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Studies in the Chemistry of Bonds between Metals. I. The Synthesis of Transition Metal Carbonyl Derivatives of Zinc and Cadmium by a Metal-Exchange Reaction

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The metal-exchange reactions of a number of transition metal carbonyl derivatives of mercury of the $\mathbf{m}_2$Hg type ($\mathbf{m}$ = $Co(CO)_4$, $Fe(CO)_2C_5H_5$, $Cr(CO)_3C_5H_5$, $Mo(CO)_3C_5H_5$, and $W(CO)_3C_5H_5$) and the mixed-metal compound $C_5H_5Fe(CO)_2HgCo(CO)_4$ with zinc and cadmium have been shown to be convenient synthetic routes to the novel zinc and cadmium analogs, $\mathbf{m}_2$Zn and $\mathbf{m}_2$Cd, and $C_5H_5Fe(CO)_2ZnCo(CO)_4$. A polar solvent such as THF was required to promote the exchange in the case of the molybednum and tungsten derivatives. The conversion of $Hg[Mn(CO)_5]_2$ to $Zn[Mn(CO)_5]_2$ occurred in diglyme at 120°. The similarity of the infrared spectra of the new zinc and cadmium compounds with those of the well-studied mercury analogs indicated that all of the compounds contain linear arrangements of covalently bonded metal atoms. Comparison of the Mössbauer parameters with the infrared data for the $M[Fe(CO)_2C_5H_5]_2$ series (M = Zn, Cd, Hg) suggested that both σ and π bonding are important in the metal–metal interactions. Mass spectra, reported for the $M[Co(CO)_4]_2$ and $M[Cr(CO)_3C_5H_5]_2$ series, gave a qualitative indication that the metal–metal bond strengths decrease in the order Zn > Cd > Hg. Detailed preparations for the mercury derivatives are described in the Experimental Section.

Introduction

Within the past 30 years there have appeared an increasing number of mercury derivatives of transition metal carbonyls of the general type $\mathbf{m}_2$Hg, where $\mathbf{m}$ represents a metal carbonyl group, *e.g.*, $\mathbf{m}$ = $Co(CO)_4$ or $Fe(CO)_2C_5H_5$, etc. Until recently these compounds have remained chemical curiosities, prepared as air-stable derivatives useful in characterization of the metal carbonyl fragment. Initially thought to contain bridging carbonyls, these derivatives have been shown to possess linear, unsupported metal–Hg–metal covalent bonds by spectroscopic[1] and X-ray crystallographic[2] studies. Structually, at least, the $\mathbf{m}_2$Hg compounds are similar to the dialkyls and diaryls of mercury, R_2Hg, which contain linear carbon–Hg–carbon covalent bonds.

From the earliest days of organometallic chemistry the organomercurials have found widespread applicability in the synthesis of other organometallic compounds and in synthetic organic chemistry in general.[3] Because of the similarity in the bonding of $\mathbf{m}_2$Hg and R_2Hg it seemed reasonable to expect that the chemical properties of the former should resemble those of the latter. Indeed, the very air stability that allows easy isolation of the $\mathbf{m}_2$Hg compounds is reflected in the fact that the dialkyls and diaryls of mercury are the only organic derivatives of the group II metals that are inert to air and water. One of the most valuable reactions of dialkyl- and diarylmercury compounds is the exchange reaction with metals more electropositive than mercury, whereby the alkyl or aryl derivative of the metal is formed (eq 1). This synthetic method has been used successfully with the alkali and alkaline earth metals—zinc, aluminum, gallium, tin, lead, antimony, bismuth, selenium, and tellurium. With cadmium, indium, and thallium, however, reversible equilibria are set up.[3] The principal advantage of the metal-exchange reaction over other synthetic routes is that mild, nonbasic conditions are employed and metallic mercury is the only other product. In order to ascertain most readily whether the metal exchange would be observed in systems containing metal–metal bonds, the reaction of $Hg[Co(CO)_4]_2$ with zinc metal was investigated initially for the following reasons: first, Dighe and Orchin[4] had shown that $Hg[Co(CO)_4]_2$ could be reduced with sodium (amalgam) even in nonpolar solvents; second, the expected product, $Zn[Co(CO)_4]_2$, had been shown to be capable of existence by Hieber and coworkers,[5,6] and although the compound had been characterized only by elemental analysis, its color and extreme air sensitivity had been noted; third, $Zn[Co(CO)_4]_2$ had taken on increased importance by the observation that it served as a catalyst for the stereospecific dimerization of bicyclo[2.2.1]heptadiene.[7] Preliminary results in this study have been described previously.[8]

$$nR_2Hg + 2M \longrightarrow 2MR_n + nHg \qquad (1)$$

Results and Discussion

Metal-Exchange Reactions.—When approximately 0.1 *M* solutions of $Hg[Co(CO)_4]_2$, $Hg[Fe(CO)_2C_5H_5]_2$, or $C_5H_5Fe(CO)_2HgCo(CO)_4$ were stirred with a tenfold excess of zinc metal in a nonpolar solvent such as hexane or toluene, under an inert atmosphere, a rapid reaction occurred at room temperature whereby the starting mercury compound was consumed virtually completely within 1 hr as indicated by thin layer

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[1] (a) G. Bor and L. Markó, *Spectrochim. Acta*, **16**, 1105 (1960); (b) H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2175 (1961).

[2] (a) R. F. Bryan and H. P. Weber, *Acta Cryst.*, **21**, A138 (1966); (b) G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc.*, *A*, 1005 (1968); (c) R. F. Bryan and A. R. Manning, *Chem. Commun.*, 1316 (1968).

[3] G. E. Coates, "Organometallic Compounds," 2nd ed, Methuen and Co. Ltd., London, 1960, Chapter 2.

[4] S. V. Dighe and M. Orchin, *Inorg. Chem.*, **1**, 965 (1962).

[5] W. Hieber and R. Breu, *Chem. Ber.*, **90**, 1259 (1957).

[6] W. Hieber and U. Teller, *Z. Anorg. Allgem. Chem.*, **249**, 43 (1942).

[7] G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966).

[8] (a) J. M. Burlitch, *J. Organometal. Chem.* (Amsterdam), **9**, P9 (1967); (b) J. M. Burlitch and A. Ferrari, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 1968, No. M-110.

chromatographic analysis.[9] From the resulting solutions the crystalline $\mathbf{m}_2Zn$ products were readily isolated in high yields. In one experiment with $Hg[Co(CO)_4]_2$ 96% of the theoretical quantity of mercury was recovered after prolonged treatment of the resulting zinc amalgam with dilute sulfuric acid. Exchange reactions with cadmium metal similarly afforded the cadmium derivatives in high yields. However the mixed-metal compound $C_5H_5Fe(CO)_2CdCo(CO)_4$ which formed readily from the mercury analog could not be isolated in a pure form because of its tendency to undergo ligand-exchange reaction to the symmetrical derivatives (eq 2). The equilibrium also could be

$$2C_5H_5Fe(CO)_2CdCo(CO)_4 \rightleftharpoons Cd[Fe(CO)_2C_5H_5]_2 + Cd[Co(CO)_4]_2 \qquad (2)$$

established from the reverse direction as shown by mass spectroscopic analysis of the residue obtained on evaporation of a solution of equimolar quantities of the symmetrical derivatives. The behavior was surprising in view of the fact that the equilibrium strongly favors the unsymmetrical derivatives for the mercury[10] and zinc analogs.

Previous observations in this laboratory and by others pointed to the photochemical instability of some of the $\mathbf{m}_2Hg$ compounds. Irradiation of a hexane solution of $Hg[Co(CO)_4]_2$ produced $Co_2(CO)_8$ and mercury[11] while irradiation of $Hg[C_5H_5Mo(CO)_2P(OCH_3)_3]_2$ gave $[C_5H_5Mo(CO)_2P(OCH_3)_3]_2$.[12] To ensure that the exchange reactions were those of the $\mathbf{m}_2Hg$ species and not of some photolysis product(s) the reactions were carried out in the dark or under dim red light. A qualitative relation of the reaction rate to the $\mathbf{m}_2Hg$ concentration was observed when a tenfold decrease in the concentration of a solution of $Hg[Co(CO)_4]_2$ resulted in a considerable quantity of starting material remaining after several hours. This is probably a surface phenomenon. Because of the extremely mild conditions under which these reactions occur and because there was no evidence of other products, we favor a mechanism that involves a direct reaction of the $\mathbf{m}_2Hg$ molecule at the metal surface without prior formation of metal carbonyl radicals or dimeric species (eq 3).

$$\mathbf{m}_2Hg + M^{II} \longrightarrow \mathbf{m}_2M^{II} + Hg \qquad (M^{II} = Zn, Cd) \qquad (3)$$

The essentially complete conversions to the cadmium derivatives was rather surprising in view of the equilibrium mixture of 75% diphenylcadmium and 25% diphenylmercury observed in the reaction of the latter with a tenfold excess of cadmium metal.[13] That the reaction described by eq 3 is reversible was demonstrated when treatment of a toluene solution of $Cd[Fe(CO)_2C_5H_5]_2$ with an excess of metallic mercury resulted in complete conversion to $Hg[Fe(CO)_2C_5H_5]_2$. A similar reaction of $Cd[Co(CO)_4]_2$ in hexane produced only 6% of $Hg[Co(CO)_4]_2$. This behavior is analogous to that observed for organic derivatives wherein $(C_6H_5)_2Cd$ was completely converted to $(C_6H_5)_2Hg$ when treated with excess metallic mercury.[13] Although the factors which govern the extent of these processes are presently unknown, it is clear that the excess of zinc and particularly of cadmium helps drive the exchange reaction to completion.

Early in the course of this investigation it was recognized that certain $\mathbf{m}_2Hg$ compounds reacted only slowly, if at all, in nonpolar solvents. For example in toluene $Hg[Cr(CO)_3C_5H_5]_2$ required 8 hr at 60° for complete conversion to the zinc analog; $Hg[Mo(CO)_3C_5H_5]_2$ failed to show any sign of reaction with zinc after 3 days at room temperature in this solvent. Following the original hypothesis that the chemical properties of the transition metal carbonyl derivatives of the main group metals should resemble the organic derivatives of these metals, we were led to carry out the metal-exchange reactions in a polar solvent since it was well known that R_2Zn and R_2Cd but not R_2Hg compounds (R = alkyl, or aryl) form complexes with various oxygen and nitrogen donors.[14] Thus coordination could be expected to favor the products in eq 3. This hypothesis was substantiated by the observation that $Hg[Cr(CO)_3C_5H_5]_2$ in tetrahydrofuran (THF) was quantitatively converted to $Zn[Cr(CO)_3C_5H_5]_2$ within 1.5 hr at room temperature. The less reactive molybdenum and tungsten analogs required 5 hr in THF at the reflux temperature for complete reaction. Similar results were obtained in the formation of the $Cd[M(CO)_3C_5H_5]_2$ (M = Cr, Mo, W) derivatives, all of which were isolated in high yield.

Very recently Mays and Robb[15] reported the failure of cadmium to replace mercury in a benzene solution of $Hg[Mo(CO)_3C_5H_5]_2$; rather the latter was formed in good yield upon treatment of $Cd[Mo(CO)_3C_5H_5]_2$ (prepared from $NaMo(CO)_3C_5H_5$ and $Cd(CN)_2$) with mercury in this solvent. These workers demonstrated the ability of the $Cd[M(CO)_3C_5H_5]_2$ derivatives (M = Mo, W) to form complexes with various nitrogen bases. In these complexes the cadmium atom is presumably four-coordinate. Evidence for some interaction with oxygen donors was mentioned[15] but these complexes were apparently too unstable to permit isolation. Significantly the mercury analogs showed little or no tendency to form complexes with either type of donor. Our results suggest that the nitrogen complexes of the $\mathbf{m}_2Cd$ derivatives could be prepared from the air-stable $\mathbf{m}_2Hg$ compounds by simply carrying out the metal-exchange reaction in the presence of the ligand in a nonpolar solvent. Such a procedure should be particularly convenient in the synthesis of the presently unknown complexes of the highly air-sensitive $\mathbf{m}_2Zn$ compounds.

Extension of the metal-exchange reaction to $Hg[Mn(CO)_5]_2$ was complicated by the very low solubility of this compound in the usual solvents. At elevated

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(9) This analytical technique was capable of detecting as little as 5% of the starting compound; the product compound decomposed rapidly on exposure to air and was observed as a dark, unmoved spot.

(10) M. J. Mays and J. D. Robb, *J. Chem. Soc., A*, 329 (1968).

(11) J. M. Burlitch and D. D. Stump, unpublished observations.

(12) M. J. Mays and S. M. Pearson, *J. Chem. Soc., A*, 2291 (1968).

(13) S. Hilpert and G. Grüttner, *Chem. Ber.*, **46**, 1675 (1913).

(14) K.-H. Thiele and P. Zdunneck, *Organometal. Chem. Rev.*, **1**, 331 (1966).

(15) M. J. Mays and J. D. Robb, *J. Chem. Soc., A*, 561 (1969).

TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR m_2Zn AND m_2Cd COMPOUNDS

Compound	Color	Mp, °C	% calcd		% found	
			C	H	C	H
$Zn[Co(CO)_4]_2$	Yellow	71–72.5	...	...	...	...
$Zn[Fe(CO)_2C_5H_5]_2$	Orange	158–159.5	40.2	2.4	39.5, 39.6	2.1, 2.1
$Zn[Cr(CO)_3C_5H_5]_2$	Yellow	225.5–227	41.1	2.2	41.5, 41.6	2.2, 2.3
$Zn[Mo(CO)_3C_5H_5]_2$	Light yellow	194–196	34.6	2.0	34.7, 34.5	1.8, 1.9
$Zn[W(CO)_3C_5H_5]_2$	White	203–205	26.2	1.4	26.4, 26.3	1.2, 1.3
$Zn[Fe(CO)_2C_5H_5][Co(CO)_4]$	Yellow-orange	72.5–73	32.0	1.2	32.5, 32.3	1.2, 1.3
$Cd[Co(CO)_4]_2$	Yellow-orange	78–80	...	...	...	...
$Cd[Fe(CO)_2C_5H_5]_2$	Red-orange	171–176	36.1	2.2	35.9, 35.7	2.2, 2.1
$Cd[Cr(CO)_3C_5H_5]_2$	Yellow	219.5–220.5	37.4	1.9	37.3, 37.4	1.9, 2.0
$Cd[Mo(CO)_3C_5H_5]_2$	Light yellow	223–224.5	32.0	1.7	32.3, 32.0	1.6, 1.6
$Cd[W(CO)_3C_5H_5]_2$	Light yellow	251.5–253	24.7	1.3	24.5, 24.5	1.4, 1.5
$Cd[Fe(CO)_2C_5H_5][Co(CO)_4]$	Yellow-orange	71–74	...	...	...	...

temperature dilute solutions could be prepared although a slow decomposition to Hg and $Mn_2(CO)_{10}$ occurred. Thus although a 77% yield of $Zn[Mn(CO)_5]_2$ was realized in one experiment upon stirring a mixture of $Hg[Mn(CO)_5]_2$ with excess zinc in diglyme for 5 hr at 120°, it was not possible to determine whether the product resulted from a direct metal-exchange process or from the known reaction of zinc with $Mn_2(CO)_{10}$ under these conditions.[16] The pentacarbonylmanganese derivatives of zinc and cadmium will be described in detail in a forthcoming publication.

Properties of the m_2Zn and the m_2Cd Compounds.—All of the compounds prepared in this study were crystalline solids with well-defined melting points. Colors were generally lighter than those of the corresponding mercury derivatives. All of the zinc derivatives were found to be quite air sensitive as solids and solutions exposed to traces of air decomposed rapidly. The solid cadmium analogs were generally more stable in this respect but strict precautions were required to handle most solutions. Solubilities of the compounds varied widely but most compounds were soluble in toluene with the cadmium derivatives being consistently less soluble than the zinc and mercury analogs. All were readily soluble in THF or acetone with unexpected enhanced air stability in the latter. It should be noted that $Zn[Co(CO)_4]_2$ and $Cd[Co(CO)_4]_2$ formed complexes with THF from which the solvent was very difficult to remove completely. Subsequent recrystallization from hexane or vacuum sublimation resulted in mixtures of low-melting solids.[17] The ability of a number of these compounds to ionize in very polar solvents such as N,N-dimethylformamide and the facile nucleophilic displacement of certain transition metal carbonyl groups from the main group metal by halide ion has been described recently.[18]

The composition of the new compounds was confirmed by C–H analysis (Table I) and by the appearance of the expected molecular ion in the mass spectrum. In cases where the transition metal had a simple isotope distribution accurate mass measurements were made on the most abundant isotope peak of the parent ion. For the compounds of complex polyisotopic transition metals the low-resolution isotope pattern of the parent ion was compared to a computer-calculated pattern. Excellent agreement was obtained by both methods and confirmed the presence of the expected number and type of metal atoms. Occasionally traces of m_2Hg analogs were observed in the spectra of the recrystallized m_2Zn and m_2Cd compounds. Apparently even with zinc the metal-exchange reaction is not quite quantitative. Isomorphous substitution is probably responsible for appearance of the mercury compound after purification—indeed $Hg[Co(CO)_4]_2$ and $Zn[Co(CO)_4]_2$ are known to crystallize in the same space group with similar packing arrangements.[2b,19]

Spectra, Structure, and Bonding.—Recently the structure of $Zn[Co(CO)_4]_2$ was shown by X-ray diffraction techniques to contain molecular units of D_{3d} symmetry with a linear arrangement of metal atoms.[19] The structure of $Hg[Co(CO)_4]_2$, also determined by X-ray diffraction,[2b] is very similar to this. The coordination around the zinc atom resembles that found in the covalent dialkyls of zinc.[20] The similarity of the infrared spectra of the $M[Co(CO)_4]_2$ compounds (M = Zn, Cd, Hg) in hexane (Table II) further substantiates their structural relationship.[21] The close coincidence of the carbonyl stretching frequencies for the zinc and mercury compounds indicates that there is not a significant difference in the net charge on cobalt. Such a situation could arise from the balancing of an inductive effect, *viz.*, $Zn^{\delta+}\rightarrow Co^{\delta-}$, with (d → p)$\pi$ bonding, *viz.*, $Zn\overset{\leftharpoonup}{-}Co$. The mass spectra of the $M[Co(CO)_4]_2$ derivatives (Table III) show the expected stepwise loss of CO from the parent ions. The greater proportion of fragments containing three metal atoms for the zinc and cadmium derivatives suggests that the metal-to-metal bonds in these compounds are stronger than those in the mercury analog, which may account for the decreased thermal and photochemical stability of the latter.

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(16) J. M. Burlitch, *Chem. Commun.*, 887 (1968).

(17) J. M. Burlitch and S. G. Earle, unpublished observations.

(18) (a) J. M. Burlitch, *J. Am. Chem. Soc.*, **91**, 4562 (1969); (b) *ibid.*, **91**, 4563 (1969).

(19) B. Lee, J. M. Burlitch, and J. L. Hoard, *ibid.*, **89**, 6362 (1967).

(20) K. S. Rao, B. P. Stoicheff, and R. Turner, *Can. J. Phys.*, **38**, 1516 (1960).

(21) In a sodium chloride cell a hexane solution of $Zn[Co(CO)_4]_2$ exhibited a weak–medium band at 2074 cm^{-1} in addition to those observed in a fluorite cell. We attribute this to complex formation with the salt of the cell walls because of similar effects observed upon interaction of $Hg[Co(CO)_4]_2$ and a soluble halide in DMF.[18b]

TABLE II
INFRARED SPECTRAL DATA

Compound	ν_{CO} soln spectra,[a,b] cm^{-1}
$Zn[Co(CO)_4]_2$	2088 s, 2033 m, 2007 vs
$Cd[Co(CO)_4]_2$	2084 s, 2021 m, 2000 vs
$Hg[Co(CO)_4]_2$	2080 s, 2030 m, 2009 vs
$Zn[Fe(CO)_2C_5H_5]_2$	1973 m, 1956 s, 1915 s
$Cd[Fe(CO)_2C_5H_5]_2$	1971 m, 1952 s, 1914 s
$Hg[Fe(CO)_2C_5H_5]_2$	1989 m, 1961 s, 1927 s
$Zn[Cr(CO)_3C_5H_5]_2$	1982 m, sh, 1970 vs, 1906 w, sh, 1892 m, 1867 s
$Cd[Cr(CO)_3C_5H_5]_2$	1976 m, 1959 vs, . . ., 1888 m, 1860 s
$Hg[Cr(CO)_3C_5H_5]_2$	1985 m, 1958 vs, . . ., 1900 m, 1883 s
$Zn[Mo(CO)_3C_5H_5]_2$	1994 m, sh, 1977 s, 1907 m, sh, 1897 m, 1873 s
$Cd[Mo(CO)_3C_5H_5]_2$[c]	
$Hg[Mo(CO)_3C_5H_5]_2$	1998 m, 1971 s, 1917 m, sh, 1908 m, 1890 s
$Zn[W(CO)_3C_5H_5]_2$	1986 m, 1969 s, 1899 m, sh, 1888 s, 1864 s
$Cd[W(CO)_3C_5H_5]_2$[c]	
$Hg[W(CO)_3C_5H_5]_2$	1992 m, 1967 s, 1912 m, sh, 1898 s, 1884 s
$Zn[Fe(CO)_2C_5H_5][Co(CO)_4]$	2083 m, 2072 w, sh, 2019 m, 1991 s, 1969 m, 1945 m, 1936 w
$Hg[Fe(CO)_2C_5H_5][Co(CO)_4]$	2077 s, 2013 s, 1997 s, 1986 s, 1979 s, sh, 1961 s, 1948 m, sh

[a] All solution spectra were observed on 0.01 *M* solutions in a sealed cell employing CaF_2 windows under an argon atmosphere. [b] Hexane solutions were employed for all compounds containing cobalt; toluene was used in all other cases. In the latter the solvent absorptions were compensated. [c] This compound was insufficiently soluble in toluene to obtain solution spectra at room temperature.

TABLE III
MASS SPECTRA OF $M[Co(CO)_4]_2$ COMPOUNDS[a]

Ion	Intensity[b] M = Zn	M = Cd	M = Hg
$MCo_2(CO)_8^+$	72	90	6.7
$MCo_2(CO)_7^+$	36	38	0.6
$MCo_2(CO)_6^+$	10	3.8	. . .
$MCo_2(CO)_5^+$	4.8	2.6	. . .
$MCo_2(CO)_4^+$	34	22	. . .
$MCo_2(CO)_3^+$	26	38	1.0
$MCo_2(CO)_2^+$	16	21	1.2
$MCo_2(CO)^+$	14	18	4.7
MCo_2^+	32	40	14
$MCo(CO)_3^+$	2.8	8.9	2.1
$MCo(CO)_2^+$	17	38	6
$MCo(CO)^+$	42	69	26
MCo^+	52	66	49
M^+	17	69	~800
$Co_2(CO)_7^+$	4.0	24	14
$Co_2(CO)_6^+$	7.5	8	11
$Co_2(CO)_5^+$	23	17	13
$Co_2(CO)_4^+$	100	100	100
$Co_2(CO)_3^+$	63	55	~100
$Co_2(CO)_2^+$	59	45	63
$Co_2(CO)^+$	12	10	25
Co_2^+	61	45	58
$Co(CO)_3^+$	10	12	29
$Co(CO)_2^+$	37	46	85
$Co(CO)^+$	61	53	77
Co^+	37	34	60
Co_2C^+	4.3	3.5	3.7
CoC^+	2.9	2.7	5.0

[a] All spectra were taken at 70 eV with a source temperature of 70–80°. [b] Intensity values refer to all elements being monoisotopic.

TABLE IV
MÖSSBAUER PARAMETERS

Compound	Isomer shift,[a] mm/sec	Quadrupole splitting,[a] mm/sec
$Hg[Fe(CO)_2C_5H_5]_2$	0.339	1.633
$Cd[Fe(CO)_2C_5H_5]_2$	0.319	1.700
$Zn[Fe(CO)_2C_5H_5]_2$	0.288	1.733

[a] Measurements were made on powdered solids at room temperature relative to sodium nitroprusside. The estimated error is ±0.006 mm/sec.

The infrared spectra of the $M[Fe(CO)_2C_5H_5]_2$ compounds are consistent with a structure of C_{2v} symmetry containing a linear arrangement of metal atoms as previously postulated for the mercury derivative.[22] The values of the carbonyl stretching frequencies together with the Mössbauer data in Table IV provide some insight into the mode of bonding in these compounds. The isomer shift (IS), indicative of the s-electron density at the iron nucleus, would be expected to be lowered both by inductive donation through the σ system $-M\rightarrow Fe(CO)_2C_5H_5$ and by $(d \rightarrow p)\pi$ interaction between the filled iron d orbitals and empty p orbitals on the main group metal, $-M\overset{\leftarrow}{-}Fe(CO)_2C_5H_5$. As expected the observed values of IS show a significant and regular decrease on going from Hg to Zn. The metal carbonyl stretching frequencies, on the other hand, are affected in the opposite way by these two types of bonding. Thus inductive donation to Fe would be expected to shift ν_{CO} to lower frequencies (in the limit, ionic species $-M^+{}^-Fe(CO)_2C_5H_5$ would result) whereas electron withdrawl in the π system would have the opposite effect and ν_{CO} would increase. The values of ν_{CO} do not vary in a regular way from $Hg[Fe(CO)_2C_5H_5]_2$ to $Zn[Fe(CO)_2C_5H_5]_2$ as would be expected if only the inductive effect or only the π interaction were operative. We conclude, therefore, that the metal-to-metal bonding in these compounds is a combination of σ and π bonding. Unfortunately the data do not permit separation of these effects to assess their relative importance. Considering the relative sizes of the orbitals involved, however, π bonding could be expected to be more important in the zinc derivatives of the metals of the first transition period.

The infrared spectra of the $M^{II}[M(CO)_3C_5H_5]_2$ (M^{II} = Zn, Cd, Hg; M = Cr, Mo, W) compounds are quite similar in the carbonyl stretching region. The spectra of $Hg[Cr(CO)_3C_5H_5]_2$ and $Hg[Mo(CO)_3C_5H_5]_2$ agree reasonably well with those reported in heptane and CS_2 by Fischer and Noack.[23] These authors interpreted these spectra in terms of a single isomer with a skew configuration of the $M(CO)_3C_5H_5$ groups about a linear M–Hg–M system. Our infrared data indicate that the zinc and cadmium analogs adopt a similar configuration. As observed in previous systems the ν_{CO} values for the three $Cr(CO)_3C_5H_5$ derivatives do not

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[22] R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.* (Amsterdam), **7**, 135 (1967).

[23] R. D. Fischer and K. Noack, *ibid.*, **16**, 125 (1969).

TABLE V
MASS SPECTRA OF $M[Cr(CO)_3C_5H_5]_2$ COMPOUNDS[a]

Ion	Intensity[b]		
	M = Zn	M = Cd	M = Hg
$MCr_2(C_5H_5)_2(CO)_6^+$	58	1.7	3.8
$MCr(C_5H_5)(CO)_3^+$	4.8	0.9	0.2
$MCr(C_5H_5)CO^+$	4.6	0.3	...
$MCr(C_5H_5)^+$	...	0.8	...
M^+	7	13	42
$Cr_2(C_5H_5)_2(CO)_4^+$	1.4	...	...
$Cr_2(C_5H_5)_2(CO)_3^+$	48	0.6	0.7
$Cr_2(C_5H_5)_2(CO)_2^+$	12	0.4	0.3
$Cr_2(C_5H_5)_2(CO)^+$	19	0.6	0.7
$Cr_2(C_5H_5)_2^+$	51	2.3	3.9
$Cr(C_5H_5)(CO)_3^+$	8.4	12	11
$Cr(C_5H_5)(CO)_2^+$	33	17	19
$Cr(C_5H_5)CO^+$	36	24	24
$Cr(C_5H_5)C^+$	4	0.6	...
$Cr(C_5H_5)^+$	100	100	100
Cr^+	93	95	90
$Cr(C_5H_5)_2^+$	145	6.4	9.6

[a] All spectra were taken at 70 eV with a source temperature of 170–175°. [b] Intensity values refer to all elements being monoisotopic.

vary in a regular way. The mass spectra of this series of compounds (Table V) are characterized by substantial loss of the main group metal which appears with two chromium atoms only in the parent ion. In contrast to the $Co(CO)_4$ series, only the zinc member of this group shows a considerably greater proportion of ions containing the central metal with one or two other metal atoms, suggesting that Zn–Cr bonds are significantly stronger than the Cd–Cr or Hg–Cr bonds. In all these spectra there were series of ions of the general formula $Cr_2(C_5H_5)_2(CO)_n$ (n = 0–4), none of which was observed in the spectrum of $[Cr(CO)_3C_5H_5]_2$.[24] The fact that these ions apparently have considerable stability lends support to the hypothesis[24] that $[Cr(CO)_3C_5H_5]_2$ dissociates before ionization in the mass spectrometer.

The mass spectra of the other π-cyclopentadienyl compounds were qualitatively similar to those given for the chromium derivatives. There were generally very few metastable ions in these spectra. None involving loss of the central metal atom was observed.

Summary

The metal-exchange reaction of transition metal carbonyl derivatives of mercury, of the type $\mathbf{m}_2Hg$, with excess zinc and cadmium metal is a convenient synthetic tool, of general applicability, for the conversion of transition metal carbonyl derivatives of mercury, $\mathbf{m}_2Hg$, into the $\mathbf{m}_2Zn$ and $\mathbf{m}_2Cd$ analogs. Although the new derivatives have been isolated in high yield, it should be emphasized that under the reaction conditions described these compounds are produced virtually quantitatively and that the filtered reaction mixtures may be used directly for most purposes. The spectra and properties of the new zinc and cadmium derivatives are consistent with structures involving linear arrangements of three metal atoms linked by nonpolar, covalent metal-to-metal bonds.

The metal-exchange reaction has been shown to be applicable to other metals such as magnesium with $\mathbf{m}_2Hg$[25] and $\mathbf{m}HgX$ (X = halogen)[26] systems. Further studies of the metal-exchange reactions and the chemical properties of the new zinc and cadmium derivatives are in progress.

Experimental Section

Preparation of Starting Materials. General Comments.—With the exception of $Hg[Co(CO)_4]_2$ which was prepared by the method of Hieber, Fischer, and Böckly[27] as described by King,[28] the preparations of the symmetrical $\mathbf{m}_2Hg$ derivatives are described in some detail because of their versatility as synthetic intermediates and the general lack of experimental details in previous reports describing their preparation and purification. The syntheses were carried out in conventional laboratory glassware under an argon atmosphere unless otherwise indicated. All of the mercury derivatives were found to be stable to air and water although air-saturated solutions in organic solvents deteriorated slowly when exposed to normal laboratory light. Consequently all manipulations (such as recrystallizations) that were carried out in the air were performed in dim red light. For long-term storage, refrigeration under an inert atmosphere was preferred. Melting points quoted were taken in sealed, argon-filled capillaries.

$Hg[Fe(CO)_2C_5H_5]_2$.[29,30]—A solution of $NaFe(CO)_2C_5H_5$ was prepared from 17.7 g (50 mmol) of $[Fe(CO)_2C_5H_5]_2$ (Strem Chemicals, Inc.; resublimed at 110° (0.001 mm)) and 3.0 g (0.13 g-atom) of sodium (amalgamated with 23 ml of Hg) in 300 ml of diglyme (Ansul Chemical Co.; triply distilled from sodium under argon) according to the general method of King.[31] The resulting dark orange solution was filtered through a 1-cm bed of degassed filter aid (Johns-Manville) in a large Fritte and added dropwise with stirring to a solution of 13.5 g (53.5 mmol) of $Hg(CN)_2$ in 1 l. of boiled, nitrogen-saturated water in a 2-l. three-necked flask. After the resulting suspension was stirred for 30 min, the brownish yellow precipitate was filtered in air, washed with two 200-ml portions of water, and then sucked dry. The crude yield was 23.4 g (85%). A 19.3-g portion of this was recrystallized from 1100 ml of boiling methanol. After filtration, slow cooling to −35° afforded 13 g of a flaky, golden-yellow solid, mp 142–143.5° (lit.[32] mp 142–144°). Rotary evaporation of the mother liquor at ambient temperature permitted the recovery of the remaining product for subsequent purification.

$Hg[Cr(CO)_3C_5H_5]_2$.—This compound, originally described by Fischer, Hafner, and Stahl,[33] was prepared by the procedure of King and Stone.[34] Recrystallization of 60 g of crude product from 1 l. of boiling 1:1 THF–methanol by slow cooling gave 30 g of yellow platelike crystals, mp 201–203°. A second crop of 11 g, mp 196–200°, was obtained on rotary evaporation (25° (~20 mm)) of the supernatant to half-volume followed by slow cooling to −35°.

$Hg[M(CO)_3C_5H_5]_2$ (M = Mo, W).—The compounds Hg[Mo-

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(24) R. B. King. *J. Am. Chem. Soc.*, **88**, 2075 (1966).

(25) J. M. Burlitch, to be submitted for publication.

(26) J. M. Burlitch and S. W. Ulmer, *J. Organometal. Chem.* (Amsterdam), **19**, P11 (1969).

(27) W. Hieber, E. O. Fischer, and E. Böckly, *Z. Anorg. Allgem. Chem.*, **269**, 308 (1952).

(28) (a) R. B. King, "Organometallic Syntheses," Vol. 1, J. J. Eisch and R. B. King, Ed., Academic Press, New York, N. Y., 1965, p 101. (b) Recrystallization of $Hg[Co(CO)_4]_2$ from warm methanol was preferred over the acetone–water mixture which occassionally led to the formation of very small crystals or an oil.

(29) The method used was a modification of that described by Fischer and Böttcher.[30] In our hands the use of methanol or THF as solvent in the preparation of $NaFe(CO)_2C_5H_5$ led to the formation of substantial quantities of $[Fe(CO)_2C_5H_5]_2$ which could only be separated from the desired product by chromatography on acid-washed alumina.

(30) E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **10b**, 600 (1955).

(31) Reference 28a, p 151.

(32) R. B. King, *J. Inorg. Nucl. Chem.*, **25**, 1296 (1963).

(33) E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allgem. Chem.*, **282**, 47 (1955).

(34) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 99 (1963).

TABLE VI

EXPERIMENTAL CONDITIONS FOR METAL-EXCHANGE REACTIONS

Compound[a]	Amt of m_2Hg, mmol	Amt of Zn or Cd, mg-atoms	Reaction solvent (ml)	Reaction temp, °C	Reaction time, hr	Recrystn solvent (ml)	Recrystn temp range, °C	Yield of 1st crop, %
$Zn[Co(CO)_4]_2$	12	60	Toluene (70)	25	1.5	*b*	25 to −80	93.5
$Zn[Fe(CO)_2Cp]_2$	2.0	20	Toluene (20)	25	1	*b*	25 to −30	74
$Zn[Fe(CO)_2Cp]_2$	4.0	40	THF (20)	25	1	Toluene	50 to −35	84
$Zn[Cr(CO)_3Cp]_2$	10	100	Toluene (120)	60	8	*b*	60 to −60	79
$Zn[Cr(CO)_3Cp]_2$	1.66	16.6	THF (20)	25	1.5	*c*	. . .	100[c]
$Zn[Mo(CO)_3Cp]_2$	2.0	20	THF (20)	70	5	Toluene (35)	50 to −60	75
$Zn[W(CO)_3Cp]_2$	2.0	20	THF (20)	70	5.5	Toluene (35)	50 to −60	58
$Zn[Fe(CO)_2Cp]$-$[Co(CO)_4]$	5.0	50	Hexane (50)	25	1	*b*	25 to −35	90
$Cd[Co(CO)_4]_2$	4.0	20	Hexane (60)	25	3	*b*	45 to −60	89
$Cd[Fe(CO)_2Cp]_2$	2.0	20	Toluene (60)	25	4	*b*	60 to −60	72
$Cd[Fe(CO)_2Cp]_2$	2.0	20	THF (30)	25	2.5	*c*	. . .	93[c]
$Cd[Cr(CO)_3Cp]_2$	2.0	20	Toluene (80)	60	16	*b*	60 to −60	85
$Cd[Mo(CO)_3Cp]_2$	2.0	20	THF (30)	70	7.5	Toluene (40)	50 to −60	85
$Cd[W(CO)_3Cp]_2$	2.0	20	THF (30)	70	17	Toluene (85)	80 to −60	56

[a] Cp = π-C_5H_5. [b] The product was crystallized from the reaction solvent. [c] The crude product which remained on evaporation of the reaction solvent had a satisfactory melting point.

$(CO)_3C_5H_5]_2$,[33] mp 201–203°, and $Hg[W(CO)_3C_5H_5]_2$,[33] mp 240–242°, were prepared in high yields by methods similar to that used for the chromium analog. The solvents employed in the preparation of the sodium salts were THF[35] and diglyme, respectively. Both products were recrystallized from boiling acetone.

$Hg[Mn(CO)_5]_2$.—Previously described[36] only as a gray-white amorphous solid, $Hg[Mn(CO)_5]_2$ was prepared by the dropwise addition of a filtered THF solution of $NaMn(CO)_5$[37] to a stirred solution of a 10% excess of $Hg(CN)_2$ in degassed THF. The resulting yellowish white, finely crystalline solid was washed with six 100-ml portions of distilled water, followed by 50 ml of methanol and 25 ml of acetone. The dry crude product (27 g, 91%) was sublimed in six portions in a large sublimator at 130° (0.001 mm). After each portion the residue was washed out with water without removing the sublimate from the probe. In this way 26.3 g (89%) of yellow, crystalline $Hg[Mn(CO)_5]_2$ was obtained. The product, which did not melt below 250°, was identified by its infrared and mass spectra. Needlelike crystals of this compound could be obtained by recrystallization from a very dilute solution in boiling toluene under nitrogen.

Preparation and Reactions of m_2Zn and m_2Cd Compounds. General Comments.—The procedures used in the syntheses of all the m_2Zn and m_2Cd compounds were similar and are illustrated by the first two preparations described below. Pertinent reaction conditions for the metal-exchange reactions are listed in Table VI. All the reactions in this section were carried out under a purified argon atmosphere in modified (two-necked) Schlenk tubes (MST). Solvents were distilled directly into the reaction vessels from appropriate drying agents. With the exception of the $Mn(CO)_5$ derivatives, the progress of the exchange reaction was conveniently followed by thin layer chromatographic (tlc) analysis on Eastman "Chromagram" silica gel plates developed with iodine. The disappearance of the air-stable m_2Hg reactant was monitored since the air-sensitive m_2Zn and m_2Cd products decomposed without elution. In most cases cyclohexane or benzene–cyclohexane mixtures served as eluents. Unless otherwise indicated, the zinc metal used was either 20 mesh (Mallinckrodt AR) or −325 mesh (Cerac Inc., Butler, Wis.); the latter type is referred to as zinc powder. The cadmium metal was −325 mesh (Cerac) powder. In our experience the form of the metal did not change the reaction rate drastically. Tetrahydrofuran (Du Pont technical grade or Fisher reagent grade) was twice distilled from potassium metal and twice degassed *in vacuo* at −78°. Toluene (Fisher reagent grade) was distilled from sodium–benzophenone. Hexane (Fisher, mixed isomers) was distilled from potassium–benzophenone. Diglyme (Ansul Chemical Co. technical grade) was triply distilled from sodium. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer; sealed cells were employed for solution spectra.

Infrared spectra of the new compounds in KBr disks are given in Table VII. The disks were prepared in a nitrogen-filled drybox (Vacuum/Atmospheres Corp.) and were recorded immediately on exposure to the air. Mass spectra were obtained on an AEI MS902 instrument[38] employing a direct-insertion probe. Carbon–hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and metal analyses by the Analytical Laboratory of the Cornell Material Science Center.

TABLE VII

INFRARED SPECTRAL DATA

Compound	ν_{CO} KBr spectra[a]
$Zn[Fe(CO)_2C_5H_5]_2$	1963 s, 1945 s, 1937 s, sh, 1980 vs, 1860 m, sh
$Cd[Fe(CO)_2C_5H_5]_2$	1963 s, 1953 s, 1940 s, sh, 1901 s, sh, 1891 s, 1858 m
$Zn[Cr(CO)_3C_5H_5]_2$	1952 s, 1878 s, 1841 s
$Cd[Cr(CO)_3C_5H_5]_2$	1966 s, sh, 1956 s, 1875 m, sh, 1836 s, 1807 s, 1715 m, sh
$Hg[Cr(CO)_3C_5H_5]_2$	1976 s, 1966 m, 1952 s, 1890 m, 1862 vs, 1842 m
$Zn[Mo(CO)_3C_5H_5]_2$	1960 s, 1892 s, 1845 s
$Cd[Mo(CO)_3C_5H_5]_2$	1980 s, sh, 1964 s, 1877 s, sh, 1846 s, 1817 s, 1730 m, sh
$Hg[Mo(CO)_3C_5H_5]_2$	2000 m, 1953 s, 1883 s, sh, 1859 vs, 1838 w, sh
$Zn[W(CO)_3C_5H_5]_2$	1945 s, 1894 m, 1825 s
$Cd[W(CO)_3C_5H_5]_2$	1975, s, sh, 1963 s, 1875 m, sh, 1845 s, 1797 s, 1720 m, sh
$Hg[W(CO)_3C_5H_5]_2$	1996 m, 1946 s, 1870 s, sh, 1851 vs, 1828 w
$Zn[Fe(CO)_2C_5H_5][Co(CO)_4]$	2073 m, sh, 2056 m, 1945 s, 1892 s
$Hg[Fe(CO)_2C_5H_5][Co(CO)_4]$	2074 s, 2004 s, 1989 s, 1961 s, 1942 s, 1912 m, sh

[a] KBr spectra were observed on disks prepared from thoroughly dried KBr in a nitrogen-filled drybox.

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[35] See ref 28a, p 145, for a description of the preparation of $NaMo(CO)_3C_5H_5$ in THF.

[36] W. Hieber and W. Schropp, Jr., *Chem. Ber.*, **93**, 455 (1960).

[37] Reference 28, p 149.

[38] Grateful acknowledgment is made to the National Institutes of Health for funds used to purchase the mass spectrometer.

Preparation of $Zn[Co(CO)_4]_2$.—Into a dry 70-ml MST, equipped with a magnetic stirrer, "fine" Fritte, and a 70-ml MST as receiving vessel, was placed 3.9 g (60 mg-atoms) of zinc powder. After the metal was flamed dry *in vacuo* and cooled, 6.5 g (12 mmoles) of $Hg[Co(CO)_4]_2$ was added followed by 35 ml of toluene, distilled in under argon. The mixture was stirred at ambient temperature for 1.5 hr during which time the color of the solution turned from deep orange to bright yellow.[39] Tlc analysis showed that all of the starting mercury compound had been consumed. After having stood for 1 hr, the mixture was filtered and slowly cooled to −80° by placing the tightly stoppered receiving MST in a small dewar containing some acetone and refrigerating the combination at −5° (3 hr), −35° (12 hr), −60° (20 hr), and −80° (3 hr). The light yellow supernatant liquid was decanted off under argon, and the yellow, prismatic crystals were dried *in vacuo* (30 min). The crystalline product weighed 4.55 g (93.5%), mp 71–72.5°, and was identified as $Zn[Co(CO)_4]_2$ by comparison of its melting point and infrared and mass spectra with those of an authentic sample prepared by a modified high-pressure procedure.[7]

Preparation of $Zn[Mo(CO)_3C_5H_5]_2$.—As described in the previous experiment a 90-ml MST was charged with 1.38 g (2.0 mmol) of $Hg[Mo(CO)_3C_5H_5]_2$, 1.3 g (20 mg-atoms) of zinc powder, and 20 ml of THF. The vessel was equipped with a cold-finger water condenser and the mixture was stirred at gentle reflux (oil bath, 73°) for 5 hr. After cooling, the light yellow reaction mixture was evaporated to dryness at reduced pressure and the resulting yellowish white residue gradually turned white upon drying *in vacuo* (20 hr). The crude product (1.13 g, 100%, mp 193–195°) was recrystallized from 35 ml of warm (50–60°) toluene by gradual cooling to −60°. This afforded 0.85 g (75%) of cream-colored crystals of $Zn[Mo(CO)_3C_5H_5]_2$, mp 194–196°.

Reaction of $Hg[Mn(CO)_5]_2$ with Zinc in Diglyme.—As described in the previous experiment an 80-ml MST, equipped with a magnetic stirrer and a cold finger, was charged with 0.590 g (1.0 mmol) of $Hg[Mn(CO)_5]_2$, 0.65 g (10 mg-atoms) of zinc turnings, and 40 ml of diglyme. Upon stirring and heating the mixture to 120°, it turned light yellow. Stirring was continued at this temperature for 5 hr during which time the starting mercury compound gradually dissolved. Mass spectroscopic analysis of the residue formed on vacuum evaporation of a small aliquot of the mixture showed that $Zn[Mn(CO)_5]_2$ was present, contaminated with a small amount of $Hg[Mn(CO)_5]_2$. After the solvent was removed *in vacuo* from the cooled and filtered reaction mixture, the resulting cream-colored residue was transferred to a small sublimator under argon and, after removal of a small amount of solvent at 50°, was sublimed at 50–110° (0.001 mm). The yellowish white sublimate, 0.35 g (77%), mp 210–212°, was identified as $Zn[Mn(CO)_5]_2$ by comparison of its melting point and mass spectrum with those of an authentic sample.[16] A similar reaction carried out using 1.3 g (20 mg-atoms) of powdered zinc and 1.18 g (2 mmol) of $Hg[Mn(CO)_5]_2$ in 20 ml of diglyme resulted in the isolation of only 0.25 g (28%) of $Zn[Mn(CO)_5]_2$. The excess zinc powder (amalgam) from the reaction mixture was washed with acetone, dried, and found to contain 0.4 g (34% recovery) of $Hg[Mn(CO)_5]_2$, isolated by sublimation and identified by its mass spectrum.

Reaction of $C_5H_5Fe(CO)_2HgCo(CO)_4$ with Cadmium.—A mixture of 1.1 g (2.0 mmol) of $C_5H_5Fe(CO)_2HgCo(CO)_4$ (prepared by the method of Dighe and Orchin[40]) and 2.24 g (20 mg-atoms) of cadmium powder in 30 ml of toluene was stirred for 1.5 hr in the dark. At the end of this period the orange color of the reaction mixture had not changed appreciably but tlc analysis showed the absence of the starting mercury compound. The filtered solution was concentrated to 10 ml by evaporation at reduced pressure and slow cooling to −60° (20 hr) afforded 0.71 g of a mixture of orange and yellow crystals, mp 71–74°. Mass spectral analysis of the finely ground solid showed that in addition to the expected product, $C_5H_5Fe(CO)_2CdCo(CO)_4$, substantial amounts of the symmetrical derivatives, $Cd[Fe(CO)_2C_5H_5]_2$ and $Cd[Co(CO)_4]_2$, were also present. When this exchange reaction was carried out in THF, a mixture of a solid and an oil was obtained upon removal of the solvent *in vacuo*. Repeated attempts to obtain a pure crystalline product by recrystallization from nonpolar solvents were unsuccessful.

Reaction of $Cd[Fe(CO)_2C_5H_5]_2$ with $Cd[Co(CO)_4]_2$.—A mixture of 0.135 g (0.297 mmol) of $Cd[Co(CO)_4]_2$ and 0.139 g (0.298 mmol) of $Cd[Fe(CO)_2C_5H_5]_2$ was prepared by weighing the solids in a nitrogen-filled drybox and dissolved in 30 ml of toluene under an argon atmosphere. The solution was stirred in the dark at ambient temperature for 3 hr. Evaporation of a 1-ml aliquot to dryness *in vacuo* left an orange-brown residue the mass spectrum of which was similar to that of the previous experiment and showed the presence of $C_5H_5Fe(CO)_2CdCo(CO)_4$ with lesser amounts of $Cd[Fe(CO)_2C_5H_5]_2$ and $Cd[Co(CO)_4]_2$. A similar experiment with the zinc analogs gave the mixed-metal compound contaminated with only very minor amounts of the symmetrical precursors.

Reaction of $Cd[Fe(CO)_2C_5H_5]_2$ with Mercury.—A mixture of 0.11 g (0.236 mmol) of $Cd[Fe(CO)_2C_5H_5]_2$ in 10 ml of toluene and 2.1 g (10.5 mg-atoms) of mercury was stirred at ambient temperature for 3 hr in the dark. This was repeated with 2.6 g (13 mg-atoms) of fresh mercury. The filtered mixture was evaporated to 4 ml at reduced pressure (25°) and then cooled slowly to −35° (8 hr). A mixture of large (3 mm), dark red, octahedral-shaped crystals and much smaller yellow-orange granular crystals was obtained. Since previous experience had shown $Hg[Fe(CO)_2C_5H_5]_2$ to be polymorphic, the crystals were ground together and a mass spectrum of this solid showed only the presence of this compound. None of the starting cadmium derivative was detected.

Reaction of $Cd[Co(CO)_4]_2$ with Mercury.—A solution of 0.156 g (0.344 mmol) of $Cd[Co(CO)_4]_2$ in 10 ml of hexane and 1.36 g (6.8 mg-atoms) of mercury were stirred at ambient temperature in the dark for 2 hr. At this time tlc analysis indicated that a small amount of $Hg[Co(CO)_4]_2$ had formed. After having been stirred for an additional 13 hr, the mixture had not changed appreciably as indicated by tlc. The filtered mixture was evaporated to dryness *in vacuo* at ambient temperature and the yellow, crystalline residue was decomposed with dilute nitric acid. Analysis of the resulting solution for mercury showed that 0.02 mmol (6%) of $Hg[Co(CO)_4]_2$ had formed.

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[39] NOTE ADDED IN PROOF.—Subsequent work with $Zn[Co(CO)_4]_2$ has shown it to be somewhat light sensitive. Solutions exposed to fluorescent laboratory light darkened appreciably in 2–4 hr.

[40] S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, **86**, 3895 (1964).