# Pentacoordinate Iridium(I) and Rhodium(I) Complexes Derived from Metal Carbonyl Anions[1]

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**Abstract:** Anionic triphenylphosphine carbonyl complexes of iridium and rhodium have been prepared by reduction of $[MCl(CO)(P(C_6H_5)_3)_2]$ (M = Ir, Rh) with sodium amalgam in tetrahydrofuran. Reaction of the resulting metallo anions with post-transition metal halides, perfluoroalkyl iodides, acetic acid, and methyl iodide afforded a series of novel five-coordinate complexes of iridium(I) and rhodium(I). Structures have been proposed for these complexes on the basis of their infrared and nmr spectra.

The research described herein[4] stems from our interest in the chemistry of complexes of metals with $d^8$ configuration[5] and our long-range interest in the synthesis of metal–metal bonds. This work also illustrates the pattern of reactions characteristic of metal carbonyl anions in which the metal possesses a basic electron pair. When this work was initiated, transition metal carbonyl anions were known for all the transition elements with the exception of osmium, rhodium, and iridium.[6] During the course of our studies an ionic trifluorophosphine complex of rhodium was described.[7]

Synthesis of compounds with covalent metal–metal bonds involving transition elements is a subject of considerable current interest.[8] Evidence for electron transport through chains of metal–metal bonds[9] provides additional impetus to this subject. The preparation of linear macromolecules comprised entirely of metal–metal bonds is a long-range goal to challenge the synthetic chemist. Even while purposeful synthetic chemistry in this area is at an early stage, at least eight methods of metal–metal bond syntheses have been reported: (1) metathetical reactions between a metal anion and a metal halide,[10] (2) elimination of carbon monoxide between metal carbonyl complexes,[11] (3) elimination of hydrogen between two metal hydrides,[12] (4) elimination of hydrogen halide between a metal hydride and a metal halide,[13] (5) insertion of electron-deficient metallic species into a metal–metal bond,[14] (6) oxidative addition of a metal halide to a basic transition metal complex,[15] (7) reaction of a metal hydride and a high-energy metal–nitrogen or metal–oxygen covalent bond,[16] (8) solid-state aggregation of thin, planar $d^8$ complexes.[17]

Reduction of the yellow tetrahydrofuran (THF) solution of chlorocarbonylbis(triphenylphosphine) iridium(I) (**1**)[18] with sodium amalgam affords a colorless solution. It is inferred from the infrared spectrum and chemical reactions of this solution that the principal species in this solution is the iridium(−I) carbonyl anion **2** (Scheme I). Attempts to isolate this anion by addition of large cations resulted in the formation of intractable materials which have infrared bands in the 2100-cm$^{-1}$ region suggesting the presence of iridium hydride bonds.

The infrared spectrum of a tetrahydrofuran solution of this intermediate anion indicates the absence of the starting complex **1** (no band at 1960 cm$^{-1}$). Two strong carbonyl bands observed at 1840 and 1860 cm$^{-1}$ are in the low-frequency region expected for carbonyl anion complexes.[6] Formulation of the intermediate anion **2** as $[Ir(CO)_3L]^-$ is based on the nature of the products derived from its reactions with various post-transition metal halides (Scheme I).

The basic character of neutral isoelectronic $d^{10}$ complexes such as tetrakis(triphenylphosphine)platinum(0) is now well documented.[19] Complexes of metals with $d^{10}$ electronic configuration often dissociate[19a] to give two or three coordinate species which are effective bases undergoing oxidative addition reactions. If this dissociative tendency of $d^{10}$ complexes extends to the anionic species **2**, the products isolated from metathetical reactions of this anion may simply result from ligands present *in situ* rather than as a product of a

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[3] Abstracted from the Ph.D. dissertation of F. Vastine, University of North Carolina, 1967.

[4] A portion of this work was described in a preliminary publication: J. P. Collman, W. R. Roper, and F. D. Vastine, *J. Am. Chem. Soc.*, **88**, 5035 (1966).

[5] J. P. Collman and W. R. Roper, *ibid.*, **88**, 3504 (1966).

[6] R. B. King, *Advan. Organometal. Chem.*, **2**, 159 (1964).

[7] T. Kruck, *Angew. Chem. Intern. Ed. Engl.*, **6**, 53 (1967).

[8] R. S. Nyholm and J. Lewis, *Sci. Progr.*, **52**, 557 (1964), and references therein.

[9] C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ülkü, *J. Am. Chem. Soc.*, **88**, 4286 (1966).

[10] (a) H. R. H. Patil and W. A. G. Graham, *ibid.*, **87**, 673 (1965); (b) A. S. Kasenally, R. S. Nyholm, and M. H. B. Stiddard, *ibid.*, **86**, 1884 (1964).

[11] (a) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966), and references therein; (b) T. Kruck and M. Höfler, *Angew. Chem. Intern. Ed. Engl.*, **3**, 701 (1964).

[12] (a) A. G. Massey, A. J. Park, and F. G. A. Stone, *J. Am. Chem. Soc.*, **85**, 2021 (1963); (b) W. P. Neumann and K. König, *Angew. Chem. Intern. Ed. Engl.*, **3**, 751 (1964).

[13] (a) R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5331 (1965); (b) B. Chiswell and L. M. Venanzi, *ibid.*, 901 (1966).

[14] (a) S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, **86**, 3895 (1964); (b) D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966), and references therein.

[15] (a) J. P. Collman and W. R. Roper, *Chem. Commun.*, 244 (1966); (b) R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1967); (c) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

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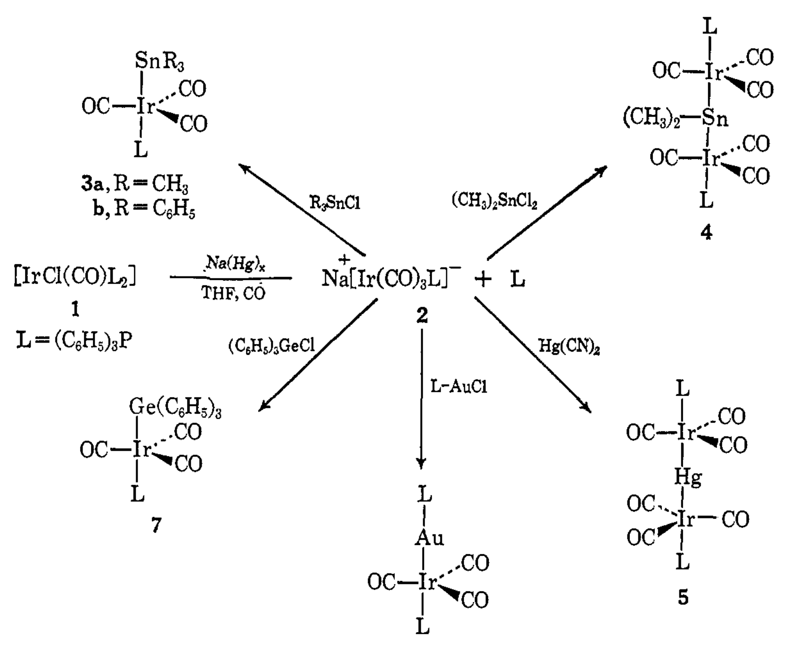
[17] (a) C. M. Harris and S. E. Livingstone, *Rev. Pure Appl. Chem.*, **12**, 16 (1962); (b) S. Yamada, *Experientia Suppl.*, **9**, 140 (1964).

[18] L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

[19] (a) C. D. Cook, C. H. Koo, S. C. Nybur, and M. T. Shiomi, *Chem. Commun.*, 426 (1967), and references therein; (b) R. Ugo, F. Cariati, and G. La Monica, *ibid.*, 868 (1966); (c) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966); (d) V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966); (e) J. McAvoy, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc.*, 1376 (1965).

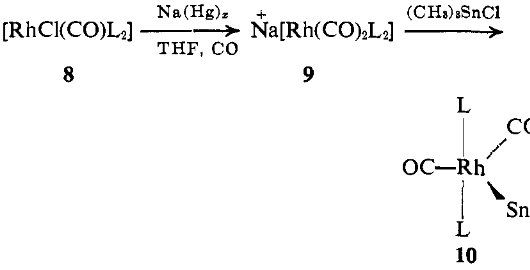
**Scheme I**



discrete anionic species. Thus the presence of an extra mole of triphenylphosphine as well as excess CO in solutions of anion **2** must be recognized in interpretation of reactions of this anion.

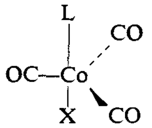
Scheme I depicts reactions between the anion **2** and several metal chlorides. The products **3–7** apparently contain metal–metal bonds. The provisional stereochemical structures depicted in Scheme I are based on infrared and nmr spectra to be discussed below. The compositions of these complexes were established by elemental analyses, and, where solubilities permitted, by osmometric molecular weights. The pale-yellow crystalline compounds are air stable with the exception of the germanium complex **7**, which gradually decomposes over a period of several weeks. The mercury complex **5** is insoluble, but the other complexes (**3**, **4**, **6**, and **7**) are soluble in halocarbons, benzene, and tetrahydrofuran.

An intermediate rhodium carbonyl anion **9** was prepared in a similar manner (eq 1). Reaction of this intermediate with trimethyltin chloride gave the five-coordinate complex **10** which has a composition different from that of the iridium analog **3a**. It is uncertain whether this difference reflects different compositions or the iridium and rhodium anions **2** and **9** or different reactivities of intermediate anions in equilibrium. In any event, the stoichiometries are consistent with the increasing affinities for carbon monoxide with the lighter transition metals.[5,20]

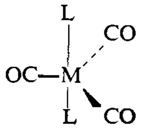


(1)

Infrared and nmr spectral data for the iridium complexes **3–7** and the rhodium complex **10** are collected in Table I. The infrared spectrum of each of these five-coordinate iridium complexes exhibits a very intense carbonyl absorption at about 1950 cm$^{-1}$ and a moderate-to-weak band at slightly higher frequencies. The most likely configuration for these five-coordinate, pseudo-d$^8$ complexes is a trigonal bipyramid;[21] however, a tetragonal pyramid is also feasible. We favor the trigonal bipyramidal arrangement with three carbonyl groups in the trigonal plane and the bulky organometal ligand and triphenylphosphine in apical positions as illustrated in Scheme I. Two infrared carbonyl absorptions observed for these compounds are in accord with $C_{3v}$ symmetry. If the organometallic groups in **3–7** are considered as pseudo-halides, these complexes are isoelectronic with five-coordinate cobalt(I) tricarbonyl compounds **11**. The infrared spectra of the related five-coordinate cobalt complexes **11** described by Hieber exhibit a strong band (E) and a weaker band (A) at higher frequency.[21] A related five-coordinate osmium(0) complex **12**[5] has $D_{3h}$ symmetry (with bulky phosphines in apical positions) as suggested by the presence of a single carbon monoxide frequency and confirmed by an X-ray diffraction study.[22] Tetragonal pyramidal arrangements with three carbonyls would be expected to give rise to more than the two peaks found in the spectra of the tricarbonyl complexes (**3–7**).



**11**, X = Br, I
($C_{3v}$)



**12**, M = Ru, Os
($D_{3h}$)

The stereochemical configuration of the rhodium-trimethyltin complex (provisionally depicted as **10**)

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[20] W. Hieber and J. Muschi, *Chem. Ber.*, **98**, 3921 (1965).

[21] W. Hieber and E. Lindener, *ibid.*, **95**, 273 (1962).

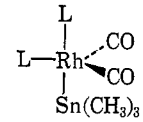
[22] J. A. Ibers, private communication.

Table I

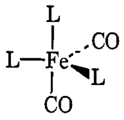
| Compound | $\gamma_{CO}$,[a] $cm^{-1}$ | Nmr, $\tau$[b] | $J_{Sn^{117}-H}$ |
|---|---|---|---|
| $[Ir(CO)_3L(Sn(CH_3)_3)]$ (**3a**) | 1950 (vs), 2010 (m) | 2.58 m (17), 9.49 d (9)[d] | 49[c] |
| $[Ir(CO)_3L(Sn(C_6H_5)_3)]$ (**3b**) | 1965 (vs), 2025 (w) | . . . | |
| $[Ir(CO)_3L]_2Sn(CH_3)_2$ (**4**) | 1950 (vs) | 2.62 m (5), 8.96 t (1) | 40 |
| $[Ir(CO)_3L]_2Hg$ (**5**) | 1945 (vs), 1985 (m) | . . . | |
| $[Ir(CO)_3L]AuL$ (**6**) | 1930 (vs), 1990 (w) | . . . | |
| $[Ir(CO)_3L]Ge(C_6H_5)_3$ (**7**) | 1955 (vs) | . . . | |
| $[Rh(CO)_2L_2(Sn(CH_3)_3)]$ (**10**) | 1930 (vs), 1975 (m) | 2.81 m (31.5), 9.86 s (9) | 46.5 |
| $[Ir(CO)_2L_2I]$ (**18**) | 1955 (s), 1935 (vs) | | |
| $[Ir(CO)_2L_2H]$ (**21**) | 1960 (s), 1915 (s) | | |
| $[Ir(CO)_2L_2(H)_2^+]PF_6^-$ (**22**) | 2085 (s), 2050 (vs) | | |
| $[Ir(CO)_2L_2(COCH_3)]$ (**24**) | 1975 (vs), 1925 (vs) | 2.63 m (33), 7.80 s (3) | |

[a] Qualitative intensities given by: vs, very strong; s, strong; m, medium; w, weak. [b] Relative area ratios given in parentheses. Multiple patterns indicated by: s, singlet; d, doublet; t, triplet; m, multiplet. [c] $J_{Sn^{117}-H}$ = 47 cps. [d] $J_{P^{31}-H}$ = 1 cps.

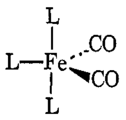
is less certain. This complex exhibits two carbonyl bands at 1970 and 1920 cm$^{-1}$. Tris(triphenylphosphine)dicarbonyliron(0) described by Hieber and Muschi[23] serves as a model five-coordinate d$^8$ dicarbonyl compound having three bulky ligands. Two carbonyl bands in its infrared spectrum are consistent with structures **13** and **14**. Structure **14** ($C_{2v}$ symmetry) was assigned to this complex on the basis of its dipole moment. Assuming that the two carbonyl groups in the rhodium–trimethyltin complex are in trigonal positions as in the isoelectronic iron(0) complex, two structures, **10** and **12**, are possible. The former is favored on the basis of an nmr argument.



**12** ($C_s$)



**13** ($C_s$)



**14** ($C_{2v}$)

The methyl signals in the nmr spectra of the iridium–trimethyltin and diiridium–dimethyltin complexes **3** and **4** (Table I) are observed as a symmetrical doublet and a symmetrical triplet presumably because of coupling with the *trans*-phosphines ($J_{P^{31}-H}$ = 1 cps). The related rhodium–trimethyltin complex exhibits a methyl singlet suggesting structure **10** ($C_{2v}$ symmetry) rather than **12** ($C_s$ symmetry). Coupling of *trans* ligands is expected to be greater than coupling of *cis* ligands.

The magnitude of the Sn$^{119}$–H coupling constants listed in Table I is related to the degree of s character in the tin-methyl bonds.[24] Holmes and Kaesz found that an increasing number of electronegative substituents on tin caused an increase in the Sn$^{119}$–H and Sn$^{117}$–H coupling constants.[24a] The $J_{Sn^{119}-H}$ value for the iridium–trimethyltin complex **3a** (49.0 cps) is about the same as that reported for $(CH_3)_3SnMn(CO)_5$[25] (48.3 cps) but smaller than that for tetramethylstannane (54.0 cps).[24a] This indicates that the electronegativity of the iridium group ($Ir(CO)_3L$) is about the same as the manganese group $Mn(CO)_5$ but less than a methyl group. The effect of replacing another methyl group by iridium is consistent with this reasoning. The coupling constant for **4** is 40.0 cps.

The analogy between the five-coordinate iridium complexes **3–7** and other five-coordinate d$^8$ systems[5] prompted us to examine reactions of these new complexes with electrophilic reagents known to oxidize five-coordinate d$^8$ complexes of iron(0), ruthenium(0), and osmium(0).[5,26] It was hoped that the integrity of the iridium–mercury or iridium–tin bonds might be maintained during oxidative addition reactions. However, this was not found to be the case. Treatment of these iridium complexes with halogens and mercuric halides resulted in oxidation of iridium and concomitant cleavage of iridium–mercury and iridium–tin bonds. These observations are summarized in eq 2–5.

$$\underset{\mathbf{5}}{Hg[Ir(CO)_3L]_2} + 4I_2 \longrightarrow \underset{\mathbf{15}}{2[IrI_3(CO)_2L]} + 2CO + HgI_2 \quad (2)$$

$$\underset{\mathbf{3b}}{[(C_6H_5)_3SnIr(CO)_3L]} + 2I_2 \longrightarrow$$
$$\underset{\mathbf{15}}{[IrI_3(CO)_2L]} + (C_6H_5)_3SnI + CO \quad (3)$$

$$\underset{\mathbf{3b}}{[(C_6H_5)_3SnIr(CO)_3L]} + 5Br_2 \longrightarrow$$
$$\underset{\mathbf{16}}{[IrBr_3(CO)_2L]} + 3C_6H_5Br + SnBr_4 + CO \quad (4)$$

$$\underset{\mathbf{3b}}{[(C_6H_5)_3SnIr(CO)_3L]} + 2HgI_2 \longrightarrow$$
$$\underset{\mathbf{17}}{[IrI(HgI)_2(CO)_2L]} + CO + (C_6H_5)_3SnI \quad (5)$$

The same triiododicarbonyliridium(III) complex **15** was formed by reaction of the mercury–iridium complex **5** with 4 moles of iodine and by reaction of the iridium–triphenyltin complex **3b** with 2 moles of iodine (eq 2 and 3). The triiodoiridium(III) complex **15** exhibits carbonyl peaks at 2070 and 2110 cm$^{-1}$. The higher frequencies of these carbonyl bands are consistent with the formulation of **15** as an iridium(III) complex. Triphenyltin iodide was isolated (eq 3) and identified by its melting point. A gas-buret analysis of reaction 3 revealed the evolution of 1 equiv of carbon monoxide. Attempts to stop these reactions at intermediate stages failed.

Bromine also cleaves phenyl–tin bonds. Thus 5 equiv of bromine is taken up by the iridium–triphenyltin complex (eq 4). Bromobenzene was detected by glpc, carbon monoxide was measured in a gas buret, and the tribromoiridium(III) complex **16** was characterized by elemental analyses and its infrared spectrum.

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(23) W. Hieber and J. Muschi, *Chem. Ber.*, **98**, 3931 (1965).

(24) (a) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961); (b) N. Flitcroft and H. D. Kaesz, *ibid.*, **85**, 1377 (1963); (c) T. F. Bolles and R. S. Drago, *ibid.*, **88**, 5730 (1966).

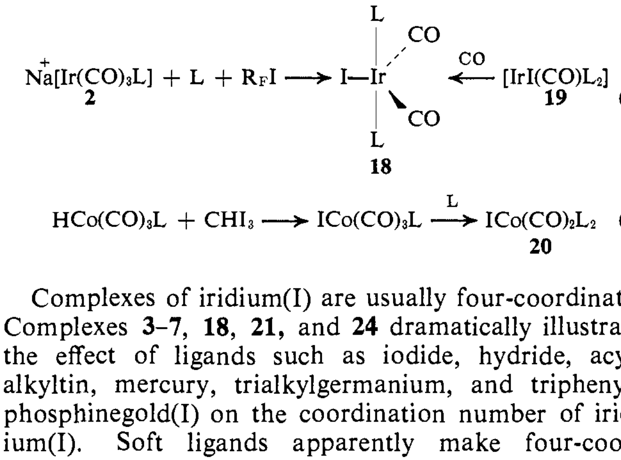
(25) W. Jetz, P. Simons, J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

(26) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **87**, 4008 (1965).

The reaction of the iridium–triphenyltin complex **3b** and 2 moles of mercuric iodide gave carbon monoxide, triphenyl iodide, and a new iridium complex containing mercury (presumably **17**). Satisfactory elemental analysis were not obtained for the iridium–mercury complex **17**; however, there is precedence for such a complex in which elemental mercury is released.[15b]

Related reactions have been reported in which manganese–mercury,[27] manganese–lead, and iron–tin bonds[28] are cleaved by halogens. On the other hand, the manganese–tin[28] bond is resistant to cleavage by halogens.

The intermediate iridium anion **2** reacted with perfluoropropyl, perfluoroethyl, and perfluorophenyl iodides to yield iodobis(triphenylphosphine)dicarbonyliridium(I) (**18**) (eq 6). These perfluoroalkyl and aryl iodides act as pseudo-halogens and are known to be polarized so that iodine bears a partial positive charge.[29] The same five-coordinate iridium(I) iodide was first prepared by Angoletta[30] by an entirely different reaction. A simple independent synthesis of **18** was achieved by carbonylating the four-coordinate iridium(I) iodide **19** which was prepared from the chloride by metathetical displacement[31] (eq 6). The analogous four-coordinate chloride **1** also reacts with an additional mole of carbon monoxide,[32] but the resulting colorless five-coordinate dicarbonyl complex (infrared bands at 1930 and 1985 cm$^{-1}$) is metastable and spontaneously loses carbon monoxide. The yellow five-coordinate dicarbonyl iodide **18** has carbonyl bands at 1995 and 1935 cm$^{-1}$. The tentative configuration depicted for **18** is based on our assumption that the phosphine groups will assume apical positions.


(6)

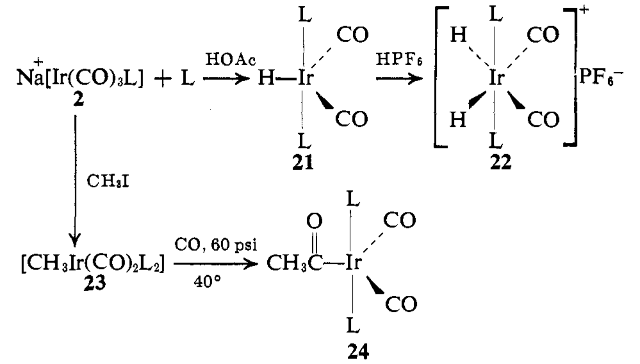
$$\mathrm{HCo(CO)_3L + CHI_3 \longrightarrow ICo(CO)_3L \xrightarrow{L} \underset{\mathbf{20}}{ICo(CO)_2L_2}} \quad (7)$$

Complexes of iridium(I) are usually four-coordinate. Complexes **3–7**, **18**, **21**, and **24** dramatically illustrate the effect of ligands such as iodide, hydride, acyl, alkyltin, mercury, trialkylgermanium, and triphenylphosphinegold(I) on the coordination number of iridium(I). Soft ligands apparently make four-coordinate d$^8$ complexes more susceptible to the addition of a fifth ligand so as to become coordinatively saturated. The greater tendency of iodobis(triphenylphosphine)carbonyliridium(I)[33] to add oxygen or carbon monoxide compared with the corresponding chloride **1** is an excellent illustration of this behavior. The great affinity of chlorobis(triphenylarsine)carbonyliridium(I) for oxygen is another example of this generalization.[34]

A structurally and electronically similar compound in which the central metal ion is cobalt has been prepared by Hieber and Duchatsch (eq 7).[35] This cobalt(I) iodide **20** exhibits two carbonyl absorption bands at 1992 and 1928 cm$^{-1}$.

Neutralization of the iridium anion **2** with acetic acid afforded a five-coordinate hydride containing two carbonyl groups and two phosphines, the second phosphine apparently acquired from uncoordinated triphenylphosphine present in the solution (Scheme II). A provisional configuration of the hydride is depicted in **21** as a trigonal bipyramid with the two phosphines *trans* ($C_{2v}$ symmetry). The infrared spectrum of **21** reveals a hydride stretching band at 2080 cm$^{-1}$ and two metal carbonyl bands at 1960 and 1915 cm$^{-1}$. The hydride was exchanged by deuterium using deuteriopropionic acid as indicated by the disappearance of the band at 2080 cm$^{-1}$. The iridium–deuterium stretching mode is apparently obscured by a phosphine absorption at 1480 cm$^{-1}$.

**Scheme II**



The fact that the iridium(I) hydride **21** is a weaker acid then acetic acid, whereas the related cobalt(I) hydride, $\mathrm{HCo(CO)_3L}$, is a strong acid,[36] illustrates an apparent trend in basic properties of d$^{10}$ metal anions within this triad. The five-coordinate hydride **21** is also a weak base undergoing protonation by hexafluorophosphoric acid to form a cationic, six-coordinate iridium(III) dihydride **22**. This reaction is an excellent example of the latent basic properties of five-coordinate d$^8$ complexes. The parallel between addition of a proton to a basic metal center and conceptional two-electron oxidation of that center is particularly clear here. This protonation should be compared with analogous reactions of five-coordinate ruthenium(0) and osmium(0) carbonyl phosphine complexes with protonic acids or Lewis acids such as mercuric halides[28] or halogens.[5,26] In all cases it is suggested that the electrophile forms a bond with the central metal in the trigonal plane. As yet neither the stereochemistry nor the question of whether such reactions are controlled by thermodynamic or kinetic parameters has been firmly established.

The elemental analysis, conductivity, and infrared spectrum of the dihydrido cation **22** are consistent with the structure formulated in Scheme II. The infrared spectrum of **22** reveals hydride stretching bands at 2180 and 2155 cm$^{-1}$ as well as carbonyl bands at 2085 and 2050 cm$^{-1}$ and $\mathrm{PF_6^-}$ absorption at 850 cm$^{-1}$. The

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(27) W. Hieber and W. Schropp, Jr., *Chem. Ber.*, **93**, 455 (1960).

(28) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962).

(29) F. G. A. Stone and P. M. Treichel, *Advan. Organometal Chem.*, 178 (1964).

(30) M. Angoletta, *Gazz. Chim. Ital.*, **90**, 1021 (1960).

(31) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).

(32) L. Vaska, *Science*, **152**, 769 (1966).

(33) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *ibid.*, **155**, 709 (1967).

(34) J. P. Collman and W. R. Roper, unpublished results.

(35) W. Hieber and H. Duchatsch, *Chem. Ber.*, **98**, 2530 (1965).

(36) M. L. H. Green, *Advan. Inorg. Chem. Radiochem.*, **6**, 115 (1965).

high frequency of the carbonyl bands is consistent with diminished electron density on the iridium(III) center. In nitrobenzene the salt **22** has a molar conductivity of 30.3 mhos which is similar to values for other 1:1 electrolytes in this solvent.[37]

A five-coordinate hydride with the same stoichiometry as **21** was obtained by treating the perchlorate analog of **22** with potassium hydroxide.[38] However, the hydride stretching frequency, 1634 $cm^{-1}$, reported for this complex is much lower than bands reported for similar four- and five-coordinate iridium(I) hydride complexes. Hydridotris(triphenylphosphine)carbonyliridium(I)[39] and similar hydrides are reported to be effective hydrogenation catalysts.[40,41] The catalytic behavior of **21** has not been tested.

Methyl iodide was found to react with a solution of the iridium anion (Scheme II). An intermediate yellow crystalline compound was isolated but not thoroughly characterized. The infrared spectrum of this metastable complex (presumably **23**) revealed two strong carbonyl bands below 2000 $cm^{-1}$ and absorption below 3000 $cm^{-1}$ characteristic of a methyl group. Carbonylation of this intermediate yielded a pale-yellow, air-stable crystalline compound formulated as an acetyl complex **24**. The infrared spectrum of **24** revealed carbonyl bands at 1975 and 1925 $cm^{-1}$ as well as an acetyl absorption at 1615 $cm^{-1}$. The latter frequency is similar to the acetyl band (1617 $cm^{-1}$) reported for $CH_3CORe(CO)_5$.[42] The nmr spectrum of **24** shows a methyl singlet at $\tau$ 7.80 (a value in accord with other acetyl complexes)[43] and a phenyl multiplet at $\tau$ 2.73. A molecular weight measurement showed the compound to be monomeric. A tentative structure having $C_{2v}$ symmetry is proposed for this acetyl derivative.

## Experimental Section

Infrared spectra were recorded in KBr disks or in solution on a Perkin-Elmer Model 237 B grating spectrophotometer or on a Perkin-Elmer Model 421 high-resolution spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A-60 spectrometer. Deuteriochloroform was used as the solvent, and tetramethylsilane ($\tau$ 10) was used as the internal reference. Carbon monoxide and nitrogen gases were separated on a Linde sieve, 13×, 20–40 mesh, column with an F & M Model 500 gas chromatograph at room temperature using helium as the carrier gas. A Perkin-Elmer Model 154 L vapor fractometer was used for the detection of bromobenzene in a benzene solution.

The tetrahydrofuran used as the solvent for the alkali metal reduction experiments was dried by refluxing in the presence of lithium aluminum hydride for 24 hr. The dried solvent was distilled under nitrogen and stored in soda pop bottles.

Group 8 metal salts were purchased from Engelhard Industries, Newark, N. J. All other chemicals and solvents used were of reagent grade quality.

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Microanalysis was performed by the Schwarzkopf Microanalytical Laboratory of Woodside, N. Y. The abbreviations used in this paper to describe relative infrared spectral intensities are v = very, w = weak, m = medium, s = strong.

**General Procedure for the Preparation of $Na[Ir(CO)_3P(C_6H_5)_3]$ (2) and $Na[Rh(CO)_2(P(C_6H_5)_3)_2]$ (8).** A quantity of sodium approximating a 20 mole ratio of sodium per mole of $M(CO)(Cl)[P(C_6H_5)_3]_2$ (M = Rh,[44] Ir[45]) was weighed in an evaporating dish under xylene. The freshly cut sodium was dropped into a dry pressure bottle previously flushed with dry nitrogen and which contained 7–8 ml of mercury (approximately a 1% amalgam). After the amalgam was formed, a solution of the desired amount of $M(Cl)(CO)[P(C_6H_5)_3]_2$ and 75 ml of dry tetrahydrofuran was added to the bottle. The bottle was then fitted to the pressure apparatus and flushed several times with carbon monoxide. The bottle was pressurized to 60 psi with carbon monoxide, heated to 60°, and stirred overnight. The bottle was then cooled and the system depressurized. After 0.5 hr a cloudy suspension in the bottle had settled and the supernatant liquid was removed with a dry syringe. The tetrahydrofuran solution was injected into a dry 300-ml single-neck flask which was flushed with nitrogen. One mole equivalent of a post transition metal halide or other reagent was added, and the solution was stirred for 15 min to 0.5 hr at room temperature. During this time the solution became cloudy, as a suspension of NaX (X = halide, CN, OAc) was formed. The solution was filtered by suction through Filter Aid, and 75 ml of methanol was added to the filtrate. The solution was evaporated to a small volume (~10–20 ml) and the precipitate was filtered. The crude product was recrystallized either from a hot benzene–methanol mixture or a warm methylene chloride–methanol mixture.

**(Triphenylphosphine)tricarbonyl(trimethyltin)iridium(I) (3a).** Trimethyltin chloride (0.51 g, 2.56 mmoles) was added to a solution of iridium anion **2** prepared from 8 ml of 1% sodium amalgam and $IrCOClL_2$ (2.0 g, 2.56 mmoles) in 75 ml of THF. Recrystallization of the pale yellow material gave 1.1 g of product (60.8%).

*Anal.* Calcd for $C_{24}H_{24}O_3PIrSn$: C, 40.98; H, 3.42; P, 4.41; mol wt, 702.8. Found: C, 41.42; H, 3.66; P, 4.46; mol wt, 718.

**(Triphenylphosphine)tricarbonyl(triphenyltin)iridium(I) (3b).** Triphenyltin chloride (0.49 g, 1.28 mmoles) was added to anion **2** prepared from sodium (0.9 g, 39 g-atoms), 7.5 ml of mercury, and $IrCOClL_2$ (1.0 g, 1.28 mmoles) in 75 ml of THF. A 0.87-g (75.8%) sample of a pale yellow material was obtained.

*Anal.* Calcd for $C_{39}H_{30}O_3PIrSn$: C, 52.66; H, 3.38; P, 3.49; mol wt, 888.8. Found: C, 52.89; H, 3.52; P, 3.26; mol wt, 896.

**Bis[(triphenylphosphine)tricarbonyliridium(I)]dimethyltin (4).** Dimethyltin dichloride (0.25 g, 1.28 mmoles) was added to a solution of anion **2** prepared from 8 ml of 1% sodium amalgam and $IrCOClL_2$ (2.0 g, 2.57 mmoles) in 100 ml of THF. The white material obtained was recrystallized several times from benzene–methanol. The yield of material was greater than 50%.

*Anal.* Calcd for $C_{44}H_{36}O_6P_2Ir_2Sn$: C, 43.04; H, 2.93; P, 5.05; mol wt, 1227. Found: C, 43.46; H, 2.99; P, 5.10; mol wt, 1250.

**Bis[(triphenylphosphine)tricarbonyliridium(I)]mercury (5).** Mercuric cyanide (0.23 g, 0.91 mmole) was added to the anion **2** prepared from 7.5 ml of 1% sodium amalgam and $IrCOClL_2$ (1.5 g, 1.93 mmoles) in 75 ml of THF. The white material that remained, after the solvent was evaporated, was washed with several large volumes of water, then ether, and finally extracted several times with hot chloroform. The white residue was used as an analytical sample.

*Anal.* Calcd for $C_{42}H_{30}HgO_6P_2Ir_2$: C, 39.40; H, 2.35; P, 4.85. Found: C, 39.62; H, 2.83; P, 4.76.

**(Triphenylphosphine)tricarbonyl(triphenylphosphinegold)iridium(I) (6).** Chlorotriphenylphosphinegold(I) (0.95 g, 1.93 mmoles) was added to anion **2** prepared from 7.5 ml of 1% sodium amalgam and $IrCOClL_2$ (1.5 g, 1.93 mmoles) in 75 ml of THF. A white product (0.93 g, 58%) was obtained.

*Anal.* Calcd for $C_{39}H_{30}AuO_3P_2Ir$: C, 46.88; H, 3.01; P, 6.21; mol wt, 998. Found: C, 46.65; H, 3.24; P, 6.13; mol wt, 990.

**(Triphenylphosphine)tricarbonyl(triphenylgermanium)iridium(I) (7).** Triphenylgermanium chloride (0.542 g, 1.6 mmoles) was added to anion **2** prepared from 7.0 ml of 1% sodium amalgam and $IrCOClL_2$ (1.25 g, 1.60 mmoles) in 75 ml of THF. The white solid (0.96 g, 71%) was recrystallized twice from benzene–methanol.

*Anal.* Calcd for $C_{39}H_{30}GeO_3PIr$: C, 55.54; H, 3.56; P, 3.68; mol wt, 842. Found: C, 55.29; H, 4.14; P, 3.72; mol wt, 877.

**Bis(triphenylphosphine)dicarbonyl(trimethyltin)rhodium(I) (10).** Trimethyltin chloride (0.360 g, 1.8 mmoles) was added to anion

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**9** prepared from 7.0 ml of 1% sodium amalgam and $RhCOClL_2$ (1.25 g, 1.81 mmoles) in 75 ml of THF. A yellow solid (900 mg, 59%) was obtained.

*Anal.* Calcd for $C_{41}H_{39}O_2P_2RhSn$: C, 58.12; H, 4.61; P, 7.32; mol wt, 847. Found: C, 58.59; H, 4.63; P, 7.19; mol wt, 722.

**Iodobis(triphenylphosphine)dicarbonyliridium(I) (18). Procedure A.** Perfluoroethyl iodide was bubbled for 2 min through a tube with a glass-fritted tip into anion **2** prepared from 7.0 ml of 1% sodium amalgam and $IrCOClL_2$ (1.25 g, 1.61 mmoles) in 75 ml of THF. The solution was stirred for 0.5 hr and then filtered. The usual work-up yielded 1.19 g (82%) of a yellow compound, mp 182–183.5° dec; ir (KBr) $\nu_{CO}$ 1995 (s) and 1935 (vs) $cm^{-1}$.

*Anal.* Calcd for $C_{38}H_{30}IO_2P_2Ir$: C, 50.65; H, 3.34; P, 6.89; I, 14.10; mol wt, 900.0. Found: C, 50.43; H, 3.40; P, 6.87; I, 14.16; mol wt, 892.

**Procedure B.** $[(C_6H_5)_3P]_2(CO)_2IrI$ was also prepared by allowing the iridium carbonyl anion to react with appropriate amounts of perfluoropropyl iodide and pentafluorophenyl iodide. The melting points and the infrared spectra of the products obtained from both reactions were identical.

**Triiodo(triphenylphosphine)dicarbonyliridium(III) (15) from Bis-[(triphenylphosphine)tricarbonyliridium(I)]mercury (5).** A 0.25-g (0.196 mmole) sample of $[(C_6H_5)_3P(CO)_3Ir]_2Hg$ was placed in a 50-ml, three-neck microflask. The flask was flushed with nitrogen, and 10 ml of benzene was added. A solution of iodine in benzene (8.0 ml of a 0.1 *M* solution) was added to the contents of the flask, and the mixture was stirred for 0.5 hr at room temperature. A precipitate settled from the solution, which was filtered. The resulting filtrate was evaporated to dryness, and the residue was recrystallized from methylene chloride–hexane to give deep red crystals; ir (KBr) $\nu$ 2110 (w), 2070 (s) $cm^{-1}$.

*Anal.* Calcd for $C_{20}H_{15}I_3O_2PIr$: C, 26.91; H, 1.68; P, 3.48; I, 42.69. Found: C, 27.11; H, 1.85; P, 3.41; I, 43.03.

**Reaction of (Triphenylphosphine)tricarbonyl(triphenyltin)iridium(I) (3b) with Iodine. A. The Preparation of Triiodo(triphenylphosphine)dicarbonyliridium(III) (15).** A 250-mg (10.28 mmoles) sample of $(C_6H_5)_3P(CO)_3IrSn(C_6H_5)_3$ was dissolved in 3 ml of tetrahydrofuran in a 50-ml, single-neck flask. The flask was flushed with nitrogen. To the solution was added 5.63 ml of a 0.1 *M* solution of iodine in tetrahydrofuran. The solution was stirred for 0.5 hr under nitrogen and then evaporated to dryness. The residue was extracted with several portions of hot hexane. The combined hexane extracts were evaporated to dryness, and the residue was recrystallized in a minimum of hot hexane. After standing several hours in the cold, 32.0 mg of triphenyltin iodide was obtained, mp 121°.

The deep red residue remaining after the initial extraction with hot hexane was recrystallized from methylene chloride–hexane. The deep red crystalline product was nonconducting in nitrobenzene; ir (KBr) $\nu_{CO}$ 2115 (m), 2075 (s) $cm^{-1}$. (These spectral features are identical with those of the product obtained from the reaction of iodine with bis[(triphenylphosphine)tricarbonyliridium(I)]mercury.)

**B. Gas-Buret Analysis of the Reaction between (Triphenylphosphine)tricarbonyl(triphenyltin)iridium(I) and Iodine.** A vial containing 200 mg (0.225 mmole) of $(C_6H_5)_3P(CO)_3IrSn(C_6H_5)_3$ was placed in a 125-ml flask which contained 0.45 mmole of iodine dissolved in 15 ml of chlorobenzene. The flask was capped with a rubber stopper, which in turn was connected to a gas buret. The vial was tipped and the flask was shaken to allow thorough mixing of the contents. During the course of the reaction, 5.08 ml of carbon monoxide (corresponding to 0.208 mmole at standard conditions) was evolved.

**Tribromodicarbonyl(triphenylphosphine)iridium(III) (16) from (Triphenylphosphine)tricarbonyl(triphenyltin)iridium(I) (3b).** A sample of $(C_6H_5)_3P(CO)_3IrSn(C_6H_5)_3$ was placed in a 50-ml, three-neck flask, which was flushed with nitrogen. A 0.1 *M* solution of bromine in benzene (11.50 ml) was added to the flask and the contents were stirred under nitrogen for 0.5 hr at room temperature.

Bromobenzene was shown to be present in the reaction solution by injecting a 20-ml portion of the solution into a 2% Carbowax on firebrick column at 159°. The bromobenzene in the reaction solution had the same retention time as a known sample.

After the vpc analysis was complete, the solid precipitate was collected on a filter and washed with hexane. This material was recrystallized from methylene chloride–hexane; ir (KBr) $\nu_{CO}$ 2070 (s) $cm^{-1}$.

*Anal.* Calcd for $C_{20}H_{15}Br_3O_2PIr$: C, 32.00; H, 2.00; Br, 31.96; P, 4.12. Found: C, 32.25; H, 2.24; Br, 33.45; P, 4.27.

**Hydridobis(triphenylphosphine)dicarbonyliridium(I) (21).** Glacial acetic acid (0.1 ml) was added to anion **2** prepared from 7.0 ml of sodium amalgam and $IrCOClL_2$ (1.0 g, 1.28 mmoles) in 75 ml of THF. After stirring for 0.5 hr the solution was worked up in the usual fashion. The yellow solid was recrystallized twice from methylene chloride–hexane to give 0.78 g (78.9%) of pale yellow needles: ir (KBr) $\nu_{M-H}$ 2050 (m); $\nu_{M-CO}$ 1960 (s), 1915 (s) $cm^{-1}$; ir ($CHCl_3$) $\nu_{M-H}$ 2080 (s) $cm^{-1}$.

*Anal.* Calcd for $C_{38}H_{31}O_2P_2Ir$: C, 58.98; H, 4.01; P, 8.02; mol wt, 773.2. Found: C, 58.43; H, 4.07; P, 7.75; mol wt, 811.

**Deuteridobis(triphenylphosphine)dicarbonyliridium(I).** A sample (100–150 mg) of $[(C_6H_5)_3P]_2(CO)_2IrH$ was placed in a 50-ml flask which was flushed with nitrogen. To the hydride was added a solution containing 4.0 ml of tetrahydrofuran, 5.0 ml of deuterium oxide, and 0.1 ml of deuteriopropanoic acid. The solution was stirred for 3–4 hr while under a nitrogen atmosphere. After the alloted time, 10 ml of deuterium oxide was added to the solution to precipitate the deuteride complex. The solution was filtered under nitrogen using a dry Schlenk tube. The residue was collected and returned to the same 50-ml flask used earlier. The exchange process was repeated for another 3–4-hr period. The reaction was worked up in the same manner. The precipitate that was collected was washed with a small amount of anhydrous diethyl ether and dried for several minutes *in vacuo* over phosphorus pentoxide.

Several milligrams of the deuteride were dissolved in 1 ml of dry chloroform, and an infrared spectrum was taken of the solution. The hydride band at 2080 $cm^{-1}$ was absent, but metal carbonyl bands appeared at 2000 and 1935 $cm^{-1}$.

**Dihydridobis(triphenylphosphine)dicarbonyliridium(I) Hexafluorophosphate (22).** Five drops of concentrated hexafluorophosphoric acid was added to a solution of 250 mg of $Ir(CO)_2HL_2$ in 10 ml of absolute ethanol. After stirring for 1 hr at room temperature, a cloudy suspension was present. The solution was filtered and the filtrate was evaporated to dryness. The crude product was twice recrystallized from boiling, absolute ethanol and yellow crystals of the salt forming upon cooling: ir (KBr) $\nu_{Ir-H}$ 2180 (s), sh 2155 (m) $cm^{-1}$; $\nu_{CO}$ 2085 (s), 2050 (vs); $\nu_{PF_6^-}$ 850 (vs) $cm^{-1}$.

*Anal.* Calcd for $C_{38}H_{32}F_6O_2P_3Ir$: C, 49.56; H, 3.48; P, 10.12; F, 12.39. Found: C, 49.72; H, 3.61; P, 10.01; F, 12.56.

**Acetylbis(triphenylphosphine)dicarbonyliridium(I) (24).** A 1.25-g (1.6 mmoles) quantity of $[(C_6H_5)_3P]_2(CO)(Cl)Ir$ in 75 ml of dry tetrahydrofuran was reduced by 7.0 ml of a 1% sodium amalgam in a pressure bottle. A stoichiometric amount of methyl iodide (0.23 g or 0.10 ml) was added and the solution was stirred for 15 min. The solution was transferred to a pressure bottle and heated to 50–60° for several hours under 50 psi of carbon monoxide The solution was cooled and filtered by suction through Celite filter aid. The filtrate was evaporated to dryness and the residue recrystallized from methylene chloride–methanol. A 1.0-g (76.9%) yield of product was obtained.

An alternative method involves evaporating the tetrahydrofuran solvent, after the anion has been allowed to react with methyl iodide, and suspending the yellow residue in 20 ml of ethanol. The suspension is warmed in a pressure bottle from 50 to 60° under 50 psi of carbon monoxide for several hours. After cooling, the suspension is filtered, and the resulting white residue is recrystallized from methylene chloride–methanol.

The nmr spectrum revealed a phenyl multiplet centered at $\tau$ 2.63 (33 protons) and a methyl singlet at $\tau$ 7.80 (3 protons): ir (KBr) $\nu_{C-H}$ 2950 (vw), 2905 (w), 2830 (vw); $\nu_{M-CO}$ 1975 (vs), 1925 (vs); $\nu_{CH_3CO}$ 1615 (s); $\nu_{C-H}$ 920 (w) $cm^{-1}$.

*Anal.* Calcd for $C_{40}H_{33}O_3P_2Ir$: C, 58.82; H, 4.04; P, 7.65; mol wt, 815.2. Found: C, 59.30; H, 4.19; P, 7.45; mol wt, 765.

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