electronic properties owing to the developing carbon–oxygen bond in the transition state.

The apparent stability differences between the carbamic acid complex intermediates (I) can also be rationalized by the π-bonding considerations. The amide species $(M'-\ddot{N}H_2)^{2+}$ generated by loss of CO_2H^+ or CO_2 from I or its conjugate base (eq 9 and 10) may very likely be more stable for $M' = Ru(NH_3)_5{}^{3+}$ than for $M' = Rh(NH_3)_5{}^{3+}$. In support, the rate[15] of base-catalyzed H–D exchange in D_2O of the $Ru(NH_3)_6{}^{3+}$ ammonia proton is about 3000 times greater than for those of $Rh(NH_3)_6{}^{3+}$. These reactions, no doubt, also go through intermediates similar to the amide complex $(M'-\ddot{N}H_2)$, and the rate differences suggest special stability for the ruthenium(III)–amide species.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Rhodium(I) and Iridium(I) Complexes with 1,1,1-Tris(diphenylphosphinomethyl)ethane

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Rhodium(I) and iridium(I) complexes of the tripodal ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, TDPME, of the type MCl(CO)(TDPME) were synthesized. The iridium(I) complex appears to be five-coordinate in the solid state but to be capable of dissociating a phosphine ligand in solution. The rhodium(I) complex is apparently a mixture of four- and five-coordinate isomers (with TDPME as either a bidentate or a tridentate ligand) both in the solid state and in solution. The existence of a facile equilibrium between four- and five-coordinate configurations of the rhodium(I) and iridium(I) complexes in solution is suggested by their rapid reaction with carbon monoxide to form dicarbonyl species. Reactions with oxygen, sulfur dioxide–oxygen, and *p*-nitrobenzoyl azide which yield (bidentate) carbonato, sulfato, and isocyanato complexes have been examined. The TDPME complexes differ significantly in reactivity from the rhodium(I) and iridium(I) complexes, *trans*-$MCl(CO)L_2$, from which they are derived. A five-coordinate d^8 iridium(I) complex with azido and carbonyl ligands in adjacent coordination sites was synthesized and found to be stable.

Introduction

Recently attention was called to a broad class of atom-transfer redox reactions which could be promoted by a metal which held both oxidant and reductant in cis positions of the coordination sphere.[2,3] Thermodynamically favorable processes between kinetically inert reactants might be facilitated with the incorporation of the potential reactants in adjacent coordination sites. Significant reactions in this group include those in which the reductant is a gas (carbon monoxide, sulfur dioxide, nitrogen oxides) and the oxidant is molecular oxygen. Stoichiometric reactions of this type have been reported from this and other laboratories.[2-6]

Although numerous examples of atom-transfer redox reactions have been reported, our knowledge of the scope and limitation of the various reactions is almost totally empirical. Yet to be established is whether or not coordination at adjacent sites is in itself sufficient to provoke a reaction. Incorporating a tridentate ligand in a d^6 or d^8 metal complex would require the other ligands in the coordination sphere to be cis to each other and thus might facilitate reactions of this type.

The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, **1**, TDPME, has been employed in several metal complex systems since it was first reported in 1962.[7-17] The geometry of the ligand is such that it can occupy three facial sites on a tetrahedron, trigonal bipyramid, square pyramid, pentagonal pyramid, or octahedron but cannot coordinate to three positions of a square plane or three meridial sites of a polyhedron. By occupying three sites of the coordination sphere, the steric relationship of the remaining ligands is often fixed. The situation is complicated if one of the phosphine groups of TDPME is not coordinated[7,9,14,15,17] or if two metals are bridged by a single TDPME ligand.[13,16] Davis and Fergusson have recently isolated and characterized two Re^{V}TDPME complexes of the same stoichiometry, one in which TDPME serves as a tridentate ligand and the other in which it serves as a bidentate ligand.[17a] As a

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[1] Visiting Scholar, Stanford University, 1968–1969.

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[15] R. B. King, L. W. Houk, and K. H. Pannell, *ibid.*, **8**, 1042 (1969).

[16] R. B. King and A. Efraty, *ibid.*, **8**, 2374 (1969).

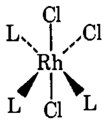
[17] (a) R. Davis and J. E. Fergusson, *Inorg. Chim. Acta*, **4**, 17 (1970); (b) R. Davis and J. E. Fergusson, *ibid.*, **4**, 23 (1970).

$$\underset{\mathbf{1}}{CH_3C[CH_2P(C_6H_5)_2]_3}$$

consequence of its tridentate character and specific geometry, complexes with degrees of substitution and stereochemistry not otherwise attainable with three unidentate ligands may be realized. TDPME reacts with nickel carbonyl at 20° to replace three CO ligands yielding Ni(CO)(TDPME); in contrast with unidentate triphenylphosphine only two CO ligands are replaced (eq 1).[11,18]

$$Ni(P(C_6H_5)_3)_2(CO)_2 + P(C_6H_5)_3 \overset{210°}{\not\longrightarrow} Ni(P(C_6H_5)_3)_3(CO) + CO \quad (1)$$

The complex $RhCl_3L_3$ (L = $(C_2H_5)_3P$, $(C_3H_7)_3P$, $(C_4H_9)_3P$, $(C_6H_5)_2CH_3P$, $(C_2H_5)_2(C_6H_5)P$, and $C_2H_5(C_6H_5)_2P$), derived from $RhCl_3$ and the appropriate ligand, has the mer configuration **2**.[19] TDPME clearly forces the fac configuration on complex **3**.



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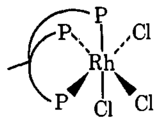
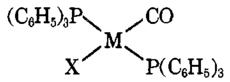


3

We report here a study of the complexes formed upon treatment of $IrCl(CO)L_2$, $IrN_3(CO)L_2$, and $RhCl(CO)L_2$ (L = $P(C_6H_5)_3$) with the tripodal ligand TDPME and their participation in several atom transfer redox reactions.

Results and Discussion

Chlorocarbonyl-1,1,1-tris(diphenylphosphinomethyl)ethaneiridium(I), IrCl(CO)(TDPME).—A benzene solution of $IrCl(CO)(P(C_6H_5)_3)_2$, **4**, when treated with an equimolar amount of TDPME, yielded a bright orange, air-sensitive powder which had an elemental analysis and molecular weight consistent with replacement of the two triphenylphosphine ligands by TDPME. The carbonyl absorption (KBr), 1900 cm^{-1}, rather low for carbonyl bonded to iridium(I), is in accord with the higher electron density expected at the metal center if all three phosphine groups are coordinated to iridium (as in structure **5a**). The isomeric structure **5b**, in which iridium(I) is four-coordinate and TDPME behaves as a bidentate ligand, would be expected to exhibit a carbonyl band above 1960 cm^{-1}. The carbonyl absorption of **4** appears at 1960 cm^{-1}; placing the carbonyl trans to a strong-field ligand such as phosphine should raise the carbonyl frequency. The trigonal-bipyramidal structure **5a** is thus tentatively assigned. The strong π acid CO ligand has tentatively been assigned to the equatorial plane because of the better π bonding in that position.



4, M = Ir, X = Cl
9, M = Rh, X = Cl
27, M = Ir, X = N_3

In contrast to the apparent behavior of TDPME, the four-coordinate carbonyl complex **4** fails to react with excess triphenylphosphine. The four-coordinate complex **6**, with nonchelated phosphines, combines with carbon monoxide but dissociates a phosphine ligand in the process (eq 2).[20]

$$\underset{\mathbf{4}}{IrCl(CO)(P(C_6H_5)_3)_2} + P(C_6H_5)_3 \not\rightleftharpoons \underset{\mathbf{6}}{IrCl(P(C_6H_5)_3)_3} + CO \quad (2)$$

A question arises as to whether the third phosphine group in **5a** is tightly bound or instead a facile equilibrium exists between four- and five-coordinate configurations (with the five-coordinate configuration favored). A saturated five-coordinate iridium(I) complex would not be expected to react rapidly with oxygen (as observed) unless it readily develops a vacant coordinate site. For example, the four-coordinate iridium(I) complex **4** reacts with molecular oxygen but the isoelectronic five-coordinate osmium(0) complex $Os(CO)_3(P(C_6H_5)_3)_2$ is inert.[6]

In solution, the carbonyl absorption of **5** is shifted only to 1912 cm^{-1} (CH_2Cl_2); thus it is unlikely that there is a significant change in the dominant coordination number. A methylene chloride solution of **5** is rapidly and irreversibly discolored when saturated with carbon monoxide, yielding a new complex with carbonyl absorptions at 2045 and 1970 cm^{-1} (CH_2Cl_2). Structure **7**, was ruled out for the dicarbonyl complex, when no metal–chlorine stretching frequency was located in the infrared spectrum and when the postulated free phosphine failed to oxidize on treatment with cumene hydroperoxide. The alternate structure, **8**, is supported by conductance values in the range reported for uni-univalent electrolytes. The tetraphenylborate salt has been isolated on treating **8** with sodium tetraphenylborate.

The reaction of **5** with carbon monoxide could be explained by dissociation of the third phosphine group to form a four-coordinate iridium(I) species, **5b**, which would rapidly take up another molecule of carbon monoxide. A complex of structure **7** is a likely (even if short-lived) intermediate in the formation of **8**; a free phosphine is available to assist with the displacement of chloride. Vaska's complex, **4**, is known to coordinate a second molecule of carbon monoxide although the five-coordinate adduct (ν_{CO} 1985 and 1935 cm^{-1}) is only stable under a pressure of carbon monoxide.[21] The higher frequency carbonyl absorptions of **8** are in accord with the proposed positive charge on the metal (Scheme I).

Chlorocarbonyl-1,1,1-tris(diphenylphosphinomethyl)ethanerhodium(I), RhCl(CO)(TDPME).—Treatment of either chlorocarbonylrhodium(I) dimer, $[RhCl(CO)_2]_2$, or $RhCl(CO)(P(C_6H_5)_3)_2$, **9**, in benzene solution with 1 equiv of TDPME per rhodium yields an air-sensitive, red-brown powder which exhibits two carbonyl bands (KBr) 2005 (m) and 1915 cm^{-1} (s). Recrystallization of the red-brown powder did not change the ratio of the two bands significantly. The molecular weight, elemental analyses, and conductance measurements are consistent with a nonelectrolyte of the formula RhCl(CO)(TDPME).

The two infrared carbonyl absorptions might be explained by a mixture of two trigonal-bipyramidal con-

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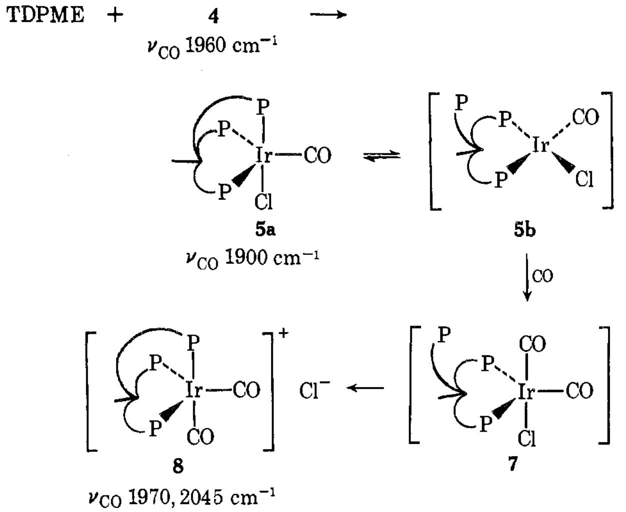
[18] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[19] J. Chatt, N. P. Johnson, and B. L. Shaw, *ibid.*, 2508 (1964).

[20] M. A. Bennett and D. A. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

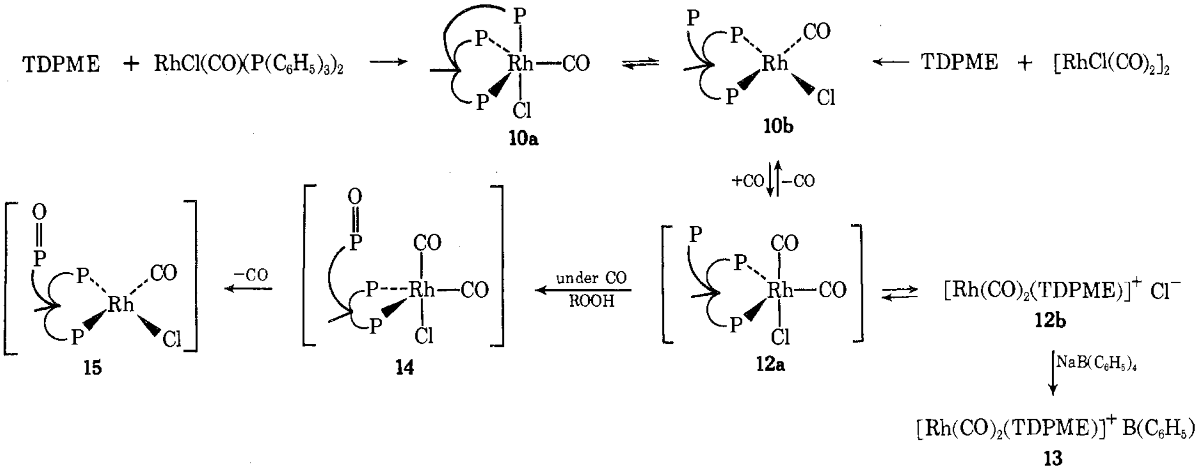
[21] L. Vaska, *Science*, **152**, 769 (1966).

Scheme I

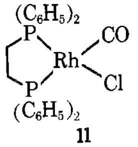


figurations (with axial and equatorial carbonyl ligands) or, alternatively, by a mixture of four- and five-coordinate rhodium(I) complexes in equilibrium (Scheme II). A facile equilibrium between four- and five-coordinate isomers would preclude separation of one isomer from the other, but characterization of the system might be aided by forcing the proposed equilibrium to one side or the other. This might be accomplished by "tying up" the free phosphine group and forcing the equilibrium to the right (Scheme II).

Scheme II



The carbonyl frequencies observed are in accord with those expected for structures such as **10a** and **10b**. Hieber has reported a ν_{CO} of 2010 cm^{-1} (CH$_2$Cl$_2$) for the 1,2-bis(diphenylphosphino)ethane complex **11** which is structurally similar to **10b**.[22] While no models for **10a** are known, the carbonyl absorption would be expected to appear at lower frequency than the absorptions for the rhodium(I) complexes **9** (1960 cm^{-1})[23]

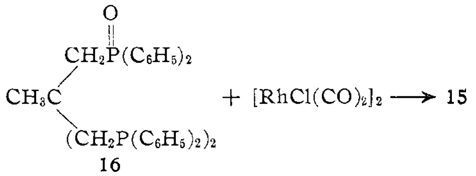


11

or **11** due to softening of the metal by the third phosphine.

The chemistry outlined in Scheme II supports our contention that RhCl(CO)(TDPME) exists as a mixture of four- and five-coordinate forms, **10a** and **10b**. Conversion of **10** to the bis-carbonyl complex **12** occurs reversibly and leaves one phosphine group on TDPME uncoordinated. Conductance measurements indicate complex **12** is a uni-univalent electrolyte; it can be converted to and isolated as the tetraphenylborate salt **13**. The uncoordinated phosphine on **12** can be oxidized using cumene hydroperoxide in methylene chloride solution (under carbon monoxide atomsphere) without oxidation of the coordinatively saturated metal. The product **14** exhibits carbonyl bands at 2050 and 1995 cm^{-1} (CH$_2$Cl$_2$) unchanged from those in **12**, but solutions of **14** exhibit phosphine oxide bands (1185, 1115, and 565 cm^{-1}). Sweeping argon through a solution of **14** yielded a new complex **15** which exhibits a single carbonyl band at 2015 cm^{-1} (CH$_2$Cl$_2$) which compares with the 2015 cm^{-1} (CH$_2$Cl$_2$) observed for **10** and is assigned to the related structure **10b**. The $\nu_{P=O}$ bands in the oxidized free ligand **16** are identical with those in complexes **14** and **15** suggesting that the phosphine oxide in **15** has little or no tendency to coordinate, a fact which is understandable on electronic and steric grounds.

An independent synthesis of **15** was achieved by treating the monoxide of TDPME, 16, with the rhodium(I) carbonyl chloride dimer (eq 3). Complex **15**



$$\mathrm{CH_3C}\begin{cases}\mathrm{CH_2\overset{O}{\overset{\|}{P}}(C_6H_5)_2} \\ \mathrm{(CH_2P(C_6H_5)_2)_2}\end{cases} + [\mathrm{RhCl(CO)_2}]_2 \longrightarrow \mathbf{15} \qquad (3)$$

16

was not isolated from solution in pure form *via* the reactions outlined in Scheme II but was contaminated with varying amounts of a material (ν_{CO} 1960–1980 cm^{-1}) which is likely a polymer similar to that observed with 1,2-bis(diphenylphosphino)ethane complexes of rhodium(I).[22] Complex **15** does not react with carbon monoxide under ambient conditions, a fact that may indicate free phosphine is necessary to assist with the expulsion of chloride (conversion of **12a** to **12b**). Complexes **14** and **15** are apparently uncharged species as indicated by their failure to form tetraphenylborates.

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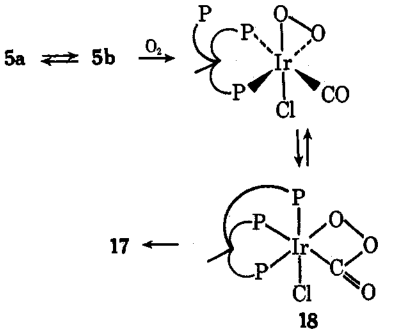
[22] W. Hieber and R. Kummer, *Chem. Ber.*, **100**, 148 (1967).

[23] D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y. ,1968, p 154.

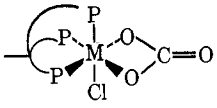
Reactions of IrCl(CO)(TDPME).—The iridium TDPME complex **5** reacts with oxygen both in the solid state and in solution. Based on the behavior of the four-coordinate iridium(I) complex **4** with oxygen, we propose that **5** adds molecular oxygen (Scheme III) *via* the four-coordinate form **5b**. Complex **4** forms a 1:1 adduct with molecular oxygen which is stable.[24] The reaction with carbon monoxide described earlier implies the existence of a facile equilibrium between the saturated and unsaturated isomers, **5a** and **5b**; and the four-coordinate unsaturated isomer should be kinetically more reactive. The oxygen adduct of **5b** would differ from that of **4** in that the former possesses cis phosphine groups and a strongly reducing free ligand in proximity to the metal center.

SCHEME III
A POSSIBLE MECHANISM FOR THE REACTION OF
IrCl(CO)(TDPME) WITH OXYGEN

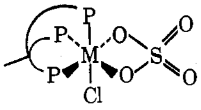


18

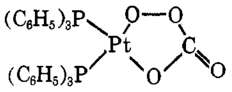
The product isolated from the reaction of **5** with molecular oxygen, an air-stable white crystalline material with carbonate absorption bands in the infrared spectrum at 1665 and 1620 cm^{-1}, has been tentatively assigned structure **17**. The disappearance of **5**, followed through changes in the infrared spectrum, is slow in the reaction with oxygen when compared to the reaction with carbon monoxide. Since no new bands were observed in the carbonyl region, it appears unlikely that the oxygen adduct of **5** has a significant lifetime. Once formed, the oxygen adduct may rearrange to carbonate with assistance from a nucleophile (the free phosphine group). Examples of nucleophilic assistance to ligand migration reactions are certainly known.[25] A perester-like complex such as **18** is a reasonable intermediate in light of the recent isolation of peroxycarbonate **19**[26] and pseudoozonide **20**.[27]



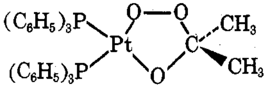
17, M = Ir
24, M = Rh



21, M = Ir
25, M = Rh



19

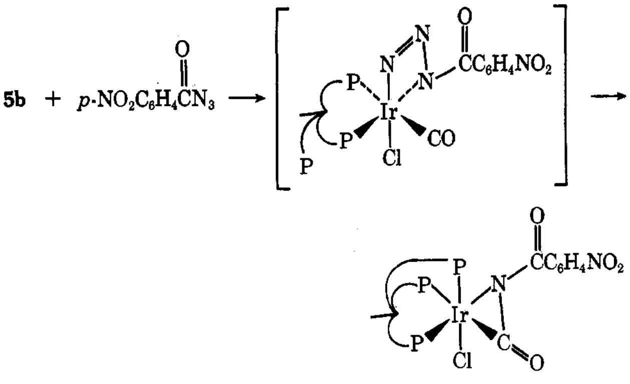


20

Stoichiometric autoxidations of sulfur dioxide to coordinated sulfate have been found to take place in the coordination sphere of group VIII metals having both d^8 and d^{10} configurations. Sulfato complexes may arise from treatment of a molecular oxygen complex with sulfur dioxide and in some case by treatment of a sulfur dioxide complex with oxygen.[4a–c,5] The well-known sulfur dioxide adducts of **4** and **9** are inert to oxygen although the oxygen adduct of **4** reacts with sulfur dioxide to form the sulfato complex.[5] It is thus noteworthy that the sulfur dioxide adduct of complex **5** observed in solution (ν_{CO} 2090 cm^{-1}) reacts with oxygen to form a sulfato complex (eq 4). The infrared spectrum (1255, 1145, 1070, 895 cm^{-1}) is consistent with that of a bidentate sulfate,[28] and structure **21** is tentatively assigned to the product.

$$\mathbf{5} + SO_2 \longrightarrow IrCl(CO)(SO_2)(TDPME) \xrightarrow{O_2} \mathbf{21} \qquad (4)$$

Earlier the coordinatively unsaturated iridium carbonyl **4** was found to react with aryl and acyl azides affording coordinated dinitrogen complexes and free isocyanates.[29] In the presence of a hydroxylic cosolvent such as ethanol the free acyl isocyanate is very rapidly trapped, but in the absence of a hydroxylic cosolvent the acyl isocyanate replaces molecular nitrogen in the coordination sphere. The TDPME iridium complex **5** reacts with *p*-nitrobenzoyl azide expelling molecular nitrogen and forming a new complex **22** whose structure is assigned on the similarity of its infrared spectrum to those of the acyl isocyanate complexes described earlier.[30] Methanol and ethanol as cosolvents fail to prevent formation of the isocyanate complex, indicating that the acyl isocyanate does not leave the coordination sphere during the course of the reaction. It seems likely that similar intermediates are formed in reactions of **4** and **5b** with acyl azides but the dangling uncoordinated phosphine in **5b** accounts for the difference in products observed for the two reactions (eq 5).



22

Both four- and five-coordinate d^8 metal complexes undergo oxidative addition reactions. Five-coordinate complexes can react either by prior dissociation of a neutral ligand (and thus react as four-coordinate unsaturated complexes) or by stepwise addition of the addendum with the second step involving irreversible

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[24] L. Vaska, *Science*, **140**, 809 (1963).

[25] *Cf.* P. Uguagliati, A. Palazzi, G. Deganello, and U. Belluco, *Inorg. Chem.*, **9**, 724 (1970).

[26] B. J. Hayward, D. M. Blake, C. J. Nyman, and G. Wilkinson, *Chem. Commun.*, 987 (1969); *J. Amer. Chem. Soc.*, **92**, 5873 (1970).

[27] R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968).

[28] See ref 6 for a discussion of the infrared spectra of bidentate and monodentate sulfates.

[29] J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, **90**, 5430 (1968).

[30] F. D. Vastine, Ph.D. Thesis, University of North Carolina, 1967.

loss of a neutral ligand.[31] Complex **5** reacts with molecular chlorine to yield the trichloroiridium(III) complex **23**, $IrCl_3(TDPME)$, with loss of carbon monoxide. In view of the results described above, it seems probable that oxidative addition occurs to the four-coordinate unsaturated isomer **5b** which should be kinetically more reactive. In solution **5** was very reactive toward a number of addenda (*e.g.*, HCl, CH_3I, HN_3, $C_6H_5SO_2Cl$, Cl_2) as evidenced by a rapid fading of the orange-red color of **5** and the disappearance of the 1900-cm^{-1} carbonyl band, but tractable products were seldom obtained. The infrared spectrum of the products often indicated the presence of more than one substance. The free phosphine of **5b** is a reactive nucleophile to the substrates mentioned above and thus **5b** has two reactive sites. Others[10,14,15,17] have noted lower than calculated carbon analyses for TDPME complexes. We observed low carbon analyses even when V_2O_5 or WO_3 was added to promote complete combustion.[16] The problem seems more acute in the presence of sulfur.

Reactions of RhCl(CO)(TDPME).—The mixture of four- and five-coordinate rhodium(I) complexes **10** also reacts with oxygen both in the solid state and in solution. Unlike the iridium case, the carbonato complex formed with rhodium is unstable. Carbonate formation as observed in the infrared spectrum (KBr) (1640 (m, br) and 1614 cm^{-1} (s, br)) is accompanied by the appearance of phosphine oxide bands (1185, 1112, and 556 cm^{-1}). Carbon dioxide was evolved during the course of the reaction. Loss of carbon dioxide from the carbonate, tentatively assigned structure **24**, may leave behind a metal oxide species which would be a potent kinetic oxidizing agent and which would readily oxidize one of the phosphine groups.

In solution the rhodium(I) complex **10** reacts with sulfur dioxide to yield a new complex which (unlike its iridium analog) has lost carbon monoxide (eq 6). The elemental analysis and molecular weight are most consistent with a 1:1 adduct with sulfur dioxide although the product is not homogeneous. The new infrared absorptions (1270, 1150, 1022, and 560 cm^{-1}) are compatible with a sulfur dioxide complex.[5,32] Treatment of this sulfur dioxide adduct with oxygen afforded a new complex for which structure **25** is proposed (eq 6).

$$\mathrm{RhCl(CO)(TDPME)} \xrightarrow[-\mathrm{CO}]{+\mathrm{SO_2}} \mathrm{RhCl(SO)_2(TDPME)} \xrightarrow{\mathrm{O_2}} \mathbf{25} \qquad (6)$$

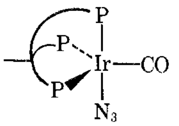
The rhodium(III)–sulfato complex appears to be less stable than its iridium(III) counterpart and as isolated contained strong phosphine oxide infrared absorptions. The four infrared peaks of **25** in the 1300–850-cm^{-1} region are consistent with a bidentate sulfato ligand.[28]

Treatment of **10** with *p*-nitrobenzoyl azide gave rise to the rapid production of nitrogen gas and a new complex analogous to the isocyanato complex obtained from **5**. The molecular weight and elemental analyses agree with the proposed formulation $RhCl(p\text{-}NO_2C_6H_4CONCO)(TDPME)$, **26**. The infrared spectrum is similar to that reported earlier for rhodium(III) complexes containing a bidentate isocyanato ligand.[29,30] Ethanol and methanol as cosolvents do not inhibit the formation of **26**.

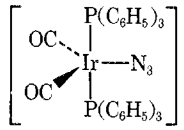
We would expect the unsaturated four-coordinate complex **10b** to be quite reactive to oxidative addition. An example is the addition of 1 equiv of hydrogen chloride to **10** to give rise to a complex which has lost carbon monoxide. The rhodium(III)–hydride stretching frequency appears in the infrared spectrum at 2030 cm^{-1}, and the molecular weight and elemental analyses agree with the formulation $RhCl_2H(TDPME)$. Although **10** reacts with a number of addenda, few result in tractable products.

Azidocarbonyl-1,1,1-tris(diphenylphosphinomethyl)ethaneiridium(I), $IrN_3(CO)(TDPME)$.—When the azido complex **27** is treated with an equimolar amount of TDPME, an air-sensitive complex can be isolated which contains new infrared absorptions at 2040 (vs) and 1900 cm^{-1} (s) attributable to the azide asymmetric stretch and carbonyl stretch, respectively. Both bands appear at lower frequency for this new complex, **28**, than for complex **27**. The low-frequency carbonyl absorption of **28** implies that all three phosphine groups of the TDPME ligand are coordinated.

The stability of **28**, with carbonyl and azido ligands occupying adjacent coordination sites on iridium(I), is noteworthy. When **27** or its rhodium(I) analog is treated with excess carbon monoxide, molecular nitrogen is liberated and a four-coordinate isocyanato complex is formed.[2,33] A reasonable hypothesis is that the initial step of the reaction involves coordination of a second carbonyl ligand to form a five-coordinate iridium(I) complex such as **29** with carbonyl and azido ligands in adjacent coordination sites. Stable d^6 metal complexes have been isolated with carbonyl and azido ligands in cis coordination sites,[2] but **28** is to our knowledge the first case of a stable d^8 metal complex in which the two potential reactants occupy adjacent coordination sites. The carbonyl and azido ligands of **28** are likely to reside in equatorial and axial coordination sites, respectively, which may be pertinent to the observed stability. The bis-carbonyl complex **29** is likely to have its two bulky phosphine ligands located in the axial coordination sites leaving the carbonyl and azido ligands in the equatorial plane.



28



29

That complex **28** also contains a labile phosphine ligand is implied by its rapid and irreversible reaction with carbon monoxide A new complex is formed which has three infrared peaks in the 1900–2200-cm^{-1} region: 2140 (m), 2045 (vs), and 1970 cm^{-1} (s). On exposure to air, complex **28** is oxidized to a stable carbonato complex which has an infrared spectrum very similar to that of carbonato complex **16**.

Experimental Section

General Information.—Microanalyses and molecular weight (osmometric) determinations were performed by Messrs. E. Meier and J. Consul, Stanford Microanalysis Laboratory. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer; only selected ir bands have been reported.

Preparative reactions were carried out under argon using

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[33] W. Beck and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, **6**, 169 (1967).

Schlenk-tube techniques. All solvents were purged with N_2 prior to their use. The tridentate ligand TDPME was prepared by the published procedure;[8] its ir and nmr spectra have been reported.[17a] Complexes $RhCl(CO)(P(C_6H_5)_3)_2$,[34] $IrCl(CO)(P(C_6H_5)_3)_2$,[35] $IrN_3(CO)(P(C_6H_5)_3)_2$,[36] and $[RhCl(CO)_2]_2$[37] were also prepared by published procedures.

Preparation of IrCl(CO)(TDPME).—To 0.67 mmol of $IrCl(CO)(P(C_6H_5)_3)_2$ in a Schlenk tube under argon was added 36 ml of dry benzene. To this yellow solution was added 0.68 mmol of TDPME and the solution immediately turned orange. The solution was heated with stirring to 55–60° and maintained at that temperature for 5 hr. On heating, the solution turned deep red; after several hours the color became lighter and a bright yellow-orange solid precipitated. The mixture was cooled to room temperature, 25 ml of *n*-hexane was added, and the mixture was placed in the freezer for 4 hr. The product was collected by filtration, washed with *n*-hexane, and dried (0.1 mm) to yield 560 mg (95%) of yellow-orange powder; ir spectrum (CsI): 1900 (vs), 270 cm^{-1} (w). The air-sensitive powder was stored in a desiccator under reduced pressure. The conductivity of a 10^{-3} *M* solution in nitrobenzene was 3.1 cm^2/ohm *M*.[38]

Anal. Calcd for $C_{42}H_{39}P_3IrClO$: C, 57.30; H, 4.47; Cl, 4.03; mol wt 880. Found: C, 57.73; H, 4.62; Cl, 4.07; mol wt 818 (CH_2Cl_2).

Reaction of IrCl(CO)(TDPME) with CO.—To 104 mg of IrCl(CO)(TDPME) in a Schlenk tube under argon was added 3 ml of dry CH_2Cl_2 and an orange-red solution was obtained. Solution samples were withdrawn at various stages and the ir spectra were recorded in 0.1-mm cells. The solution under argon was sampled and ν_{CO} 1912 cm^{-1} (vs) was observed. Carbon monoxide was bubbled through the solution for *ca.* 20 sec (not long enough to effect the complete color change); ν_{CO} 2045 (s), 1970 (s), and 1912 cm^{-1} (m). Then CO was bubbled through the solution until the color had faded to a pale yellow and no further color change was noted (*ca.* 2 min); ν_{CO} 2045 (s) and 1970 cm^{-1} (s). The solution was purged with argon and sampled again; ν_{CO} 2045 (s) and 1970 cm^{-1} (s). The spectrum remained unchanged even after stirring under argon for 11 hr; temperatures as high as 70° likewise failed to reverse the CO addition. Attempts to crystallize or precipitate the product from solution were unsuccessful. The solvent was evaporated *in vacuo* to a pale yellow solid which was thoroughly washed with ether and dried under reduced pressure; ir spectrum (CsI): 2035 (s) and 1955 cm^{-1} (s). The pale yellow powder appears to be air stable. The conductivity of a 10^{-3} *M* solution in nitrobenzene was 21.3 cm^2/ohm *M*, this value is at the lower end of the range generally observed for uni-univalent electrolytes.

Anal. Calcd for $C_{43}H_{39}P_3IrClO_2$: C, 56.86; H, 4.33; Cl, 3.90; mol wt 908. Found: C, 56.31; H, 4.38; Cl, 3.73; mol wt 730 (CH_2Cl_2).

When the reaction with CO was run in methanol solution and a solution of 1 equiv of sodium tetraphenylborate in a minimal amount of methanol was added, a yellow precipitate immediately deposited. The precipitate was collected by filtration and was thoroughly washed with methanol. A yellow powder was obtained; ir spectrum (KBr): 2040 (s), 1955 (s), 1575 (w), and 610 cm^{-1} (m).

Anal. Calcd for $BC_{67}H_{59}P_3IrO_2$: C, 67.5; H, 4.99. Found: C, 66.05; H, 5.08.

Preparation of RhCl(CO)(TDPME).—To a solution of 0.1 mmol of $[RhCl(CO)_2]_2$ in 2 ml of dry benzene was added 0.2 mmol of TDPME in 5 ml of benzene. Upon addition of TDPME a gas was evolved and the solution turned dark red-brown. After stirring for 20 min at room temperature, 15 ml of *n*-hexane was added slowly. The mixture was cooled overnight and then filtered under argon, and the residue was washed with *n*-hexane and dried at 0.1 mm; a red-brown powder was obtained; yield 197 mg (99%); ir spectrum (CsI): 2005 (m), 1915 (s), 272 cm^{-1} (w); conductivity (7.0) measured in 10^{-3} *M* nitrobenzene indicates the material to be virtually a nonelectrolyte.[38]

The air-sensitive powder is soluble in CH_2Cl_2 and pyridine, slightly soluble in benzene, acetonitrile, and methanol, and insoluble in toluene, acetone, and tetrachloroethylene. It reacts with $CHCl_3$. Samples recrystallized from CH_2Cl_2–*n*-hexane gave analyses with a high chlorine content suggesting complexation with CH_2Cl_2.

Anal. Calcd for $C_{42}H_{39}P_3RhOCl$: C, 63.77; H, 4.97; Cl, 4.48; P, 11.75; mol wt 791. Found: C, 63.79; H, 5.01; Cl, 4.59; P, 11.29; mol wt 840 (in CH_2Cl_2).

Using the same procedure as above, treatment of *trans*-$RhCl(CO)(P(C_6H_5)_3)_2$ with TDPME yielded a product identical with that described above.

Reaction of RhCl(CO)(TDPME) with CO.—When CO was bubbled into the dark red-brown solution of RhCl(CO)(TDPME) in CH_2Cl_2, there was a rapid fading of the color. In nitrobenzene solution the color change was accompanied by a significant increase in the conductivity (7.0 to 14.8).[38] In CH_2Cl_2 solution the color change was accompanied by a change in the carbonyl region of the ir spectrum: the 2010- and 1940-cm^{-1} bands were replaced by bands at 2060 and 1995 cm^{-1}. Bubbling N_2 or argon through the solution (with the aid of gentle heating) brought back the dark color, a decrease in intensity of the 2060- and 1995-cm^{-1} bands, and a reappearance of the 2010- and 1940-cm^{-1} bands. The cycle can be repeated, but an anomalous band appears at 1970 cm^{-1} after the sample has been in solution a while and it gradually increases in intensity.

Reaction of $RhCl(CO)_2$(TDPME) with $NaB(C_6H_5)_4$.—CO was bubbled into the rust-colored suspension of 0.1 mmol of RhCl(CO)(TDPME) in 5 ml of methanol; after 2 min a yellow solution was obtained. With the solution under a positive pressure of CO, a solution of 0.1 mmol of $NaB(C_6H_5)_4$ in 2 ml of CH_3OH was added; a yellow precipitate deposited immediately. The mixture was filtered and the precipitate was thoroughly washed with CH_3OH and dried. A yield of 79% of yellow-orange powder was obtained; ir spectrum (KBr): 2048 (s), 1975 (s), 1575 (w), 610 cm^{-1} (m).

Anal. Calcd for $C_{67}H_{59}P_3RhO_2B$: C, 72.97; H, 5.39. Found: C, 72.46; H, 5.41.

Reaction of $RhCl(CO)_2$(TDPME) with Cumene Hydroperoxide.—To 0.1 mmol of RhCl(CO)(TDPME) in a Schlenk tube (fitted with a rubber septum) under argon was added 2 ml of dry CH_2Cl_2. The atmosphere above the red-brown solution was exchanged for CO. After stirring for a few minutes under CO the color of the solution changed to yellow. After 20 min, 0.1 mmol of cumene hydroperoxide in 0.5 ml of CH_2Cl_2 was added to the yellow solution while maintaining a slight positive pressure of CO. Solution samples were withdrawn at intervals and their ir spectra were recorded in 0.1-mm cells. No color change was observed upon hydroperoxide addition. Four hours after hydroperoxide addition, the ir spectrum [ν_{CO} 2060 (vs) and 1995 cm^{-1} (vs)], contained phosphine oxide bands: 1185 (m), 1115 (m), and 565 cm^{-1} (m). Five hours later the ir spectrum indicated only a slight increase in the intensity of the phosphine oxide bands. The CO above the solution was exchanged for argon (by repeatedly evacuating and filling). The solution was heated to *ca.* 40° for 5 min and then stirred at room temperature for 1 hr; ir spectrum: ν_{CO} 2015 (vs) and 1970 cm^{-1} (m)—no band at 1940 cm^{-1}. The intensity of the 1970-cm^{-1} band varied from run to run. The argon above the solution was exchanged for CO and the ir spectrum was recorded after 1 hr: ν_{CO} 2070 (s), 2015 (sh, m), 1995 (s), 1970 cm^{-1} (sh, m). The CO atmosphere was exchanged for argon again and after 0.5 hr the ir spectrum was recorded: ν_{CO} 2015 (s) and 1970 cm^{-1} (m).

If a methanolic solution of 1 equiv of $NaB(C_6H_5)_4$ was added to the "oxidized" solution *ca.* 12 hr after hydroperoxide addition, a small amount of yellow precipitate was obtained which was identified by its ir spectrum as unoxidized $[RhCl(CO)_2(TDPME)]B(C_6H_5)_4$.

Preparation of the Monoxide of TDPME.—To 1.0 mmol of TDPME in 30 ml of acetone was added 95 μl of 30% hydrogen peroxide. After stirring 6 hr at room temperature, tlc analysis (silica gel, 1:1 C_2H_5OAc–C_6H_6) indicated the presence of approximately equal amounts of starting material and the monoxide with smaller amounts of the di- and trioxides. (Increasing the ratio of hydrogen peroxide to TDPME only increased the yield of di- and trioxides.) The solution was concentrated *in vacuo* to a viscous oil and chromatographed over silica gel. The unreacted TDPME was eluted with benzene and the monoxide with 40:60 C_2H_5OAc–C_6H_6. The monoxide (250 mg) was concentrated to a viscous oil which was crystallized with difficulty from hexane. A white powder was obtained, mp 127–128°; ir spectrum (KBr): 1185, 1112, 560 cm^{-1}; nmr spectrum (C_6D_6): 1.25 (3H, s), 2.75–2.92 (6H, m), 7.03–7.17 (20H, m), 7.40–8.03 ppm (10H, m).

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(35) J. P. Collman, C. T. Sears, Jr., and M. Kubota, *ibid.*, **11**, 101 (1968).

(36) W. Beck, W. P. Fehlhammer, P. Pollman, and H. Schachl, *Chem. Ber.*, **102**, 1979 (1969).

(37) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 211 (1965).

(38) Conductivities are reported in cm^2/ohm *M* at ambient temperature in 10^{-3} *M* nitrobenzene solutions.

Anal. Calcd for $C_{41}H_{39}P_3O$: C, 76.87; H, 6.14. Found: C, 76.95; H, 6.29.

Reaction of $[RhCl(CO)_2]_2$ with the Monoxide of TDPME.—To 0.24 mmol of the monoxide of TDPME and 0.12 mmol of rhodium chlorocarbonyl dimer in a Schlenk tube was added 8 ml of dry benzene. A gas was immediately evolved. After 15 min at room temperature, an aliquot was removed; the ir spectrum (CH_2Cl_2) showed 2015 cm^{-1} (s) as the only peak in the carbonyl region. After stirring 10 hr at room temperature, a yellow solid had precipitated. The product was collected by filtration under argon and was washed with 20 ml of *n*-hexane. A yield of 84 mg of air-stable yellow powder was obtained; ir spectrum (KBr): 2002 (s), 1180 (m), 1110 (m), 580 (m), 565 cm^{-1} (m). A second crop of 104 mg (97% total yield) was also obtained.

Anal. Calcd for $C_{42}H_{39}RhP_3O_2Cl$: C, 62.51; H, 4.87; Cl, 4.39. Found: C, 60.16; H, 4.81; Cl, 4.13.

Reaction of IrCl(CO)(TDPME) with O_2.—Air was bubbled through the orange-red solution of 0.1 mmol of IrCl(CO)(TDPME) in 3 ml of CH_2Cl_2. Solution samples were withdrawn at intervals and their ir spectra were recorded in 0.1-mm cells. As air was bubbled in, weak bands appeared at 2045 and 1970 cm^{-1}, the band at 1915 cm^{-1} diminished, and broad absorptions appeared at 1670–1650 and 1625 cm^{-1}. The spectrum recorded after 2 hr contained only a moderate intensity absorption at 1915 cm^{-1}. After 20 hr the 1915-cm^{-1} band was very weak, the ν_{CO_3} bands were of moderate intensity, and phosphine oxide bands had appeared.

If IrCl(CO)(TDPME) was exposed to air in the solid state, the 1900-cm^{-1} band disappeared and ν_{CO_3} bands at 1655 and 1620 cm^{-1} appeared. Recrystallization of a sample (which no longer showed a 1900-cm^{-1} absorption) from ethanol–*n*-hexane yielded a white microcrystalline powder; ir spectrum (CsI): 1620 (m), 1655 (m), 350 (w), 330 (w), and 290 cm^{-1} (w).

Anal. Calcd for $C_{42}H_{39}P_3IrClO_3$: C, 55.29; H, 4.31; Cl, 3.80. Found: C, 55.42; H, 4.43; Cl, 3.89.

Reaction of IrCl(CO)(TDPME) with SO_2 and O_2.—Sulfur dioxide gas was bubbled for 3 min into a solution of 300 mg of IrCl(CO)(TDPME) in 6 ml of CH_2Cl_2. The orange-red solution faded to yellow-orange almost immediately. Solution samples were withdrawn at intervals and their ir spectra were recorded in 0.1-mm KBr cells. After 40 min the original ν_{CO} at 1910 cm^{-1} had been replaced by strong band at 2090 cm^{-1}; the strongest bands in the spectrum could be attributed to free SO_2. After 12 hr, air was bubbled through the solution. The ir spectrum recorded 20 minutes later showed a greatly diminished ν_{CO} at 2090 cm^{-1}. After 2 hr, a white precipitate began to form. After 5 hr, the mixture was filtered to yield 110 mg of white powder and a second crop of 78 mg was obtained from the filtrate. The powder was recrystallized from CH_2Cl_2–*n*-hexane (it is only very sparingly soluble in CH_2Cl_2) to yield white crystals; ir spectrum (CsI): 1255 (s), 1145 (vs), 1070 (sh, w), 895 (m), 648 (s), 610 (w), and 290 cm^{-1} (w).

Anal. Calcd for $C_{41}H_{39}P_3IrClSO_4$: C, 51.93; H, 4.15; Cl, 3.73; S, 3.37. Found: C, 50.25; H, 4.17; Cl, 3.88; S, 3.40.

Reaction of IrCl(CO)(TDPME) with *p*-Nitrobenzoyl Azide.—To 0.068 mmol of IrCl(CO)(TDPME) in a Schlenk tube under argon was added 6 ml of CH_2Cl_2 and 0.5 ml of ethanol. To this solution at 0–5° 16 mg (a slight excess) of *p*-nitrobenzoyl azide was added. Stirring was continued at 0–5° for 1 hr and then at room temperature. After 5 hr 18 ml of *n*-hexane was added and the mixture was placed in the freezer overnight. The mixture was filtered under argon, and the residue was washed with *n*-hexane and dried (0.1 mm) to yield 42 mg (59%) of a salmon-colored hygroscopic powder; ir spectrum (KBr): 1620 (m), 1525 (s), 1400 (w), 1360 (m), 1340 (s), 1165 (w), 995 (s), and 870 cm^{-1} (w).

Anal. Calcd for $C_{49}H_{43}P_3IrClN_2O_4$: C, 56.35; H, 4.15; N, 2.68; Cl, 3.39. Found: C, 55.37; H, 4.12; N, 2.47; Cl, 3.49.

Reaction of IrCl(CO)(TDPME) with Cl_2.—A solution of 220 mg of IrCl(CO)(TDPME) in 15 ml of CH_2Cl_2 in a Schlenk tube under argon was saturated with Cl_2. The orange-red solution immediately turned pale yellow. After 19 hr at room temperature the yellow color still remained. The solution (under a positive pressure of argon) was heated to 60° and was then maintained at 45° for a total of 42 hr after which time a white crystalline material had precipitated. The product was collected by filtration and was recrystallized from boiling acetonitrile. Sparingly soluble white crystals were obtained; ir spectrum (CsI): no absorptions in the 1600–2900-cm^{-1} region; 300 (w) and 260 cm^{-1} (w).

Anal. Calcd for $C_{41}H_{39}P_3IrCl_3$: C, 53.34; H, 4.26; Cl, 11.52. Found: C, 52.89; H, 4.25; Cl, 11.35.

Reaction of RhCl(CO)(TDPME) with O_2.—(A) Oxygen was bubbled into a solution of 0.1 mmol of RhCl(CO)(TDPME) in 2 ml of CH_2Cl_2 until all the solvent had evaporated (20 min). The residue was a brown powder which contained a residual carbonyl absorption at 1965 cm^{-1} (w), carbonate bands at 1660–1540 cm^{-1} (m, br), and phosphine oxide bands at 1185, 1115, 560, and 540 cm^{-1}. If RhCl(CO)(TDPME) in the solid state was exposed to air for several days, its red-brown color faded and its ir spectrum changed to that described above.

(B) A 26-ml serum bottle containing 0.15 mmol of RhCl(CO)(TDPME) was flushed with O_2 until a negligible amount of N_2 was indicated by vpc (Poropak Molecular Sieve 5A columns connected in tandem). A 5-ml volume of CH_2Cl_2 was injected. Within 5 min the solution changed from red-brown to brown. Samples of gas (0.5 ml) were withdrawn and analyzed by vpc. A slow evolution of CO_2 (nearly complete after 6 hr) was observed. After 27 hr, 1 ml of methanol containing 6 drops of concentrated hydrochloric acid was added, the clear brown solution precipitated a bright yellow-orange solid, and a further quantity of CO_2 was evolved. Evaporation of the sample on the rotary evaporator and trituration with methanol gave a yellow-orange powder which was filtered and dried; ir spectrum (KBr): 2090 (w), 1180 (m), 1113 (w), 710 (m), 565 (m), and 385 cm^{-1} (w).

(C) A solution of 0.153 mmol of RhCl(CO)(TDPME) in 3 ml of CH_2Cl_2 was cooled to 0–5° and air was slowly bubbled through. Solution samples were withdrawn and their ir spectra were run in 0.1-mm cells. After 2 min, new peaks had appeared at 2050 (w) and 1600 cm^{-1} (w, br); at 20 min the carbonyl region appeared at 2050 (m), 2015 (m), 1990 (m), 1940 (w), and 1615 cm^{-1} (w, br), and phosphine oxide peaks were evident at 1185, 1112, and 556 cm^{-1}. After 1 hr, the carbonyl region appeared at 2050 (m), 2015 (w, sh), 1990 (m), 1970 (m, sh), 1615 cm^{-1} (m, br). The 2050-cm^{-1} band may be due to an oxygen adduct, or more likely the 2050- and 1995-cm^{-1} bands are due to some biscarbonyl material present as an impurity. The 1970-cm^{-1} band may be attributed to the polymer obtained if the TDPME ligand bridges two metal centers. *n*-Hexane was added to the brown solution (to the cloud point) and after 3 days at 0° a tan powder was obtained; ir spectrum (KBr): 1640 (m, br), 1616 (s, br), 1188 (w), 1112 (w), 708 (w), and 556 cm^{-1} (w).

Reaction of RhCl(CO)(TDPME) with SO_2 and with SO_2–O_2.—Sulfur dioxide gas was bubbled into a suspension of 0.15 mmol of RhCl(CO)(TDPME) in 5 ml of benzene. Within 1 min the solid dissolved and the solution faded to a pale orange color. After stirring an additional 10 min, 10 ml of ether was added, precipitating a bright yellow-orange solid. The product was filtered under N_2, washed with ether, and dried (0.1 (0.1 mm) to yield 124 mg (85%); ir spectrum (KBr): 1310 (w), 1270 (w), 1150 (m), 1022 (s), and 560 cm^{-1} (m).

Anal. Calcd for $C_{41}H_{39}P_3RhSO_2Cl$: C, 59.54; H, 4.75; Cl, 4.27; S, 3.88; mol wt 827. Found: C, 55.78; H, 4.53; Cl, 4.63; S, 3.35; mol wt 1250 (CH_2Cl_2).

If the experiment above was repeated except that, after stirring the SO_2 adduct for 10 min, O_2 was bubbled into the clear solution, a yellow-orange precipitate formed. After cooling overnight at 0° the mixture was filtered and the residue was washed with benzene and dried to yield 112 mg (91% as the monomeric sulfate) of yellow powder; ir spectrum (KBr): 1240 (m), 1138 (s), 905 (w), 875 (w), and 638 cm^{-1} (m) (also phosphine oxide bands of moderate intensity).

Anal. Calcd for $C_{41}H_{39}P_3RhClSO_4$: C, 57.32; H, 4.58; S, 3.73; Cl, 4.13; mol wt 859. Found: C, 56.83; H, 4.59; S, 3.63; Cl, 4.30; mol wt 1160 (CH_2Cl_2).

Reaction of RhCl(CO)(TDPME) with *p*-Nitrobenzoyl Azide.—The addition of *p*-nitrobenzoyl azide to 1 equiv of RhCl(CO)(TDPME) in CH_2Cl_2–methanol under argon led to the rapid and complete evolution of N_2 (<20 min, followed by vpc) and the disappearance of both starting materials (followed by ir). In a preparative run, 0.21 mmol of *p*-nitrobenzoyl azide was added to a solution of 0.20 mmol of RhCl(CO)(TDPME) in 5 ml of CH_2Cl_2–1 ml of ethanol at 0–5°. After 30 min at 0–5°, 10 ml of *n*-hexane was added which precipitated an orange powder. The precipitate was collected by filtration, washed with *n*-hexane, and dried (0.1 mm) to yield 141 mg (74%) of orange powder; ir spectrum (CsI): 1675 (m), 1635 (m), 1522 (s), 1402 (m), 1385 (m), 1342 (s), 1170 (w), 1015 (w), 872 (w), 850 (m), 660 (w), and 281 cm^{-1} (w).

Anal. Calcd for $C_{49}H_{43}P_3RhN_2O_4Cl$: C, 61.61; H, 4.54; N, 2.93; Cl, 3.71; mol wt 955. Found: C, 60.90; H, 4.52; N, 2.89; Cl, 3.71; mol wt ($CHCl_2$) 996.

Reaction of RhCl(CO)(TDPME) with HCl.—A sample of 0.1 mmol of RhCl(CO)(TDPME) was placed in a 6-ml serum bottle and flushed and evacuated with N_2; to this was added 3 ml of CH_2Cl_2. Dry HCl gas, 2.5 ml (0.103 mmol at 760 mm (25°)), was added and the red-brown color of the solution immediately faded to a bright yellow. After stirring for 1 hr at room temperature, *n*-hexane was added to the cloud point. After cooling for 12 hr at 0°, yellow microcrystals formed. These were filtered, washed with *n*-hexane, and dried (65° (0.1 mm)) to yield 47 mg (59%); ir spectrum (CsI): 2030 (w), 800 (w), 298 (w), and 286 cm^{-1} (w).

Anal. Calcd for $C_{41}H_{40}P_3RhCl_2$: C, 61.59; H, 5.04; Cl, 8.87; mol wt 799. Found: C, 61.13; H, 5.30; Cl, 8.95; mol wt (CH_2Cl_2) 815.

Reaction of RhCl(CO)(TDPME) with Cl_2.—Chlorine gas was bubbled into the red-brown suspension of 110 mg of RhCl(CO)(TDPME) in 6 ml of dry benzene. After a few minutes the solution turned yellow. After sitting at room temperature for 10 min, the suspension was filtered and the residue was washed with ether and with benzene and then dried at 65° (0.1 mm). A yellow powder was obtained; ir spectrum (CsI): no carbonyl bands, 300 (w), 288 (w), and 275 cm^{-1} (w).

Anal. Calcd for $C_{41}H_{39}P_3RhCl_3$: C, 59.05; H, 4.71; Cl 12.75. Found: C, 56.47; H, 4.55; Cl, 13.47.

Preparation of IrN_3(CO)(TDPME).—To 0.19 mmol of IrN_3(CO)$(P(C_6H_5)_3)_2$ in a Schlenk tube was added 14 ml of dry benzene. To this bright yellow solution was added 0.19 mmol of TDPME. The solution, which immediately became orange, was stirred at room temperature for *ca.* 12 hr by which time an orange solid had precipitated. A total of 20 ml of *n*-hexane was added in small aliquots and the mixture was filtered under argon. The precipitate was washed with *n*-hexane and dried (0.1 mm) to yield 147 mg (88%) of an air-sensitive orange powder; ir spectrum (KBr): 2040 (vs), 1900 (s), and 1275 cm^{-1} (w).

Anal. Calcd for $C_{42}H_{39}P_3N_3O$: C, 56.88; H, 4.43; N, 4.74. Found: C, 56.45; H, 4.43; N, 4.36.

Reaction of IrN_3(CO)(TDPME) with CO.—To 40 mg of IrN_3(CO)(TDPME) in a Schlenk tube under argon was added 1.5 ml of dry CH_2Cl_2. The argon atmosphere above the solution was exchanged for CO (by repeatedly evacuating and filling); after stirring under CO for *ca.* 5 min, the solution changed from orange to pale yellow. Solution samples were withdrawn at intervals and their ir spectra were recorded in 0.1-mm KBr cells. After 0.5 hr, the 2040 (vs) and 1905 cm^{-1} (s) bands had been replaced with new peaks at 2140 (m), 2045 (s), and 1970 cm^{-1} (s); after 4 hr the spectrum remained the same but after 17 hr a weak absorption at 2230 cm^{-1} had appeared. The CO atmosphere above the solution was exchanged for argon and the solution was heated to 70°, but no changes were observed in the ir spectrum. After stirring under CO for 17 hr, a small amount of white solid precipitated from solution. Attempts to isolate homogeneous products from this run or larger scale runs were unsuccessful. The powders obtained often contained strong isocyanate and/or carbonate bands in addition to a band at *ca.* 2040 cm^{-1} (probably azide).

Reaction of IrN_3(CO)(TDPME) with O_2.—A sample of IrN_3(CO)(TDPME) was exposed to air for several days. A pale yellow powder was obtained which was only sparingly soluble in CH_2Cl_2; ir spectrum (KBr): 2040 (vs), 1665 (s, br), 1620 (m), and 1280 cm^{-1} (w).

Anal. Calcd for $C_{42}H_{39}P_3IrN_3O_3$: C, 54.90; H, 4.28; N, 4.57. Found: C, 55.70; H, 4.44; N, 4.20.

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The Preparation of Some Cobalt Carbonyl Complexes Containing Ligand-Bridged Metal Atoms

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The complexes $LCo_2(CO)_6$, $LCo_2(CO)_4HCCC_6H_5$, ffars$Co_2(CO)_5$, $CH_3CCo_3(CO)_7$ffars, and $Co_4(CO)_8$(ffars)$_2$ are described, and ligand-bridged structures are assigned to them on the basis of their infrared spectra. The ligands L and ffars are fluorocarbon-bridged ditertiary arsines and phosphines.

Introduction

Tertiary phosphine and arsine derivatives of dicobalt octacarbonyl often exist in solution as an equilibrium mixture containing both carbonyl-bridged and nonbridged forms. As a result these species tend to have complicated infrared spectra in the carbonyl stretching region.[1] This behavior is the same as that of the parent dicobalt octacarbonyl which has been shown, from a study of the carbonyl infrared spectrum, to exist in pentane solution at room temperature as ~45% bridged form and ~55% nonbridged form.[2,3] Other tertiary phosphine derivatives of dicobalt octacarbonyl such as $[(C_6H_5)_3PCo(CO)_3]_2$ and $[(C_4H_9)_3PCo(CO)_3]_2$ exist in solution[4] and in the solid state[5] in the nonbridged form only. This may be a result of steric interaction between the very bulky organophosphine groups. Other ligands, such as 1,2-bis(diphenylphosphino)ethane, which might be expected to fix the dicobalt carbonyl moiety in a

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