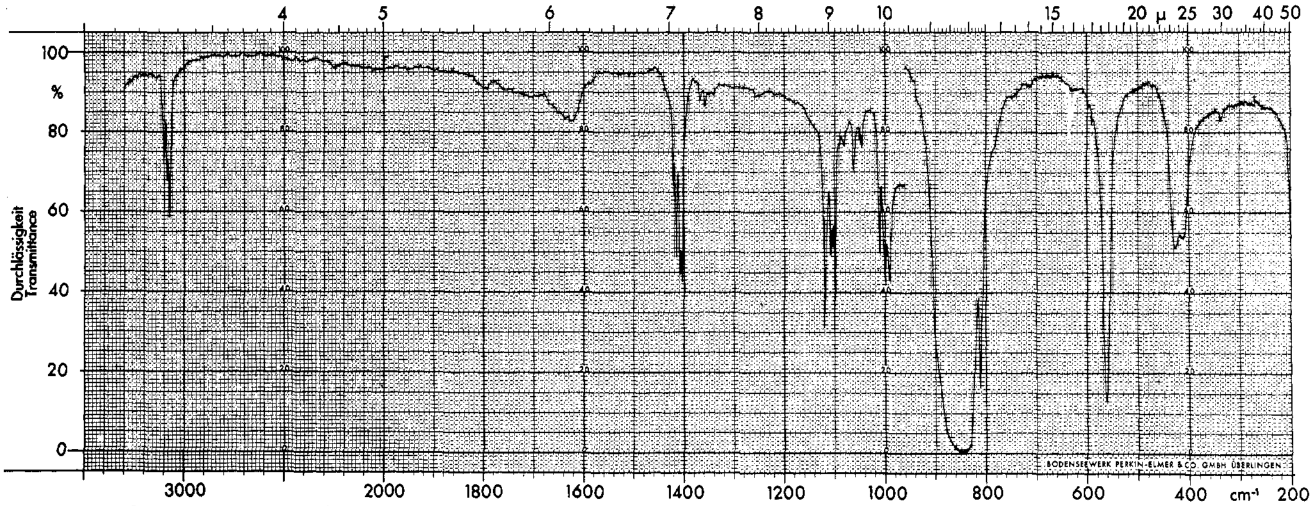

Figure 1.—Infrared spectrum of $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2](PF_6)_2$: KBr pellet in the 4000–450-cm^{-1} region; Nujol mull in the 450–200-cm^{-1} region.

absorption spectrum in aqueous solution as reported by Wilkinson.[3] However, it is clear that Wilkinson's formulation[3,4] of this compound as $[Ru(cp)_2]ClO_4$ is incorrect, because the yellow perchlorate salt is diamagnetic and contains an appreciable amount of mercury (14.53%). Nevertheless, we have confirmed Wilkinson's finding[4] that one-electron equivalent per ruthenocene is associated with electrochemical production of the salt. This finding is equally explicable in terms of a mercury oxidation

$$Hg(0) \xrightarrow{-2e^-} Hg(II)$$

as it is an oxidation of ruthenocene, because the analytical data for the compound indicate that the Ru:Hg ratio is approximately 2. A hexafluorophosphate salt can be prepared from the perchlorate by simple anion exchange. The physical properties of these compounds (*vide infra*) taken with the analytical data suggested that we were dealing with impure salts of $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]^{2+}$. Formulation of the cation as a ruthenocene adduct of mercuric ion led us to carry out homogeneous reactions of ruthenocene and appropriate mercuric salts. These reactions provided pure samples containing the cation produced electrochemically.

The yellow crystalline product from the reaction of ruthenocene and mercuric cyanide in ethanol in the presence of perchloric acid gave analytical data in excellent agreement with the formula $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2](ClO_4)_2$. A change of the mole ratio of the reactants did not change the composition of the product. The physical properties of this material are essentially the same as those found for the perchlorate from the electrochemical oxidation of ruthenocene. Conversion to an analytically pure PF_6^- salt was readily accomplished. Other salts may be prepared by employing directly the corresponding acids (*e.g.*, HBF_4) in place of perchloric acid. The compounds $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]X_2$ ($X^- = ClO_4^-, PF_6^-, BF_4^-$) are all diamagnetic.

Assuming that the hexafluorophosphate salt is a 1:2 electrolyte in nitromethane solution, its molecular weight by vapor pressure osmometry was found to be 843. This value is in satisfactory agreement (−11.6%) with the theoretical value of 953. Thus it is reasonably certain that the salts contain $[(cp)_2\text{–}Ru\text{–}Hg\text{–}Ru(cp)_2]^{2+}$ and not some larger cation cluster.

The only nonsolvent peaks in the proton nmr spectra of the perchlorate salt of $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]^{2+}$ in nitromethane and acetonitrile are sharp singlets at 5.63 and 5.48 ppm, respectively, downfield of internal TMS. The evidence from both nmr and magnetic susceptibility experiments thus supports a ring-unsubstituted, symmetrical Ru(II)–Hg(II)–Ru(II) structure for the cation. The single proton peak for $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]^{2+}$ occurs at ~1 ppm lower field than the proton resonance for ruthenocene (4.42 ppm downfield of TMS for a 5% solution in CCl_4). This shift is consistent with a base–acid interaction between ruthenocene and the mercuric ion which would remove d-electron density from the ruthenium atom.

The infrared and Raman spectra of $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]X_2$ ($X^- = ClO_4^-, PF_6^-, BF_4^-$) are essentially the same except for absorptions attributable to the different anions. Typical spectra are shown in Figures 1 and 2, and the data are compared in Table I with analogous spectral results for ruthenocene. A strong Raman band at 110 cm^{-1} was observed both in solid samples and solutions containing the cation. This band is not present in ruthenocene and may be assigned to the symmetrical Ru–Hg–Ru stretching mode in $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2]^{2+}$. The next higher energy band (338 cm^{-1} for PF_6^-; 336 cm^{-1} for ClO_4^-) may be assigned as the symmetrical ring–metal–ring stretch,[8–10] ω_4, which is observed at 330 cm^{-1} in ruthenocene. The ir band at ~190 cm^{-1} is assigned to the ring–metal–ring bending vibration, ω_{22}. The ring–metal–ring bending mode of ruthenocene is calculated to appear at ~185 cm^{-1} by using the ω_4/ω_{22} ratio of ferrocene. This ratio is 1.78 for ferrocene and is 338/190 = 1.78 for $[(cp)_2Ru\text{–}Hg\text{–}Ru(cp)_2](PF_6)_2$. The higher energy vibrational bands (>400 cm^{-1}), representing various localized ring motions in the mercury compounds, appear at almost the same positions as they do in the ruthenocene spectrum. However, it may be noted that the infrared bands at 407 and 1001 cm^{-1} for the perchlorate (410 and 1002 cm^{-1} for PF_6^-) correspond to two Raman-active vibrations in ruthenocene (402 and 996 cm^{-1}) that have become ir active,

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

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

(10) J. Brunvoll, S. J. Cyvin, and L. Schäfer, *J. Organometal. Chem.*, **27**, 107 (1971).

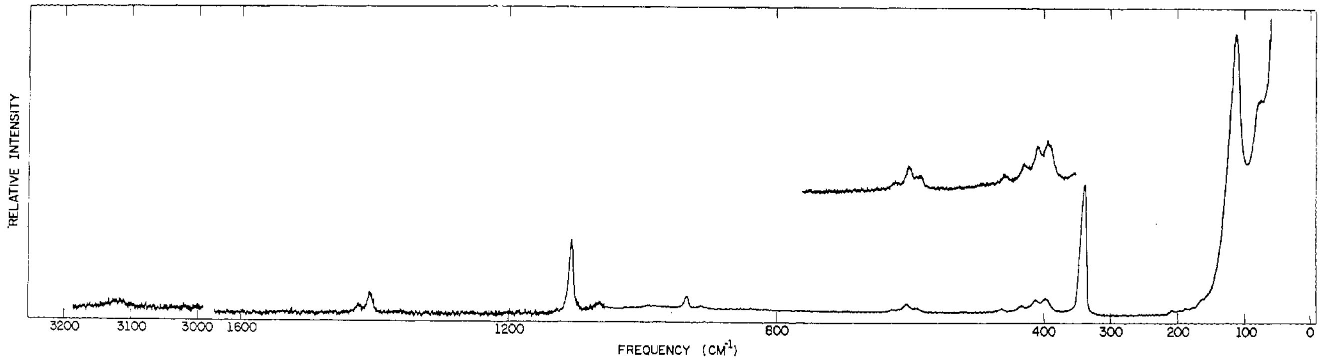

Figure 2.—Raman spectrum of a solid sample of [$(cp)_2Ru$–Hg–$Ru(cp)_2$]$(ClO_4)_2$.

TABLE I

INFRARED AND RAMAN DATA FOR VARIOUS [$(cp)_2Ru$–Hg–$Ru(cp)_2$]X_2 SALTS[a]

$Ru(cp)_2$		$X^- = ClO_4^-$		$X^- = PF_6^-$		$X^- = BF_4^-$	
Ir	R	Ir	R	Ir	R	Ir	R
			111 s		110 s		113 s
		~190 s		~190 s		~190 s	
	330 s		336 s		338 s		338 s
379 w							
	402 m	407 m	393 w	410 m	393 w	410 m	393 w
			410 w		410 w		410 w
446 s		427 m	430 w	425 m	430 w	425 m	430 w
			460 w				
	600 w	585 w	602 w	585 w	602 w	585 w	604 w
806 s							
819 w							
862 m		850 m		853 m		853 m	
			930 w				
	996 w						
1002 s		1005 m[b]		1012 s[b]		1005 m	
1050 w	1056 m	1050 m	1062 w	1062 w[b]	1070 w	1075 m	
1100 s	1105 s		1107 m	1100 s[b]	1108 m	1110 m	1109 m
	1200 w						
	1360 w						
1402 s	1408 m	1405 s	1407 w	1408 s[b]	1408 w	1407 s	1408 w
		1420 s[b]	1423 w	1423 s[b]	1423 w	1422 s	1423 w
1620 w							
1660 w							
1675 w							
1755 w							
1790 w							
3080 m	3085 w	3105 s[b]	3130 w	3128 s[b]	3130 w	3115 m	3120 w
	3103 w						
	3110 w						

[a] Band positions were taken from the Nujol mull spectra. Absorptions of the anions were not included. [b] This band shows further structure in a KBr pellet.

TABLE II

ELECTRONIC ABSORPTION BANDS OF RUTHENOCENE AND [$(cp)_2Ru$–Hg–$Ru(cp)_2$]$^{2+}$ ION

$Ru(cp)_2$[a]				[$(cp)_2Ru$–Hg–$Ru(cp)_2$]$^{2+}$		
System	Assignment	$\bar{\nu}$, cm^{-1}	ϵ	$\bar{\nu}$, cm^{-1}	ϵ	$\nu_{1/2}$, cm^{-1}
I	$^1A_{1g} \rightarrow a^3E_{1g}$	26,000	~5			
				26,700[b]	4,400	
II	$\rightarrow \left\{\begin{array}{l} a^1E_{1g} \\ ^1E_{2g} \end{array}\right.$	31,000	200			
				31,200 (31,500)[c]	35,000	4,300 (2,500)[c]
III	$\rightarrow b^1E_{1g}$	36,000	150			
IV		42,000	2,000	42,600[b]	15,000	
V		46,100	4,200	46,500[b]	25,000	
VI	$\rightarrow {}^1A_{2u}$	>51,300	>50,000	>50,000	>30,000	

[a] From ref 6. [b] Shoulder whose intensity (ϵ) is not corrected for tailing by its neighboring band. The position of the 26,700-cm^{-1} band was taken from the resolved spectrum at 77°K (see Figure 3). The others were estimated from the inflection points. [c] The values in parentheses refer to low-temperature (77°K) data for the 31,200-cm^{-1} band.

presumably due to the lower molecular symmetry. In summary, the ir and Raman results are entirely consistent with the formulation of the cation as a ruthenocene adduct of Hg(II).

The electronic absorption spectra of [$(cp)_2Ru$–Hg–$Ru(cp)_2$]$(PF_6)_2$ both at room temperature and at 77°K are shown in Figure 3. The band positions and intensities for the cation and $Ru(cp)_2$ are compared in

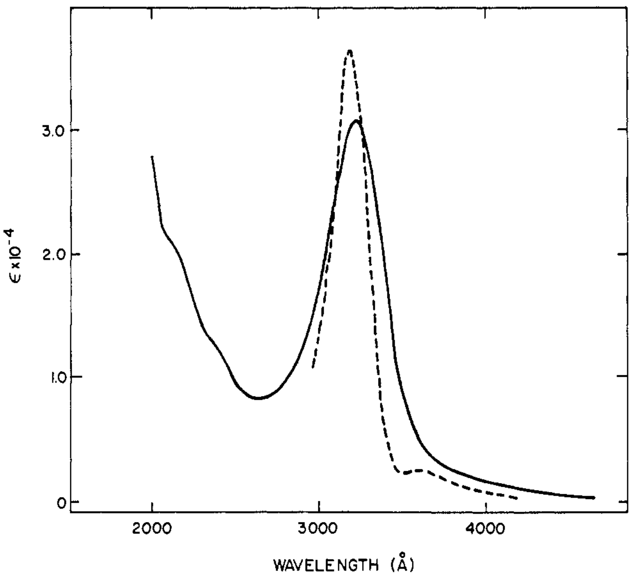

Figure 3.—Electronic absorption spectra of $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2](PF_6)_2$: —, 0.01 *M* $HClO_4$ aqueous solution at 300°K; ---, dissolved in solvent mixture of propionitrile, ethanol, and ethyl ether (1:1:3) at 77°K (the intensity is not to scale in this case).

Table II. The room-temperature electronic absorption spectrum of $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2](PF_6)_2$ was measured in acidic aqueous solution (0.01 *M* $HClO_4$), as the cation is unstable in organic solvents at that temperature.[8] However, no decomposition was noticed at 77°K in the organic solvent mixture used (propionitrile, ethanol, ethyl ether). The most striking spectral feature of the $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$ ion is the strong band at 31,200 cm^{-1} (ϵ 35,000). This band, which is not present in the spectrum of $Ru(cp)_2$, blue shifts by $\sim$300 cm^{-1} and dramatically sharpens (the half-width changes from 4300 to 2500 cm^{-1}) in going from room temperature to 77°K. Therefore, it is reasonable to assign the 31,200-cm^{-1} band to a transition associated with the Ru–Hg–Ru bonded unit. Similar changes in band shapes and positions have been observed on lowering the temperature for metal–metal transitions in $M_2(CO)_{10}$ (M = Mn, Re) complexes.[11] The 26,700-cm^{-1} band in the $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$ spectrum is relatively intense and most likely has a different origin from the lowest spin-forbidden d–d ($^1A_{1g} \rightarrow a^3E_{1g}$) ruthenocene band. However, the bands in ruthenocene attributable to charge-transfer transitions (IV, V, VI) are found in essentially the same positions in the Ru–Hg bonded cation. This result provides additional evidence for the Ru(II)–Hg(II) formulation.

It may be pointed out that formation of $[(cp)_2Ru\text{-}Hg\text{-}Ru(cp)_2]^{2+}$ in the reaction of ruthenocene and mercuric ion is not surprising in view of the known basicities of bis(cyclopentadienyl)metal complexes.[12] Many metallocenes are easily protonated, although others, including those in the iron group, require strong acids.[13,14] Some mixed cyclopentadienylcarbonyl complexes have also been found to show metal basicity. For example, certain anionic cyclopentadienylcarbonylmetal complexes will displace halide from alkyl and acyl halides.[15] On the other hand, mercuric halides have been used as Lewis acids in reactions with various transition metal bases. Simple adducts, partially dissociated HgX^+ complexes, and completely halide-displaced metal–mercury–metal bonded complexes result from such reactions. An example of the last class is the compound $[Co(CO)_4]_2Hg$.[16] Another example of a Co–Hg–Co bonded complex is the recently isolated $K_6[HgCo_2(CN)_{10}]\cdot 2H_2O$,[17] in which mercuric cyanide was employed in the preparation instead of mercuric halides. Observation of unusually strong adsorption of pentacyanocobaltate(II) on a mercury electrode during electrochemical oxidation led to the preparation of the above Co–Hg bonded complex by a homogeneous reaction.[17]

In the absence of acid ferrocene does not react with mercuric cyanide to form $[(cp)_2Fe\text{-}Hg\text{-}Fe(cp)_2]^{2+}$. However, under similar conditions ferrocene reacts with mercuric halides to yield adducts as well as oxidation products.[18] The adducts, $Fe(cp)_2\cdot n HgX_2$, are believed to contain one or more Fe–Hg bonds. Ruthenocene also forms similar adducts with mercuric halides without the oxidation that accompanies the reaction with ferrocene.

Acknowledgments.—Research at the California Institute of Technology was supported by the National Science Foundation. We gratefully acknowledge the assistance of Professor F. C. Anson and Dr. Hong Sup Lim in carrying out the electrochemical experiments and Mr. Josef Nemeth for assistance in the molecular weight determinations.

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(11) R. Levenson and H. B. Gray, unpublished work; R. Levenson, Ph.D. Thesis, Columbia University, New York, N. Y., 1970.

(12) D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970).

(13) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(14) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5249 (1960).

(15) R. E. Dessy, R. L. Pohl, and R. B. King, *ibid.*, **88**, 5121 (1966).

(16) D. J. Cook and R. D. W. Kemmitt, *Chem. Ind.* (*London*), 946 (1966); I. N. Nowell and D. R. Russell, *Chem. Commun.*, 817 (1967).

(17) H. S. Lim and F. C. Anson, *Inorg. Chem.*, **10**, 103 (1971).

(18) D. N. Hendrickson and Y. S. Sohn, unpublished results.