$(OH_2)_2^{3+}$ seems very much out of order. Despite the presence of the azomethine groups the *trans*[14]diene ligand seems quite flexible; certainly the steric differences between the macrocyclic ligands are too small to be obvious from examination of molecular models of *cis*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ and *cis*-Co(tet*b*)$(OH_2)_2^{3+}$. A more likely hypothesis is that the presence of Co–N-(imine) bonds in the *trans*[14]diene complex stabilizes a $CoLOH_2^{3+}$ intermediate.

The kinetic stability of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$ is to be contrasted with the rapidity of reaction 1. A further and even more remarkable contrast is that Cl^- *inhibits* the *cis* → *trans* isomerization of Co(cyclam)$(OH_2)_2^{3+}$.[8] It should also be noted (1) that Co–O bond breaking should lead to *cis* → *trans* isomerization (even in the absence of Cl^-); (2) that *cis*-Co(tet*b*)$ClOH_2^{2+}$ cannot be detected as a transient in reaction 1 and has not been prepared by other methods; (3) that Co–Cl bonds are generally about as labile as Co–OH_2 bonds;[29] and (4) that *trans*-Co(tet*b*)$(OH_2)_2^{3+}$ does not seem to be an important product of reaction 1. These considerations suggest that reaction 1 may proceed by means of a nucleophilic attack of Cl^- at the organic backside of *cis*-Co(tet*b*)$(OH_2)_2^{3+}$.

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(29) Reference 23, Chapter 3.

Chlorotris(triphenylphosphine)iridium(I) and Related Complexes. Oxidative Addition Reactions and Hydrogen Abstraction from the Coordinated Ligand[1]

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Abstract: The preparation, properties, and reactions of a series of complexes of general formula $IrClL_3$ are described, where L is $(C_6H_5)_3P$, $(C_6D_5)_3P$, (*o*-$DC_6H_4)_3P$, (*p*-$FC_6H_4)_3P$, (*p*-$CH_3OC_6H_4)_3P$, (*p*-$CH_3C_6H_4)_3P$, $(C_6H_5)_3As$, and $(C_6H_5)_3Sb$. The complex $IrCl(Ph_3P)_3$ differs from the analogous rhodium compound in two principal ways: (i) triphenylphosphine is not so readily lost in solution; (ii) the reaction with hydrogen is irreversible and occurs without displacement of triphenylphosphine, so that $IrCl(Ph_3P)_3$ does not function as a homogeneous hydrogenation catalyst. Reactions with CO, PF_3, NO, and HCl are described. Reaction of $IrCl(Ph_3P)_3$ with chlorine gives initially an iridium(III) complex $IrCl_3(Ph_3P)_2$, which appears to be five-coordinate in solution, and with excess chlorine or nitrosyl chloride the iridium(IV) complex $IrCl_4(Ph_3P)_2$ is formed. This and the analogous triphenylarsine complex are characterized by far-infrared, magnetic susceptibility, and esr measurements. Metal–chlorine stretching frequencies are reported for the new compounds and used where possible to assign stereochemistries. Unlike their rhodium analogs, the iridium(I) complexes $IrClL_3$ isomerize on heating in solvents to octahedral hydrido aryls of iridium(III), the stereochemistry of which is inferred from infrared and proton nmr measurements. It is shown that the isomerization arises by transfer of one hydrogen atom from the *ortho* position of an aromatic ring of the coordinated ligand to the metal, with the formation of a metal–carbon σ bond at the *ortho* position. In the triarylphosphine series, the rate of isomerization depends on the substituent *para* to phosphorus in the order F < H < OCH_3 < CH_3. On the basis of the small kinetic isotope effect, a three-center mechanism is suggested for the hydrogen transfer. The reactions of the hydrides are generally similar to but slower than those of the parent iridium(I) complexes. Some of these reactions apparently proceed *via* the iridium(I) complex formed by return of the hydrogen to the ligand. The iridium(I)–iridium(III) tautomerism is compared with similar situations involving Fe(0)–Fe(II) and Ru(0)–Ru(II), and a brief analogy is drawn with metal-catalyzed H–D exchanges in aromatic hydrocarbons.

The ability to undergo oxidative addition reactions with a variety of simple molecules and to catalyze the homogeneous hydrogenation of olefins and acetylenes are features of a number of d^8 metal complexes, notably $IrCl(CO)(Ph_3P)_2$[3] and $RhCl(Ph_3P)_3$.[4,5] On the basis of the limited data presently available, it appears that (a) iridium(I) complexes undergo oxidative addition more readily than rhodium(I) complexes, and (b) oxidative addition is assisted by the presence of good σ-donor ligands on the metal. We therefore decided to attempt the preparation of $IrCl(Ph_3P)_3$, expecting

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(1) Preliminary communication: M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967); presented in part at the Symposium on Transition Metal Complexes of Hydrogen, Oxygen, and Nitrogen and Homogeneous Catalysis, Osaka, Japan, Sept 22, 1967.

(2) Author to whom enquiries should be addressed at the Research School of Chemistry, Australian National University, Canberra, Australia.

(3) L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, **83**, 2784 (1961).

(4) M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (London), 846 (1965).

(5) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

Table I. Analytical Data and Ir–Cl Stretching Frequencies in Complexes of General Formula $IrClL_3$[a]

Formula of complex	Color	% C		% H		% Cl/Br		% P		ν(Ir–Cl), cm^{-1}	Other bands, cm^{-1}
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
$IrCl\{(C_6H_5)_3P\}_3$	Orange	63.7	63.7	4.8	4.7	3.5	3.4	9.1	9.2[c]	282 s	420 s, 321 w, 243 w, 223 m
$IrBr\{(C_6H_5)_3P\}_3$	Red–brown	61.8	62.0	4.3	4.3	7.6	7.4				414 s, 320 w, 220 w
$IrCl\{(C_6D_5)_3P\}_3$	Orange	61.2	59.5			3.3	3.4	8.8	8.2	nm	nm
$IrCl\{(o\text{-}DC_6H_4)_3P\}_3$	Orange	63.4	62.7	3.5	5.5[b]	3.5	3.5			nm	nm
$IrCl\{(p\text{-}FC_6H_4)_3P\}_3$	Orange	55.0	55.2	3.1	3.0	3.0	3.1	7.9	7.8	283 s	430 s, 350 w, 340 w, 240 w, 233 w
$IrCl\{(p\text{-}CH_3OC_6H_4)_3P\}_3$	Orange	58.9	56.1	5.0	4.9	2.8	2.7			284 ms	445 vs, 438 vs
$IrCl\{(p\text{-}CH_3C_6H_4)_3P\}_3$	Orange	66.7	67.2	5.6	5.7	3.1	3.0			279 s	440 vs, 420 ms, 353 m
$IrCl\{(C_6H_5)_3As\}_3$	Orange–red	56.6	55.6	4.0	4.4	3.1	3.2			nm	nm
$IrCl\{(C_6H_5)_3Sb\}_3$	Red	50.4	51.4	3.5	3.9	2.8	2.6			nm	nm

[a] Abbreviations: s, strong; vs, very strong; m, medium; ms, medium strong; w, weak; nm, not measured. [b] H + D. [c] Mol wt, calcd 1015; found (C_6H_6) 800–850, ($CHCl_3$) 700–750.

that it would be more reactive than either $IrCl(CO)(Ph_3P)_2$ or $RhCl(Ph_3P)_3$ and hoping that it would be an even better homogeneous hydrogenation catalyst.

The reaction of the metal chloride in ethanol with excess triphenylphosphine, which provides an easy preparation of $RhCl(Ph_3P)_3$,[4,5] cannot be used to make $IrCl(Ph_3P)_3$, since the initially formed hydrido complex $IrHCl_2(Ph_3P)_3$,[6] unlike its rhodium analog,[7] does not readily eliminate HCl; this can only be achieved with a reagent such as $(CH_3)_3SnN(CH_3)_2$.[8] During the course of our work, the presence of $IrCl(Ph_3P)_3$ in the solution obtained by treating the nitrogen complex $IrClN_2(Ph_3P)_2$ with triphenylphosphine was suggested,[9] and later the desired complex was isolated.[10] Following our initial communication,[1] we now report the preparation and properties of a series of complexes of general formula $IrCl(ligand)_3$ and details of their isomerization to hydrido complexes of iridium(III).

Results

We[1] first isolated $IrCl(Ph_3P)_3$ by heating the 1,5-cyclooctadiene complex $[IrCl(C_8H_{12})]_2$[11] with excess triphenylphosphine in ligroin; a similar method has been used to make $RhCl(Ph_3P)_3$.[12] In the first stage of the reaction, which occurs at room temperature, the halogen bridges of the diene complex are split, giving $IrCl(C_8H_{12})(Ph_3P)$;[11] on heating, the diene is displaced and $IrCl(Ph_3P)_3$ precipitates as orange crystals. Since $[IrBr(C_8H_{12})]_2$ is unstable, an indirect method has to be used to make $IrBr(Ph_3P)_3$. On heating with lithium bromide, $IrCl(C_8H_{12})(Ph_3P)$ is converted to the corresponding bromo complex, and this, when heated with excess triphenylphosphine in ligroin, gives orange crystalline $IrBr(Ph_3P)_3$. Using triphenylarsine and triphenylstibine, the analogous diene complexes $IrCl(C_8H_{12})(Ph_3M)$ (M = As, Sb) can be obtained,[13] but the diene cannot be replaced, presumably owing to the poorer σ donor ability of these ligands compared with triphenylphosphine.

The most convenient starting point for making the complexes $IrClL_3$ (L = triarylphosphines, Ph_3As, and Ph_3Sb) is the cyclooctene complex $IrCl(C_8H_{14})_2$.[14] The olefin is smoothly displaced from this compound on stirring with excess ligand in petroleum ether (bp 60–80°) at room temperature and the products are precipitated as orange or red crystals. Table I lists the complexes prepared in this way with pertinent analytical and far-ir data. It may be noted that olefin displacement from $[RhCl(C_2H_4)_2]_2$ and $RhCl(C_8H_{14})_2$ provides a general method for making the corresponding rhodium(I) complexes.[15,16]

The complexes $IrCl(Ph_3P)_3$ and $IrBr(Ph_3P)_3$ are isomorphous with $RhBr(Ph_3P)_3$ and with the metastable orange modification of $RhCl(Ph_3P)_3$,[4,5] as judged by visual comparison of X-ray powder patterns; a red modification of $IrCl(Ph_3P)_3$ analogous to the stable modification of $RhCl(Ph_3P)_3$[4,5] could not be made. The iridium(I) compounds are appreciably more air sensitive than the rhodium(I) compounds, darkening in air after a day; the ir spectra then show bands due to triphenylphosphine oxide. *In vacuo* or under nitrogen (with which it does not react), $IrCl(Ph_3P)_3$ is stable indefinitely. The orange triphenylarsine and maroon triphenylstibine complexes react rapidly with oxygen. After a few hours in air they change to beige powders and their ir spectra then show a strong band at *ca.* 840 cm^{-1} which is attributed to coordinated O_2.[17,18] Even under anaerobic conditions, it is difficult to obtain $IrCl(Ph_3As)_3$ and $IrCl(Ph_3Sb)_3$ completely free from oxygen, and their reactions have been studied by using solutions prepared *in situ* in degassed solvents. The extreme sensitivity toward oxygen of $IrCl(CO)(Ph_3As)_2$ compared with that of $IrCl(CO)(Ph_3P)_2$ has been briefly noted elsewhere.[19]

The ir spectra of the new iridium(I) complexes show a strong band at ~280 cm^{-1} (Table I), which is absent from the spectrum of $IrBr(PPh_3)_3$ and can be assigned to ν(Ir–Cl). This value is considerably lower than the value observed for ν(IrCl) in $IrCl(CO)(Ph_3P)_2$ (~320 cm^{-1}).[20,21] A similar difference has been noted pre-

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(6) L. Vaska, *J. Amer. Chem. Soc.*, **83**, 756 (1961).

(7) A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc., A*, 1670 (1966).

(8) D. J. Cardin and M. F. Lappert, *Chem. Commun.*, 1034 (1967).

(9) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **88**, 3459 (1966).

(10) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *ibid.*, **90**, 5430 (1968).

(11) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610 (1966).

(12) K. Ohno and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 99 (1968).

(13) H. C. Volger, K. Vrieze, and A. Praat, *J. Organometal Chem.* (Amsterdam), **14**, 429 (1968).

(14) B. L. Shaw and E. Singleton, *J. Chem. Soc., A*, 1683 (1967). The molecular weight of this compound has not been determined owing to its insolubility, but it is presumably dimeric by analogy with the ethylene-rhodium(I) complex $[RhCl(C_2H_4)_2]_2$ (R. Cramer, *Inorg. Chem.*, **1**, 722 (1962)).

(15) J. T. Mague and G. Wilkinson, *J. Chem. Soc., A*, 1736 (1966).

(16) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *ibid.*, 1054 (1968).

(17) L. Vaska, *Science*, **140**, 809 (1963); L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

(18) W. P. Griffith and T. D. Wickins, *J. Chem. Soc., A*, 397 (1968).

(19) J. P. Collman and W. R. Roper, unpublished results cited by J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, **90**, 2282 (1968).

viously between the values of ν(Rh–Cl) in $RhCl(Ph_3P)_3$ and $RhCl(CO)(Ph_3P)_2$.[21] Studies on a series of octahedral iridium(III) complexes[21–23] have shown that ν(Ir–Cl) occurs in the range 278–262 cm^{-1} (Cl *trans* to P or As) and 303–310 cm^{-1} (Cl *trans* to CO). Our results suggest that a similar correlation is valid for planar iridium(I) complexes.

A solution of $IrCl(Ph_3P)_3$ in nitrobenzene is nonconducting, and molecular weights measured osmometrically in benzene and chloroform (*ca.* 0.02 *M* solutions) are 800–850 and 700–750, respectively, compared with the calculated value of 1015. Under the same conditions, the molecular weight of $RhCl(Ph_3P)_3$ is half the calculated value, which has hitherto been assumed to be due to the complete dissociation of one molecule of triphenylphosphine in solution.[4,5] Thus, the results apparently indicate that the iridium(I) complex is incompletely dissociated in solution. Unfortunately, however, the molecular weight determinations are not reliable because of slow isomerization to the hydrido complex (see later), which is evidenced by the lightening in color of the solution. Another approach to studying the possible dissociation of $IrCl(Ph_3P)_3$ and its analogs is to attempt the detection of free ligand in solution by nmr.[24] The ^{19}F chemical shifts at 30° of $(p\text{-}FC_6H_4)_3P$ ($\sim$0.1 *M* solution in C_6D_6) and of *trans*-$PdCl_2[(p\text{-}FC_6H_4)_3P]_2$ (saturated solution, $\sim$0.1 *M*, in $CDCl_3$) are -48.33 ± 0.05 and -53.78 ± 0.05 ppm, respectively, relative to C_6F_6 as internal standard. A saturated solution ($\sim$0.1 *M*) of $IrCl[(p\text{-}FC_6H_4)_3P]_3$ in benzene shows two absorptions in a 2:1 intensity ratio at -49.70 and -50.91 ppm; no resonance due to free ligand is observed until some ligand is added to the solution. Under these conditions, therefore, the complex $IrCl[(p\text{-}FC_6H_4)_3P]_3$ and presumably its analogs do not measurably dissociate, but the experiment clearly does not rule out the possibility of dissociation at concentration <*ca.* 0.1 *M*. In the case of $RhCl(Ph_3P)_3$, ^{31}P nmr studies[24] suggest that dissociation is <5% at concentration >10^{-2} *M*, in unexplained contradiction to the molecular weight results. On the basis of our molecular weight and nmr data, we can only conclude that any dissociation of $IrCl(Ph_3P)_3$ and its analogs is less than that occurring in solutions of $RhCl(Ph_3P)_3$.[25] This conclusion is supported by the observation that, whereas $RhCl(Ph_3P)_3$ on heating or *in vacuo* loses triphenylphosphine giving a dimeric species $[RhCl(Ph_3P)_2]_2$,[4,5] $IrCl(Ph_3P)_3$ isomerizes to a hydride without loss of triphenylphosphine (see later).

Reactions of $IrClL_3$. (a) π-Bonding Ligands. The quantitative reactions of $IrCl(Ph_3P)_3$ with CO and with PF_3 at room temperature and pressure to give $IrCl(CO)(Ph_3P)_2$ and $IrCl(PF_3)(Ph_3P)_2$, respectively, resemble the corresponding reactions of $RhCl(Ph_3P)_3$. However, $IrCl(Ph_3P)_3$, unlike $RhCl(Ph_3P)_3$, does not react with ethylene at 25°(1 atm), again indicating the firmer bonding of triphenylphosphine in the iridium(I) compound. In benzene solution, nitric oxide reacts with $IrCl(Ph_3P)_3$ to give pale brown crystals which analyze for $IrCl(NO)_2(Ph_3P)_2$; these are monomeric in chloroform and nonconducting in nitrobenzene. The ir spectrum shows a strong band assignable to ν(NO) at 1600 cm^{-1}, but there are also intense bands at 1410, 1310, and 824 cm^{-1} which are characteristic of a N-bonded nitro group.[26] This suggests that the compound should be formulated as $IrCl(NO)(NO_2)(Ph_3P)_2$, the nitro group arising from adventitious oxygen or NO_2 (no attempt was made to purify the NO). The compound is clearly not identical with the previously prepared compound $IrCl(NO)_2(Ph_3P)_2$,[27] for which ν(NO) is reported to be 1495–1540 cm^{-1}. The compound may be regarded as an example of five-coordinate iridium(III), if the NO is imagined to be a mononegative ligand.

(b) Hydrogen. The complexes $IrCl(Ph_3M)_3$ (M = P, As, and Sb) react instantaneously and irreversibly with hydrogen or deuterium giving the colorless light-sensitive dihydrides or dideuterides $IrH_2(D_2)Cl(Ph_3M)_3$. The triphenylphosphine complex is identical (ir and X-ray powder pattern) with that prepared by heating iridium chloro salts with the ligand in ethanol.[6] The triphenylphosphine and triphenylarsine complexes show two bands due to ν(Ir–H), which suggests that the hydrogens are mutually *cis;* nmr studies on the triphenylphosphine complex[28] indicate that this has the meridional configuration. Surprisingly, the complex $IrH_2Cl(Ph_3Sb)_3$ shows only one band due to ν(Ir–H) at 2090 cm^{-1}; unfortunately we could not obtain a sufficiently concentrated solution for nmr measurement. It is of interest that $IrCl(Ph_3P)_3$ dehydrogenates ethanol to acetaldehyde and gives the same dihydride as that obtained in the reaction with hydrogen. On prolonged boiling in higher boiling alcohols, $IrCl(CO)(Ph_3P)_2$ is formed. The dehydrogenation probably proceeds *via* an ethanol or ethoxide complex, hydride ion being transferred to the metal from the α carbon atom.[29,30]

As noted in our preliminary communication,[1] and subsequently confirmed,[10] the complex $IrCl(Ph_3P)_3$ does not catalyze the homogeneous hydrogenation of olefins. This marked difference from $RhCl(Ph_3P)_3$ probably reflects two factors: (1) the iridium complex does not so readily provide a vacant site by loss of triphenylphosphine for the approach of the olefin; (2) iridium–hydrogen bonds are stronger than rhodium–hydrogen bonds, so that hydrogen is not so readily transferred from the dihydride to the olefin.[5]

(c) Hydrogen Chloride. The complexes $IrCl(Ph_3M)_3$ (M = P, As, and Sb) react immediately at 25° (1 atm) with HCl giving pale yellow crystals of general formula $IrHCl_2(Ph_3M)_3$. The triphenylphosphine complex has ν(Ir–H) at 2230 cm^{-1}, indicating that H is *trans* to Cl, and the compound is apparently identical with the so-called β isomer which has been assigned the meridional configuration on the basis of nmr studies.[28] In agreement with this, the far-ir spectrum shows bands due to ν(Ir–Cl) at 253 cm^{-1} (Cl *trans* to H) and 275 cm^{-1} (Cl *trans* to Ph_3P). The stereochemistry of the tri-

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(20) L. Vaska, *J. Amer. Chem. Soc.*, **88**, 5325 (1966).

(21) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(22) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 6789 (1965).

(23) B. L. Shaw and A. C. Smithies, *ibid.*, *A*, 2784 (1968).

(24) D. R. Eaton and S. R. Suart, *J. Amer. Chem. Soc.*, **90**, 4170 (1968).

(25) Attempts to apply the ^{19}F nmr method to the study of $RhCl[(p\text{-}FC_6H_4)_3P]_3$ have been frustrated by the broadness of the observed signal, presumably caused by traces of Rh(II); see ref 5.

(26) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 154.

(27) L. Malatesta, M. Angoletta, and G. Caglio, *Angew. Chem. Intern. Ed. Engl.*, **2**, 739 (1963).

(28) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

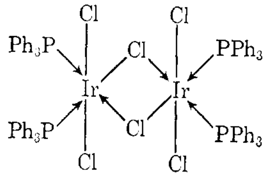
(29) L. Vaska, *J. Amer. Chem. Soc.*, **84**, 4989 (1962).

(30) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

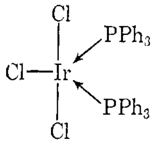
phenylarsine and triphenylstibine complexes is probably similar. It is worth noting for comparison that $RhCl(Ph_3P)_3$ reacts with HCl to give a five-coordinate hydride $RhHCl_2(Ph_3P)_2$,[31] and only gives $RhHCl_2(Ph_3P)_3$ in the presence of excess triphenylphosphine.[7]

(d) Chlorine. Excess chlorine reacts with a benzene solution of $IrCl(Ph_3P)_3$ giving an air-stable orange crystalline solid of empirical formula $IrCl_3(Ph_3P)_2$ (A) and a violet solution from which purple crystals of formula $IrCl_4(Ph_3P)_2$ can be isolated. The same complexes are obtained by chlorination of $IrHCl_2(Ph_3P)_3$. A yellow crystalline compound of formula $IrCl_3(Ph_3P)_2$ has been described as resulting from treatment of $IrH_3(Ph_3P)_3$ in CCl_4 with excess chlorine,[32] and at the time our work started, the compound $IrCl_4(Ph_3P)_2$ had only been mentioned as a product of chlorination of $IrH_2Cl(Ph_3P)_3$.[6] After our work was complete, the preparation of a range of complexes of general formula $IrCl_4$(tertiary phosphine)$_2$ was reported.[33]

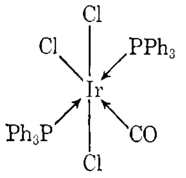
We find that A is insoluble in most organic solvents except chloroform and dichloromethane in which it is monomeric. From these solutions, ether precipitates yellow crystals B of the same formula as A, but having a different X-ray powder pattern and far-ir spectrum. Remarkably, the color of B changes from yellow to brown when it is *in vacuo* and returns to yellow at 1 atm. No evidence could be found from the ir spectrum for the presence of coordinated water, oxygen, hydrogen, etc. The bands at ~330 cm^{-1} in the spectra of A and B are typical of ν(Ir–Cl) (Cl *trans* to Cl), while the bands in the region 280–230 cm^{-1} could be due either to ν(Ir–Cl) (Cl *trans* to P) or to bridging chlorine modes, or to both. Both A and B may therefore be dimeric in the solid state with mutually *cis*-phosphines and bridging chlorines (I), while in solution the structure may be five-coordinate, as in II. The complex reacts with CO at 25° (1 atm) to give a monomeric iridium(III) carbonyl complex $IrCl_3(CO)(Ph_3P)_2$ [ν(CO) 2100 cm^{-1}], which is not identical with the product obtained by chlorination of $IrCl(CO)(Ph_3P)_2$[34] and shown by far-ir spectroscopy[21] to have configuration III. The far-ir spectrum of the new compound shows bands due to ν(IrCl) at 324 cm^{-1} (Cl *trans* to Cl) and 275 cm^{-1} (Cl *trans* to Ph_3P), indicating that the triphenylphosphines are mutually *cis* (configuration IV). This result also supports the suggestion that the triphenylphosphines are mutually *cis* in A and B. The complex $IrCl_3(Ph_3P)_2$ also reacts with pyridine to give monomeric $IrCl_3(C_5H_5N)(Ph_3P)_2$ and with triphenylphosphine to give $IrCl_3(Ph_3P)_3$. Both compounds show strong bands at ~330 cm^{-1} in their far-ir spectra indicating *trans*-chlorine atoms, and molecular weight measurements suggest that the *tris*-phosphine complex is dissociated in solution.



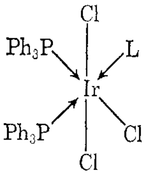
I



II



III



IV, L = CO, C_5H_5N, or Ph_3P

The violet complex $IrCl_4(Ph_3P)_2$ can be obtained in good yield by treatment of $IrCl_3(Ph_3P)_2$ with excess chlorine, and also by treating $IrCl(Ph_3P)_3$ with nitrosyl chloride. The analogous triphenylarsine complex is prepared by chlorination of either $IrCl(Ph_3As)_3$ or $IrHCl_2(Ph_3As)_3$, but there is no sign of an intermediate $IrCl_3(Ph_3As)_2$. Chlorination of $IrCl(Ph_3Sb)_3$ gives a maroon insoluble compound which has not been investigated further. The magnetic moments of $IrCl_4(Ph_3P)_2$ and $IrCl_4(Ph_3As)_2$ at room temperature are 1.68 and 1.75 BM, respectively, as expected for a spin-paired d^5 electron configuration (Ir(IV)). The magnetic susceptibilities over a temperature range obey the Curie law and show no temperature-independent paramagnetism (Table II). The rather low value for μ_{eff} derived from the variable-temperature measurements on $IrCl_4(Ph_3P)_2$ is probably caused by decomposition to Ir(III) occurring in the solid state. The triphenylarsine complex is noticeably more stable in this respect, but both complexes decompose slowly in solution, especially in strong light. The far-ir spectrum of $IrCl_4(Ph_3P)_2$ shows only one strong band due to ν(Ir–Cl) at 329 cm^{-1}, indicating that the complex has the *trans* configuration (*cf.* ν(Pt–Cl) in *trans*-$PtCl_4[(C_2H_5)_3P]_2$ at 340 cm^{-1}).[35] The corresponding band in $IrCl_4(Ph_3As)_2$ could not be located owing to obscuring ligand absorption. On treatment with CO at 25° (1 atm), the complex $IrCl_4(Ph_3P)_2$ gives the known compound $IrCl_3(CO)(Ph_3P)_2$ (configuration III), showing that the *trans* configuration of the triphenylphosphines is retained during the reduction.

Table II. Variation of Magnetic Susceptibilities of *trans*-$IrCl_4(Ph_3M)_2$ (M = P, As) with Temperature

Temp, °K	$\chi_M^{corr} \times 10^6$	μ_{eff}, BM
	(i) *trans*-$IrCl_4(Ph_3P)_2$	
107	2971	1.60
140	2134	1.55
164	1796	1.54
194	1447	1.50
230	1335	1.51
250.5	1247	1.59
286	1122	1.61
	Av	1.58 ± 0.04
	(ii) *trans*-$IrCl_4(Ph_3As)_2$	
95	4041	1.74
124	2960	1.72
153.5	2453	1.74
184	2053	1.74
214.5	1773	1.75
249	1545	1.76
281.5	1345	1.75
	Av	1.75 ± 0.01

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(31) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 1347 (1967).

(32) M. Angoletta and A. Araneo, *Gazz. Chim. Ital.*, **93**, 1343 (1963).

(33) J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc., A*, 2636 (1968).

(34) L. Vaska and J. W. Di Luzio, *J. Amer. Chem. Soc.*, **84**, 680 (1962).

(35) D. M. Adams and P. J. Chandler, *J. Chem. Soc., A*, 1009 (1967).

Table III. g Values Derived from Esr Spectra of Iridium(IV) Complexes

Band	Temp, °K	Complex	Form	g_x	g_y	g (rms) $g_z = 0$	g (rms) $g_z = 0.4$
X	295	*trans*-$IrCl_4(Ph_3P)_2$	Powder	2.52	2.52	2.06	2.07
X	295	*trans*-$IrCl_4(Ph_3As)_2$	Powder	2.56	2.56	2.09	2.10
X	77	*trans*-$IrCl_4(Ph_3P)_2$	Glass	2.50	2.50	2.04	2.05
X	77	*trans*-$IrCl_4(Ph_3As)_2$	Glass	2.50	2.50	2.04	2.05
Q	295	*trans*-$IrCl_4(Ph_3P)_2$	Powder	2.50	2.50	2.04	2.05
Q	295	*trans*-$IrCl_4(Ph_3As)_2$	Powder	2.48	2.48	2.02	2.04

The esr spectra of $IrCl_4L_2$ (L = Ph_3P, Ph_3As) have been recorded both in the powder form at room temperature (X and Q band) and in a toluene–chloroform glass at 77° K (X band). The low-frequency spectra are broad and asymmetric (Figure 1). Multiplying the spectrometer frequency by almost four only doubled the minimum–maximum separation. This appears to eliminate an interpretation based on three similar unresolved g values, which is also not consistent with the spin-only value for the magnetic moment. An explanation of the results is that one g value is very low ($\sim$0.4, the lower limit of the spectrometer) and that the observed transitions are for the $g_\perp$ orientations. Indeed, the esr spectrum of $IrCl_4(Ph_3As)_2$ shows a broad band centered at $g \sim 0.4$. The observed g values are given in Table III, from which it is clear that g_{rms} varies little with the value 0 or 0.4 assigned to g_z. The esr spectra of $IrCl_4L_2$ are similar to that observed for ferricytochrome C[36] but differ from those of the carborane analogs of ferricinium cation.[37] Similar esr results have recently been reported for $IrCl_4[(n\text{-}C_3H_7)_3M]_2$ (M = P or As).[38]

Hydrogen Abstraction from the Coordinated Ligand. On heating $IrCl(Ph_3P)_3$ in a number of solvents (benzene, acetone, chloroform, and cyclohexane have been used) for several hours, it is converted into a colorless, monomeric, diamagnetic, nonconducting complex of the same empirical formula. The ir spectrum shows bands at 2200 and 817 cm^{-1} assignable to ν(Ir–H) and δ(Ir–H), respectively, showing that an iridium hydride is formed. The complex obtained on heating $IrCl(Ph_3P)_3$ in C_6D_6 and $(CD_3)_2CO$ is identical (ir and X-ray powder pattern) with that obtained in C_6H_6 and $(CH_3)_2CO$, and there is no sign of a band in the 1600 cm^{-1} region due to ν(Ir–D). However, when the fully deuterated complex $IrCl[(C_6D_5)_3P]_3$ is heated in benzene or cyclohexane, the resulting colorless complex, which is isomorphous (X-ray powder pattern) with the new hydride, shows no band at 2200 cm^{-1} in the ir, but instead shows two new bands at 1600 and 1540 cm^{-1} which are absent from the spectrum of $IrCl[(C_6D_5)_3P]_3$. The latter is assigned to ν(Ir–D) (ratio ν(Ir–H)/ν(Ir–D) = 1.43, calcd 1.41), the former to a ring ν(CC) mode. The infrared spectral evidence therefore establishes unequivocally that $IrCl(Ph_3P)_3$ isomerizes to a hydride by abstracting hydrogen from coordinated triphenylphosphine. The ir spectra are discussed in more detail below.

Similar hydrides are obtained on heating the analogous iridium(I) complexes of p-fluoro-, p-methyl-, and p-methoxyphenylphosphine, and of triphenylarsine and triphenylstibine in organic solvents (Table IV). The period of heating is $\sim$2 hr for the triarylphosphine complexes and $\sim$6 hr for the triphenylarsine and triphenylstibine complexes. All the new hydrides are air stable in the solid state. The solutions are slowly decomposed by air and light, and the $(p\text{-}FC_6H_4)_3P$ derivative rapidly decomposes in boiling cyclohexane.

Table IV. Analytical Data for Hydrides Derived from $IrClL_3$

Ligand (L)	% C Calcd	% C Found	% H Calcd	% H Found	% Cl Calcd	% Cl Found
$(C_6H_5)_3P$	63.7	63.9	4.8	4.8	3.5	3.7[a]
$(C_6D_5)_3P$	61.3	61.2			3.2	3.0
$(o\text{-}DC_6H_4)_3P$	63.4	63.8			3.5	3.0
$(p\text{-}C_6H_4)_3P$[e]	55.1	55.2	3.1	3.4	3.0	3.55
$(p\text{-}CH_3OC_6H_4)_3P$	58.9	59.3	5.0	4.9	2.8	3.3[b]
$(C_6H_5)_3As$	56.6	56.9	4.0	4.2	3.1	3.2[c]
$(C_6H_5)_3Sb$	50.4	52.2	3.5	4.2	2.8	4.1[d]

[a] P, calcd 9.1, found 8.7; mol wt, calcd 1015, found (C_6H_6) 950, 980. [b] P, calcd 8.1, found 8.1. [c] Mol wt, calcd 1146, found (C_6H_6) 1220. [d] Mol wt, calcd 1287, found (C_6H_6) 1437. [e] Sample heated at 110° (10^{-4} mm) to remove benzene of crystallization.

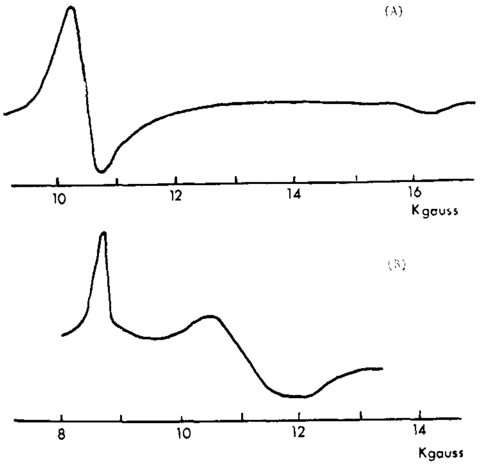

Figure 1. Esr spectra of powdered iridium(IV) complexes at room temperature: (A), *trans*-$IrCl_4(Ph_3As)_2$; (B), complex obtained by chlorination of $IrHCl[(C_6H_4)Ph_2P](Ph_3P)_2$.

The presence of an iridium–hydrogen bond in these compounds is confirmed by the appearance of high-field lines in their nmr spectra. The triphenylphosphine complex shows an eight-line spectrum due to ^{31}P–^{1}H coupling centered at δ −18.7 ppm relative to $(CH_3)_4Si$ (Figure 2), and the triphenylarsine and triphenylstibine complexes show singlets at δ −19.9 and −22.7 ppm, respectively (Table V). The measured ratios of the areas of the high-field lines *vs.* the aromatic proton resonances were 1 to 50 ± 10 and 1 to 60 ± 15 for the

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(36) I. Salmeen and G. Palmer, *J. Chem. Phys.*, **48**, 2049 (1968).

(37) A. H. Maki and T. E. Berry, *J. Amer. Chem. Soc.*, **87**, 4437 (1965).

(38) A. Hudson and M. J. Kennedy, *J. Chem. Soc., A*, 1116 (1969).

Table V. Proton Nmr and Ir Spectral Data on Hydrides Derived from $IrClL_3$

L	δ_H, ppm rel to TMS[a]	Solvent	No. of scans	No. of lines	Spacing, Hz	ν(Ir–H), cm^{-1}			δ(IrH), cm^{-1}, Nujol	ν(IrCl), cm^{-1}
						Nujol	C_6H_6	$CHCl_3$		
$(C_6H_5)_3P$	−18.7	C_6H_6	430	8	15,6,6,6,6,6,15	2200	2188, 2223 sh	2204, 2260 sh	819	254
$(C_6H_5)_3As$	−19.9	C_6H_6	266	1		2170	nm	nm	805	257
$(C_6H_5)_3Sb$	−22.7	$CDCl_3$	1	1		2152	nm	nm	805	nm
(*p*-$FC_6H_4)_3P$	−17.2	C_6H_6	1	*c*		2208	2184, 2215 sh	nm	*d*	255
(*p*-$CH_3OC_6H_4)_3P$	−18.7	C_6H_6	348	4[b]	12, 18, 12	2206	2198, 2220 sh	nm	*d*	251
(*p*-$CH_3C_6H_4)_3P$	nm[e]					2208	2190, 2220 sh	nm	*d*	255

[a] In accordance with the recommendation of the ASTM, values upfield of $(CH_3)_4Si$ are taken as negative. [b] Overlapping 1:2:1 triplets. [c] Could not be resolved owing to insufficient solubility and decomposition of sample. [d] Masked by ligand absorption. [e] Not measured.

triphenylphosphine and triphenylstibine complexes, respectively (calculated for a monohydride, 1 to 44), showing that only one hydrogen atom is abstracted from the ligand. For convenience in this discussion, we shall assume that the hydrogen comes from the *ortho* position of one of the phenyl groups, and that the iridium forms a σ bond to the carbon atom at that position in order to complete sixfold coordination; the evidence for this will be discussed below. The hydrides derived from $IrCl(Ph_3M)_3$ (M = P, As, and Sb) are therefore formulated as $IrHCl[(o\text{-}C_6H_4)Ph_2M](Ph_3M)_2$, but we shall use the abbreviated notation "IrHCl(ligand)$_3$."

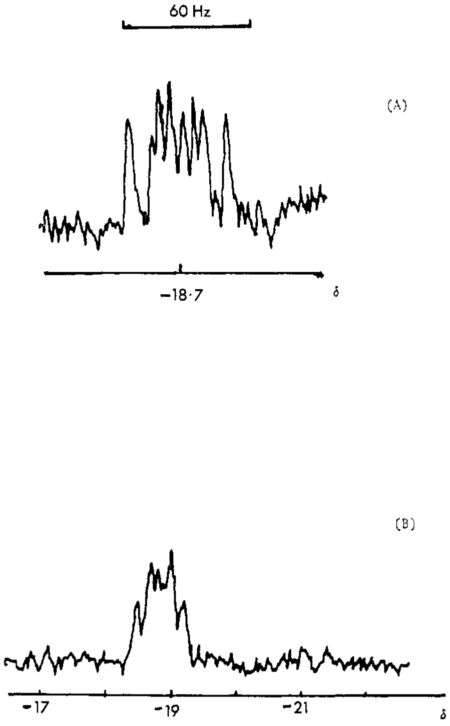
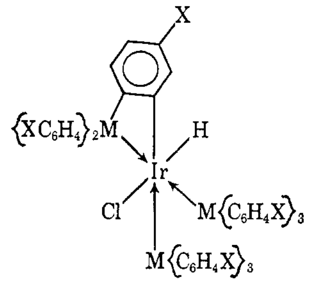


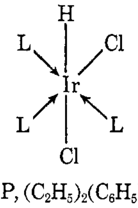
Figure 2. High-field nmr signals in hydrides obtained by isomerization of $IrClL_3$: (A) L = $(C_6H_5)_3P$; (B) L = (*p*-$CH_3OC_6H_4)_3P$.

The stereochemistry of octahedral iridium(III) hydrides containing tertiary phosphines can be determined from the position and multiplicity of the high-field lines.[39] Specifically, when the ligands are $(C_2H_5)_3P$ and $(C_2H_5)_2(C_6H_5)P$, δ_H = −20 to −22 ppm and J_{P-H} = 11–21 Hz for H *cis* to P, and δ_H = −10 to −15 ppm and J_{P-H} = ~160 Hz for H *trans* to P. The corresponding values for hydrides containing $(C_6H_5)_3P$ are δ_H = −19 ppm and J_{P-H} = 14 Hz (H *cis* to Ph_3P) and δ_H = −12 to −15 ppm and J_{P-H} = 164 Hz (H *trans* to Ph_3P).[28] Thus, the position of the high-field signal in the nmr spectrum of "$IrHCl(Ph_3P)_3$" (Figure 2) and the small splittings (Table V) indicate that the hydrogen is *trans* to chlorine and is mutually *cis* to three inequivalent phosphorus atoms (configuration V). The high-field line of the hydride derived from IrCl[(*p*-$CH_3OC_6H_4)_3P]_3$ is similar to that of the triphenylphosphine complex, except that the central multiplets are closer together (Figure 2). The profile thus resembles a pattern of two overlapping 1:2:1 triplets (J_{P-H} = 12 and 18 Hz), which is the pattern observed in hydrides of configuration VI,[20,39] in which the mutually *trans*-phosphines are equivalent.

Infrared data also support configuration V for the new hydrides. The value of ν(Ir–H) (2200 cm^{-1}) in "$IrHCl(Ph_3P)_3$" is characteristic of H *trans* to Cl, while the low value of ν(Ir–Cl) (~250 cm^{-1}) is characteristic of Cl *trans* to H. Moreover, ν(Ir–H) shifts to higher frequency in more polar solvents when H is *trans* to Cl, but is almost insensitive to solvent when H is *trans* to P or As.[40] The solvent shifts observed for "$IrHCl(Ph_3P)_3$" (Table V) are clearly consistent with hydrogen being *trans* to chlorine. It has also been noted that the hydride $IrHCl_2[(C_2H_5)_2(C_6H_5)P]_3$ (configuration VI) shows *two* bands due to ν(Ir–H) in benzene solution,[39] possibly owing to some type of solvent interaction, and we also observe that the bands due to ν(Ir–H) in the



V, M = P, As, or Sb; X = H
M = P; X = *p*-CH_3, *p*-CH_3O, or *p*-F



VI, L = $(C_2H_5)_3P$, $(C_2H_5)_2(C_6H_5)P$, or $(C_6H_5)_3P$

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(39) J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).

(40) D. M. Adams, *Proc. Chem. Soc.*, 431 (1961).

new hydrides show broadening and shoulders in solution.

The Origin of the Abstracted Hydrogen Atom. Unless one of the phenyl rings is highly nonplanar, the only reasonable source for the hydrogen atom which migrates to the metal is the *ortho* position adjacent to the phosphorus atom, even though this forms a presumably strained four-membered planar chelate ring. Moreover, X-ray studies of five complexes of the noble metals have revealed a fairly close intramolecular contact between the metal atom and one or more *ortho* hydrogen atoms of phenyl groups of the coordinated ligands, *viz.* $RuCl_2(Ph_3P)_3$, (2.59 Å),[41] the red modification of *trans*-$PdI_2[(CH_3)_2(C_6H_5)P]_2$ (2.84, 2.85 Å),[42] $[Ir(CO)(diphos)_2]^+Cl^-$ (diphos = $Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh_2$) (~3.1, 3.3 Å),[43] $RhCl(CS)(Ph_3P)_2$ (3.01, 3.01, 3.10, and 3.24 Å),[44] and $RuHCl(Ph_3P)_3$ (2.85 Å).[45] However, it must be noted that in none of these cases is hydrogen transferred to the metal, and in only one case, $RuHCl(Ph_3P)_3$, is there evidence for exchange between the metal-bound hydrogen and the *ortho* positions.[46] Loss of hydrogen from the *ortho* position of an aromatic ring of a coordinated ligand with concomitant formation of a metal–carbon σ bond to that position has been previously reported in the reaction of aromatic azo compounds with $Ni(C_5H_5)_2$,[47] $Fe_2(CO)_9$,[48] and platinum and palladium salts,[49] but in these cases the hydrogen atom does not migrate to the metal.

The ir spectra of the iridium hydrido complexes provide evidence for a change in the substitution pattern of one of the phenyl groups of the ligand. Bands at 1565 and 1570 cm^{-1} due to ν(CC) in the spectrum of $IrCl(Ph_3P)_3$ are replaced by bands at 1556, 1567, and 1582 cm^{-1} in the spectrum of the derived hydride. Likewise, there is a new band at 1600 cm^{-1} in the spectrum of the deuteride from $IrCl[(C_6D_5)_3P]_3$, and a new band at 1552 cm^{-1} in the spectrum of the hydride from $IrCl[(p\text{-}FC_6H_4)_3P]_3$. The hydride "$IrHCl(Ph_3P)_3$" also shows a strong band at 728 cm^{-1}, which is in the range characteristic of C–H out-of-plane deformations for *ortho*-disubstituted aromatics,[50] but this band does not appear in the spectra of all the other hydrides. This is to be expected in the case of the hydrides containing *para*-substituted triarylphosphines, because the δ'(CH) modes for 1,4 and 1,2,4 substitution fall in the same range,[50] but in the case of "$IrHCl(Ph_3As)_3$" and "$IrHCl(Ph_3Sb)_3$," the expected band is probably masked by strong ligand absorption at 730 cm^{-1}. It may be noted that in three other cases where hydrogen is abstracted from coordinate arenes or from phenyl groups of coordinated ligands, a band in the region of 700–750 cm^{-1} has been observed (Table VI).

Table VI. Aromatic C–H Deformation Frequencies in Complexes Containing σ-Bonded *ortho*-Disubstituted Aryl Groups

Complex	δ(CH), cm^{-1}	Ref
$RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2$	737, 814	53
$FeH[(C_6H_4)PhPCH_2CH_2PPh_2](Ph_2PCH_2CH_2PPh_2)$	728	54
$Rh[(C_6H_4)Ph_2P](Ph_3P)_2$	746	59

In an attempt to prove conclusively that the *ortho* position is involved in hydrogen abstraction, the complex $IrCl[(o\text{-}DC_6H_4)_3P]_3$ has been synthesized. On heating in cyclohexane, it is converted into a colorless complex showing a band due to ν(Ir–H) at 2200 cm^{-1} and five bands in the 1550–1600 cm^{-1} region of the ir. Unfortunately, in this case, we cannot distinguish the bands due to ν(Ir–D) (expected value 1556 cm^{-1}) and those due to ν(CC) vibrations; since only one *ortho* position is deuterated, the intensity of the band due to ν(Ir–D) is expected to be half that of the ν(Ir–D) band in "$IrDCl[(C_6D_5)_3P]_3$." The spectrum of the hydride–deuteride derived from $IrCl[(o\text{-}DC_6H_4)_3P]_3$ also shows medium or strong bands in the C–H deformation region at 789, 755, 728, 716, 650, and 643 cm^{-1} which are absent from the spectrum of the parent compound. Hydrogen abstraction from the *ortho* position would leave three adjacent hydrogen atoms, which should show two ranges of absorption at 810–750 and 725–680 cm^{-1};[50] some of the listed bands are obviously assignable on this basis. Deuterium abstraction from the *ortho* position gives an *ortho*-disubstitution pattern, and a band at 728 cm^{-1} would therefore be expected. The appearance of this band, in conjunction with the complex spectrum in the 1550–1600 cm^{-1} region, suggests that both deuterium and hydrogen have been transferred to the metal in $IrCl[(o\text{-}DC_6H_4)_3P]_3$.

We have also compared the extinction coefficients of the bands due to ν(Ir–H) in "$IrHCl(Ph_3P)_3$" and the hydride/deuteride from $IrCl[(o\text{-}DC_6H_4)_3P]_3$. The ratio should be 2:1 if hydrogen and deuterium abstraction are equally probable. The value measured in benzene solution is 1.5:1. However, the ratio of intensities of the bands in the hydride/deuteride at 2260 cm^{-1} due to ν(C–D) and 2200 cm^{-1} due to ν(Ir–H) changes from 1:2.6 in a Nujol mull to ~1:1 in benzene solution. Also, as mentioned earlier, the ν(Ir–H) band broadens in solution; the band widths at half-height for "$IrHCl(Ph_3P)_3$" in a Nujol mull and in benzene solution are 20 and 90 cm^{-1}, respectively. Thus the intensity of the ν(Ir–H) band in the hydride/deuteride will be enhanced by the proximity of the ν(C–D) absorption (the two modes may also be vibrationally coupled); hence the ratio of extinction coefficients of ν(Ir–H) in "$IrHCl(Ph_3P)_3$" and the hydride/deuteride must be greater than 1.5. This result is consistent with abstraction of hydrogen and deuterium from the *ortho* position in the latter compound.

The rate of hydrogen abstraction in the iridium(I)–phosphine complexes can be measured by following the appearance of the band due to ν(Ir–H) at *ca.* 2200 cm^{-1} in deoxygenated benzene. The triphenylarsine and triphenylstibine complexes are too air sensitive for this procedure to be reliably employed. The reactions all

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(41) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

(42) (a) N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Commun.*, 237 (1965); (b) N. A. Bailey and R. Mason, *J. Chem. Soc., A*, 2594 (1968).

(43) J. A. J. Jarvis, R. H. B. Mais, P. G. Owston, and K. A. Taylor, *Chem. Commun.*, 906 (1966).

(44) J. L. de Boer, D. Rogers, A. C. Skapski, and P. G. H. Troughton, *ibid.*, 756 (1966).

(45) A. C. Skapski and P. G. H. Troughton, *ibid.*, 1230 (1968).

(46) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc., A*, 3143 (1968).

(47) J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, **85**, 1544 (1963).

(48) M. M. Bagga, W. T. Flannigan, G. R. Knox, P. L. Pauson, F. J. Preston, and R. I. Reed, *J. Chem. Soc., C*, 36 (1968).

(49) A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, **87**, 3272 (1965).

(50) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958, pp 77–78.

show the expected first-order kinetics; the half-lives are given in Table VII. The rates are in the order L = $(p\text{-}FC_6H_4)_3P < (C_6H_5)_3P = (o\text{-}DC_6H_4)_3P < (p\text{-}CH_3OC_6H_4)_3P < (p\text{-}CH_3C_6H_4)_3P$. The rate of hydrogen abstraction for L = $(o\text{-}DC_6H_4)_3P$ could not be measured as accurately as for the other complexes owing to interference from ν(C–D), but the near identity of this rate with that for L = $(C_6H_5)_3P$ suggests that there is little or no kinetic isotope effect in the isomerization.

Table VII. Rate Data for Hydrogen Abstraction in $IrClL_3$[a]

Ligand (L) in $IrClL_3$	$t_{1/2}$, min
$(p\text{-}FC_6H_4)_3P$	130
$(o\text{-}DC_6H_4)_3P$	66
$(C_6H_5)_3P$	57
$(p\text{-}CH_3OC_6H_4)_3P$	45
$(p\text{-}CH_3C_6H_4)_3P$	39

[a] 1.44×10^{-3} *M* solutions in benzene at 39.5 ± 0.5°.

Reaction of the Hydrides Derived from $IrClL_3$. It was hoped that the reactions of the new hydrides would provide evidence for the presence of the metal–carbon σ bond to the *ortho* position of the aromatic ring, since such bonds can often be cleaved by a variety of reagents, such as hydrogen, hydrogen halides, and halogen. In fact, most of the reactions of the hydrides are similar to those of the parent iridium(I) complexes, except that they take place less readily. Thus, "$IrHCl(Ph_3P)_3$" does not react with hydrogen, hydrogen chloride, or carbon monoxide at room temperature (*cf.* $IrCl(Ph_3P)_3$), but in refluxing benzene the products are $IrH_2Cl(Ph_3P)_3$, $IrHCl_2(Ph_3P)_3$, and $IrCl(CO)(Ph_3P)_2$, respectively. The hydride "$IrHCl(Ph_3P)_3$" also reacts with refluxing ethanol to give acetaldehyde and $IrH_2Cl(Ph_3P)_3$. In the initial stages of the reaction, a transient orange color develops in the solution, which may indicate that the reaction proceeds *via* $IrCl(Ph_3P)_3$ as the reactive intermediate, *i.e.*, with hydrogen migration from the metal back to the ligand.

Reaction of $IrHCl[(C_6H_4)Ph_2P](Ph_3P)_2$ with deuterium could in principle occur by two routes: (i) cleavage of the metal–carbon σ bond to give $IrHDCl[(C_6H_4D)](Ph_2P)_2$, with incorporation of one deuterium atom in the *ortho* position of one of the phenyl rings. The initially formed hydride–deuteride could isomerize to $IrDHCl[(C_6H_4D)Ph_2P](Ph_3P)_2$ and disproportionate to a mixture of dihydride and dideuteride;[51] Ir–H could also exchange with D_2.[51] (ii) The hydrogen on the metal could migrate back to the ligand, giving $IrCl(Ph_3P)_3$, which reacts with deuterium giving $IrD_2Cl(Ph_3P)_3$. In practice, the reaction with deuterium in refluxing benzene gave variable results under similar experimental conditions. The complexes isolated were always isomorphous with $IrH_2Cl(Ph_3P)_3$, but in some cases strong bands due to both ν(Ir–H) and ν(Ir–D) were observed (2200, 2110 and 1579, 1515 cm^{-1}, respectively); in other cases the Ir–D bands were much stronger than the Ir–H bands, and in one case bands due to ν(Ir–D) only were observed. The variability of results may be a consequence of differing rates of gas flow, which was not controlled. In the case in which only the dideuteride was formed, the final product was treated with CO in refluxing benzene. The mass spectra of the isolated triphenylphosphine and $IrCl(CO)(Ph_3P)_2$ showed no peak at *m/e* 263, indicating that monodeuteriotriphenylphosphine, $(C_6H_4D)(C_6H_5)_2P$, was absent. This result suggests that mechanism ii must be operative in this particular experiment, but clearly mechanism i may be operative in the other experiments.

The complex "$IrHCl(Ph_3P)_3$" also reacts with DCl in refluxing benzene giving $IrDCl_2(Ph_3P)_3$ [ν(Ir–D) = 1600 cm^{-1}]. The same complex can be made by treating $IrHCl_2(Ph_3P)_3$ with DCl. The mass spectrum of $IrHCl_2(Ph_3P)_3$ shows only peaks due to triphenylphosphine, but the spectra of the dideuteride prepared by both routes show peaks due to mono- and dideuteriotriphenylphosphine (*m/e* 263, 264). The most likely explanation of this result is that deuterium is transferred from metal to ligand in the mass spectrometer, since it seems less likely that this could occur in the reaction of DCl with $IrHCl_2(Ph_3P)_3$. We are currently investigating the reaction of "$IrHCl(Ph_3P)_3$" with DCl to see if deuterium is incorporated in the ligand.

Reaction of $IrHCl[(C_6H_4)Ph_2P](Ph_3P)_2$ with excess chlorine would be expected to give an iridium(IV) complex containing (*o*-chlorophenyl)diphenylphosphine, *e.g.*, $IrCl_4(Ph_3P)[Ph_2(o\text{-}ClC_6H_4)P]$ resulting from cleavage of the metal–hydrogen and metal–carbon σ bonds and oxidation of the metal. If hydrogen migration to the metal preceded chlorine addition, or if the chelate triphenylphosphine were displaced, the known complex $IrCl_4(Ph_3P)_2$ should be formed. When the reaction is carried out in benzene, a blue solution is rapidly formed from which dark blue crystals can be isolated. We have been unable to obtain completely satisfactory analytical data for this compound, although the figures fit approximately for $IrCl_4(Ph_3P)_2$. The ir spectrum shows a strong absorption at ~1100 cm^{-1} characteristic of coordinated phosphine oxide,[52] and the magnetic moment at room temperature is 1.76 ± 0.09 BM. The esr spectrum is similar to that of $IrCl_4(Ph_3P)_2$. The bands in the uv and visible spectrum differ appreciably in position and intensity from those of $IrCl_4(Ph_3P)_2$ (Table VIII). The spectrum of a solution of "$IrHCl(Ph_3P)_3$" in dichloromethane treated with chlorine suggests that ~12% of *trans*-$IrCl_4(Ph_3P)_2$ is formed in addition to the blue compound. By contrast, chlorination of "$IrHCl(Ph_3As)_3$" in benzene gives only *trans*-$IrCl_4(Ph_3As)_2$.

Table VIII. Electronic Spectra of Iridium(IV) Complexes[a]

Complex[b]	Bands, cm^{-1} × 10^{-3} (extinction coefficient)
trans-$IrCl_4(Ph_3P)_2$	17.6 (2370), 16.3 sh (1325)
trans-$IrCl_4(Ph_3As)_2$	18.1 (2670), 16.3 sh (1216)
Ir(IV) complex from "$IrHCl(Ph_3P)_3$" + Cl_2	26.0 (2100), 12.8 (2450)

[a] Abbreviations: sh, shoulder. [b] Measured on *ca.* 10^{-3} to 10^{-4} *M* solutions in CH_2Cl_2.

Discussion

The most thoroughly studied examples of hydrogen abstraction from ligand to metal are those involving

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(51) L. Vaska, *Chem. Commun.*, 614 (1966); G. G. Eberhardt and L. Vaska, *J. Catal.*, **8**, 183 (1967).

(52) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

square-planar ditertiary phosphine complexes of ruthenium(0) and iron(0) (d^8), which are in tautomeric equilibrium with octahedral hydrido alkyls or aryls of the divalent elements (d^6)

$$\mathrm{Ru(C_{10}H_8)(Me_2PCH_2CH_2PMe_2)_2} \rightleftharpoons \textit{cis}\text{-}\mathrm{RuH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2}^{53} \quad (1)$$

$\mathrm{C_{10}H_8}$ = naphthalene; Me = methyl

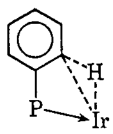
$$\mathrm{Ru(Me_2PCH_2CH_2PMe_2)_2} \rightleftharpoons \textit{cis}\text{-}\mathrm{RuH(CH_2PMeCH_2CH_2PMe_2)(Me_2PCH_2CH_2PMe_2)}^{53} \quad (2)$$

$$\mathrm{Fe(Ph_2PCH_2CH_2PPh_2)_2} \rightleftharpoons \textit{cis}\text{-}\mathrm{FeH[(C_6H_4)PhPCH_2CH_2PPh_2](Ph_2PCH_2CH_2PPh_2)}^{54} \quad (3)$$

In these cases, spectroscopic studies suggest that the predominant species in the solid state and in solution is the hydride. In solution, a small amount of the very reactive zerovalent tautomer may be formed. Equations 1 and 2 apparently react entirely in the zerovalent form with iodine, but both tautomers react with DCl.[53] In the reaction of system 3 with DCl, 80% of reaction occurs with the zerovalent form and 20% with the hydrido aryl form. Reaction with ethylene to give $\mathrm{Fe(Ph_2PCH_2CH_2PPh_2)_2(C_2H_4)}$ occurs entirely with the zerovalent tautomer.

The iridium(I) system appears to be similar to the iron(0) and ruthenium(0) systems, except that it has proved possible for the first time to isolate the more reactive low-valent tautomer. Although conversion to the hydridoaryliridium(III) complex is essentially complete and irreversible in the solid state, our preliminary studies indicate that some reactions can proceed *via* the iridium(I) tautomer. The extent to which this occurs with different ligands on iridium and with various reagents is a subject for future investigation. Clearly, the low-valent tautomer in these systems need not be the more reactive of the pair. Thus, the deuterium–hydrogen exchange which occurs at the *ortho* positions of phenyl groups of triphenylphosphine in $\mathrm{CoH(N_2)(Ph_3P)_3}$,[55] $\mathrm{RuH_2(N_2)(Ph_3P)_3}$,[56] and $\mathrm{RuHCl(Ph_3P)_3}$[46] may proceed *via* reactive hydrido aryls of cobalt(III) and ruthenium(IV), respectively. The reversible loss of hydrogen from the complexes $\mathrm{FeH_2N_2[(C_2H_5)(C_6H_5)_2P]_3}$[57] and $\mathrm{RuHCl[(PhO)_3P]_3}$,[58] and the irreversible loss of methane from $\mathrm{Rh(CH_3)(Ph_3P)_3}$,[59] to give *ortho*-bonded phenyl species may likewise involve intermediate hydrido aryls of iron(IV), ruthenium(IV), and rhodium(III).

The process of hydrogen abstraction in the complexes of Ir(I), Ru(0), and Fe(0) may be regarded as a special case of oxidative addition to a square-planar metal complex, or as the insertion of the metal into a C–H bond. If this is regarded as an electrophilic attack on the metal, the reactions should be assisted by electron-releasing groups in the *para* position of the phenyl ring, a trend which is apparent from the rate data (Table VII). The fact that $\mathrm{IrCl[(\textit{p}\text{-}CH_3OC_6H_4)_3P]_3}$ isomerizes more slowly than $\mathrm{IrCl[(\textit{p}\text{-}CH_3C_6H_4)_3P]_3}$ indicates that inductive and mesomeric effects can affect the charge on the metal. It has been noted previously that electron-releasing groups in the *para* positions increase the rates of hydrogenation of cyclohexene using catalysts of the type $\mathrm{RhCl[(aryl)_3P]_3}$.[16] Moreover, the lack of any marked kinetic isotope effect in the isomerization of $\mathrm{IrCl(Ph_3P)_3}$, and the fact that addition of the C–H bond to the metal gives exclusively a *cis* adduct, suggests a three-center mechanism for the migration of hydrogen between ligand and metal, with a transition state similar to VII. This is similar to the transition state suggested for the transfer of hydrogen from $\mathrm{RhH_2Cl(Ph_3P)_2}$ (solvent) to olefins in the hydrogenation of olefins catalyzed by $\mathrm{RhCl(Ph_3P)_3}$.[5]



VII

Finally, we note the analogy between hydrogen transfer between metal and coordinated ligand and the dissociative π-complex mechanism proposed for the hydrogen–deuterium exchange of aromatic compounds on metal surfaces.[60] Especially relevant to the case of $\mathrm{IrCl(Ph_3P)_3}$ is the observed H–D exchange at the *ortho* positions of aniline and phenol with $\mathrm{D_2O}$ on nickel-kieselguhr.[61]

Experimental Section

Physical Measurements. Infrared spectra in the range 4000–400 $\mathrm{cm^{-1}}$ were measured on samples prepared in Nujol and hexachlorobutadiene mulls using the following grating instruments: Perkin-Elmer 337 (London), Perkin-Elmer 457, and Perkin-Elmer 225 (Canberra). In the range 450–200 $\mathrm{cm^{-1}}$ samples were run as Nujol mulls between high density polythene windows on a Grubb-Parsons DM2 spectrophotometer (London) or a Perkin-Elmer 225 instrument (Canberra). Proton resonance spectra (0–10 ppm downfield of $\mathrm{(CH_3)_4Si}$ as internal reference) were measured on a Varian Associates HA-100 at 100 MHz. The high-field lines were recorded at 60 MHz on Perkin-Elmer R10 and JEOL C60 HL instruments, using $\mathrm{(CH_3)_4Si}$ as internal reference; a computer of average transients technique was used for the triarylphosphine and triphenylarsine complexes. ^{19}F spectra were recorded on the Varian HA-100 instrument at 94.07 MHz. Electron-spin resonance spectra were measured on Varian 4502 (X band) and 4503 (Q band) instruments. Ultraviolet and visible spectra were measured on a Unicam SP-800 spectrophotometer. Mass spectra were recorded on a GEC/AEI MS-902 instrument.

X-Ray powder photographs of specimens *ca.* 1 mm thick were recorded on Ilford Industrial 9 film in a Nonius Guinier Mark II camera using nickel-filtered Cu Kα radiation from a Philips PW 1009 X-ray generator. Molecular weights were measured at 25° in Analar solvents (*ca.* 0.02 *M*) using a vapor pressure osmometer (Model 301A, Mechrolab) calibrated with benzil. Molecular conductivities were measured on *ca.* 10^{-3} *M* solutions in Analar nitrobenzene at 25° using a Wayne–Kerr Universal Bridge, Type B-221, and dip-type bright platinum electrodes. The cell constant was determined using aqueous potassium chloride solution. Magnetic susceptibilities at room temperature were measured on powdered samples in a Gouy tube calibrated with $\mathrm{Hg[Co(NCS)_4]}$. Melting points (uncorrected) were measured on a Gallenkamp hot-stage apparatus using samples sealed in evacuated capillaries. Microanalyses were carried out in the following laboratories: Max-Planck Institut für Kohlenforschung, Mülheim, Germany; Weiler and Strauss, Oxford, England; Department of Chemistry, University College London; John Curtin School of Medical Research, Canberra (Dr. Joyce Fildes and associates); and the Ana-

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(53) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(54) G. Hata, H. Kondo, and A. Miyake, *J. Amer. Chem. Soc.*, **90**, 2278 (1968).

(55) G. W. Parshall, *ibid.*, **90**, 1669 (1968).

(56) W. H. Knoth, *ibid.*, **90**, 7172 (1968).

(57) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).

(58) W. H. Knoth and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 2400 (1969).

(59) W. Keim, *J. Organometal. Chem.* (Amsterdam), **14**, 179 (1968).

(60) J. L. Garnett and W. A. Sollich, *Aust. J. Chem.*, **18**, 1003 (1965), and references cited therein.

(61) C. J. McDonald and J. S. Shannon, *ibid.*, **20**, 297 (1967).

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General. Unless stated otherwise, all reactions were carried out in an atmosphere of nitrogen, and all complexes were washed with ether or pentane and dried at 25° (10^{-3} mm). Ether was sodium dried and THF was distilled from $LiAlH_4$ and stored under nitrogen.

Ligands. Triphenylphosphine, triphenylarsine, and triphenylstilbene were used as received. The *para*-substituted triphenylphosphines were prepared as described in the literature.[62]

Pentadeuteriotriphenylphosphine. Pentadeuteriobromobenzene was prepared by brominating hexadeuteriobenzene, following the procedure of Vogel.[63] Phosphorus trichloride (2.94 g, 0.0215 mol) in 20 ml of ether was added over a period of 100 min to the Grignard reagent from pentadeuteriobromobenzene (11.6 g, 0.0716 mol) in 20 ml of ether and magnesium (2.1 g, 0.09 g-atom). The mixture was hydrolyzed at 0° with D_2O (10 ml) and evaporated to dryness. The residue was extracted with five 100-ml portions of boiling *n*-hexane and solvent evaporated to give colorless crystals (4.2 g, 71%): mp 76°, isomorphous with triphenylphosphine (mp 77°). *Anal.* Calcd for $C_{18}D_{15}P$: C, 78.0; P, 11.2. Found: C, 77.6; P, 11.3.

Mono-*o*-deuteriotriphenylphosphine. *o*-Deuteriochlorobenzene was first prepared as follows. A Grignard reagent prepared from *o*-bromochlorobenzene (50 g, 0.261 mol) in 70 ml of ether and magnesium (6.9 g, 0.287 g-atom) was hydrolyzed with deuterioacetic acid (CH_3CO_2D) (19.1 g, 0.313 mol) in 50 ml of ether at *ca.* −10° with vigorous stirring. The mixture was filtered and the residue was washed with 100 ml of ether. The ethereal solution was washed successively with two 50-ml portions of 10% aqueous $NaHCO_3$ and two 50-ml portions of water, and dried ($MgSO_4$). Distillation gave 14 g (34%) of *o*-deuteriochlorobenzene: bp 133–135° (760 mm).

Phosphorus trichloride (2.06 g, 0.0185 mol) in 20 ml of THF was added to the Grignard reagent prepared by refluxing *o*-deuteriochlorobenzene (9.7 g, 0.0617 mol) and magnesium (1.63 g, 0.068 g-atom) in 25 ml of THF for 5 hr. The mixture was worked up as described for $(C_6D_5)_3P$ to give colorless crystals (2.0 g, 66.5%), mp 76–77°, isomorphous with triphenylphosphine. *Anal.* Calcd for $C_{18}H_{12}D_3P$: C, 81.6; H, 6.8; P, 11.7. Found: C, 81.5; H, 6.9; P, 11.6.

Chlorotris(triphenylphosphine)iridium(I), $IrCl(Ph_3P)_3$ from μ,μ'-Dichloro-bis(1,5-cyclooctadiene)diiridium(I) $[IrCl(C_8H_{12})]_2$. Triphenylphosphine (1.42 g) was heated under reflux with $[IrCl(C_8H_{12})]_2$ (0.25 g) in 30 ml of petroleum ether (bp 80–100°) for 1 hr. The orange crystalline product (0.60 g, 73%) was filtered and stored *in vacuo.* The complex is soluble in benzene and chloroform, less soluble in acetone, and slightly soluble in ether and alcohol. It melts with decomposition at 212°.

Bromotris(triphenylphosphine)iridium(I) $IrBr(Ph_3P)_3$ from Chloro-1,5-cyclooctadiene(triphenylphosphine)iridium(I), $IrCl(C_8H_{12})(Ph_3P)$. The complex $IrCl(C_8H_{12})(Ph_3P)$ (0.3 g) was heated with lithium bromide (0.5 g) in 10 ml of acetone under reflux for 1 hr. The solution was evaporated to dryness at 25° (15 mm) and the residue was washed with water. It was then dissolved in acetone (10 ml), dried ($MgSO_4$), and evaporated to dryness. Recrystallization from acetone–petroleum ether (bp 60–80°) gave red-brown crystals (0.4 g, 80%) of $IrBr(C_8H_{12})(Ph_3P)$. These were then refluxed with excess triphenylphosphine (0.75 g) in 20 ml of petroleum ether (bp 80–100°) for 1 hr, giving red-brown crystals (0.48 g, 74%) of $IrBr(Ph_3P)_3$, isomorphous with $IrCl(Ph_3P)_3$.

General Procedure for the Preparation of the Complexes $IrClL_3$ from Chlorobis(cyclooctene)iridium(I), $IrCl(C_8H_{14})_2$. A suspension of $IrCl(C_8H_{14})_2$ (0.3 g, 1 mol) and excess ligand (~6 mol) in 30 ml of petroleum ether (bp 60–80°) was stirred at room temperature. The solution immediately turned orange and orange or red crystals precipitated. After 8 hr, the product was filtered and stored *in vacuo.* Yields were 70–80%. Analytical data are in Table I.

Reaction of $IrCl(Ph_3P)_3$ with CO to give $IrCl(CO)(Ph_3P)_2$. To 10 ml of benzene saturated with CO at room temperature and pressure was added 0.3 g of $IrCl(Ph_3P)_3$. The color of the solution changed almost immediately from red-brown to yellow. Carbon monoxide was passed for 30 min and 30 ml of petroleum ether (bp 40–60°) added to precipitate a yellow solid. Recrystallization from chloroform–ethanol (1:1) gave lemon yellow crystals (0.21 g, 81%), isomorphous with an authentic sample of *trans*-$IrCl(CO)(Ph_3P)_2$ [ν(CO) 1970 cm^{-1}]. *Anal.* Calcd for $C_{37}H_{30}ClOP_2Ir$: C, 56.9; H, 3.9. Found: C, 56.9; H, 3.7.

Preparation of Chloro(phosphorus trifluoride)bis(triphenylphosphine)iridium(I). The above procedure was repeated using phosphorus trifluoride in place of carbon monoxide. Recrystallization from benzene–petroleum ether (bp 60–80°) (1:1) gave yellow crystals of $IrCl(PF_3)(Ph_3P)_2$ (82%), mp 134° dec, isomorphous with $RhCl(PF_3)(Ph_3P)_2$.[64] The complex is soluble in benzene, chloroform, and ether, and insoluble in pentane. *Anal.* Calcd for $C_{36}H_{30}ClF_3P_3Ir$: C, 51.4; H, 3.6; Cl, 4.2; P, 11.0; mol wt, 840. Found: C, 51.1; H, 3.6; Cl, 4.3; P, 9.1; mol wt ($CHCl_3$), 827

Preparation of Chloronitro(nitrosyl)bis(triphenylphosphine)iridium(III) from Nitric Oxide and $IrCl(Ph_3P)_3$. Nitric oxide (Matheson) was passed through 20 ml of sodium-dried benzene which had been flushed with nitrogen for 2 hr. Addition of 0.3 g of $IrCl(Ph_3P)_3$ caused the initially dark red solution to turn orange within 2 min. After 1 hr, beige crystals of the product (0.19 g, 78%) were obtained by slow addition of petroleum ether (bp 60–80°). The complex is soluble in chloroform and acetone, insoluble in ether. It melts at 210° (darkening at 170°). *Anal.* Calcd for $C_{36}H_{30}O_3ClN_2P_2Ir$: C, 52.2; H, 3.7; Cl, 4.3; N, 3.4; mol wt, 828. Found: C, 53.6; H, 3.7; Cl, 4.3; N, 3.3; mol wt ($CHCl_3$), 824. The molar conductance is 0.3 $ohm^{-1}\,cm^2$.

Reaction of $IrCl(Ph_3P)_3$ with Hydrogen to Give Dihydridochlorotris(triphenylphosphine)iridium(III). To 20 ml of benzene saturated with hydrogen at 25° (1 atm) was added $IrCl(Ph_3P)_3$ (0.4 g). The solution turned pale yellow within 10 min. After 2 hr the product was precipitated with 30 ml of petroleum ether and recrystallized from benzene to give colorless crystals (0.30 g, 75%) isomorphous with an authentic sample of $IrH_2Cl(Ph_3P)_3$. *Anal.* Calcd for $C_{54}H_{47}ClP_3Ir$: C, 63.8; H, 4.7; Cl, 3.5. Found: C, 65.0; H, 4.4; Cl, 3.1. The ir spectrum showed bands (cm^{-1}) due to ν(Ir–H) at 2215 s and 2110 s (Nujol). The corresponding dideuteride was prepared similarly in 80% yield using deuterium. *Anal.* Calcd for $C_{54}H_{45}D_2ClP_3Ir$: C, 63.8; H, 4.7; Cl, 3.5. Found: C, 63.7; H, 4.9; Cl, 3.3. Bands due to ν(Ir–D) were seen at 1584 s, and 1520 s cm^{-1}.

Reaction of $IrCl(Ph_3As)_3$ with Hydrogen to Give Chlorodihydridotris(triphenylarsine)iridium(III). The complex $IrCl(Ph_3As)_3$ was prepared *in situ* from 0.14 g of $IrCl(C_8H_{14})_2$ and 0.35 g of triphenylarsine in deoxygenated benzene (20 ml). Hydrogen was bubbled through the solution, which rapidly turned pale yellow. Addition of petroleum ether (bp 60–80°; 30 ml) precipitated a pale cream solid, which was recrystallized from benzene–petroleum ether (bp 60–80°) to give colorless, light-sensitive crystals (0.18 g, 71%), mp 183° dec. *Anal.* Calcd for $C_{54}H_{47}As_3ClIr$: C, 56.4; H, 4.1; Cl, 3.1; mol wt, 1149. Found: C, 57.7; H, 4.6; Cl, 3.2; mol wt ($CHCl_3$), 1081. Ir maxima (cm^{-1}) at 2160 m and 2120 s were due to ν(Ir–H) and those at 814 m and 869 s were due to δ(Ir–H) (Nujol).

Reaction of $IrCl(Ph_3Sb)_3$ with Hydrogen to Give Chlorodihydridotris(triphenylstibine)iridium(III). The procedure was as described above, using triphenylstibine in place of triphenylarsine. The complex was obtained in 68% yield as off-white crystals after recrystallization from benzene–petroleum ether. It melts at 145° dec, is soluble in chloroform, and insoluble in ether. *Anal.* Calcd for $C_{54}H_{47}ClSb_3Ir$: C, 50.3; H, 3.7; Cl, 2.8; mol wt, 1289. Found: C, 50.2; H, 3.7; Cl, 2.8; mol wt ($CHCl_3$), 1268. Ir maxima (cm^{-1}) are at 2090 vs [ν(Ir–H)] and 810 s [δ(Ir–H)] in Nujol.

Reaction of $IrCl(Ph_3P)_3$ with Hydrogen Chloride to Give Hydridodichlorotris(triphenylphosphine)iridium(III). Benzene (10 ml) was saturated with HCl and $IrCl(Ph_3P)_3$ (0.5 g) added; the red-brown solution immediately turned yellow. After 30 min, 15 ml of petroleum ether (bp 60–80°) was added and the precipitate recrystallized from benzene–petroleum ether (1:1) to give pale yellow crystals (0.35 g, 68%). *Anal.* Calcd for $C_{54}H_{46}Cl_2P_3Ir$: C, 61.7; H, 4.4; Cl, 6.7. Found: C, 61.2; H, 4.1; Cl, 7.1. A band due to ν(Ir–H) was seen at 2230 s cm^{-1}.

The analogous deuterio compound was prepared by using DCl in place of HCl. *Anal.* Calcd for $C_{54}H_{45}DCl_2P_3Ir$: C, 61.7; H, 4.4. Found: C, 61.7; H, 5.3. A band due to ν(Ir–D) was seen at 1600 cm^{-1}.

Reaction of $IrCl(Ph_3As)_3$ with Hydrogen Chloride to Give Hydridodichlorotris(triphenylarsine)iridium(III). To a solution of $IrCl(Ph_3As)_3$ prepared *in situ* from $IrCl(C_8H_{14})_2$ (0.10 g) and triphenylarsine (0.27 g) in deoxygenated benzene (20 ml) was added a solution of HCl in ethanol (1.1 mol). The solution immediately turned

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(62) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

(63) A. I. Vogel, "Elementary Practical Organic Chemistry," Longmans, London, 1961, p 228.

(64) P. A. Longstaff, Thesis, University of London, 1968.

yellow. Petroleum ether (bp 60–80°) (10 ml) was added and the solution evaporated to $\sim$15 ml at 25° (15 mm), giving pale yellow crystals (0.20 g, 78%). *Anal.* Calcd for $C_{54}H_{46}As_3Cl_2Ir$: C, 54.8; H, 3.8; Cl, 6.0; mol wt, 1183. Found: C, 55.4; H, 4.3; Cl, 6.1; mol wt, 1081. A band due to ν(Ir–H) was seen at 2185 cm^{-1} (Nujol).

Reaction of $IrCl(Ph_3Sb)_3$ with Hydrogen Chloride to Give Hydridodichlorotris(triphenylstibine)iridium(III). The reaction was carried out as above, using 0.1 g of $IrCl(C_8H_{14})_2$ and 0.62 g of triphenylstibine in 10 ml of benzene. Recrystallization from benzene–petroleum ether (bp 60–80°) gave 0.16 g (62%) of pale yellow crystals. *Anal.* Calcd for $C_{54}H_{46}Cl_2Sb_3Ir$: C, 48.9; H, 3.4; Cl, 5.4; mol wt, 1324. Found: C, 48.0; H, 3.4; Cl, 6.0; mol wt ($CHCl_3$), 1268. The complex is more soluble in organic solvents than its triphenylphosphine and triphenylarsine analogs, and is slightly soluble in ether. A band due to ν(Ir–H) was seen at 2098 s cm^{-1} (Nujol).

Reaction of $IrCl(Ph_3P)_3$ with Ethanol. The complex $IrCl(Ph_3P)_3$ (0.5 g) was heated under reflux with 10 ml of pure deoxygenated ethanol for 1 hr. A slow stream of nitrogen was passed continuously through the mixture and into 10 ml of Brady's reagent. At the boiling point, the solution turned yellow and after 1 hr was colorless. An orange-yellow precipitate formed in the Brady's reagent, which was filtered off and recrystallized from ethanol; mp and mmp 165° (lit.[65] value for acetaldehyde 2,4-dinitrophenylhydrazone, 168°). The iridium complex was isolated by evaporating the solvent at 15 mm and recrystallizing the residue from chloroform–petroleum ether (bp 60–80°) to give colorless crystals (0.44 g, 88%) isomorphous with an authentic sample of $IrH_2Cl(Ph_3P)_3$. *Anal.* Calcd for $C_{54}H_{47}ClP_3Ir$: C, 63.8; H, 4.7; Cl, 3.5. Found: C, 63.7; H, 5.0; Cl, 4.1. No precipitate formed in the Brady's reagent when the experiment was repeated in the absence of $IrCl(Ph_3P)_3$.

Reaction of $IrCl(Ph_3P)_3$ with Chlorine to Give Trichlorobis(triphenylphosphine)iridium(III) and *trans*-Tetrachlorobis(triphenylphenylphosphine)iridium(IV). The complex $IrCl(Ph_3P)_3$ (0.5 g) was dissolved in benzene (30 ml) under nitrogen and chlorine was bubbled through the solution. The initially red-brown solution lightened in color and then darkened. After 5 min, orange crystals precipitated from the purple solution. After 30 min, these were filtered and washed with benzene. The yield of $IrCl_3(Ph_3P)_2$ was 0.12 g (30%), mp 224–230° dec. *Anal.* Calcd for $C_{36}H_{30}Cl_3P_2Ir$: C, 52.5; H, 3.7; Cl, 12.8; P, 7.5; mol wt, 824. Found: C, 52.4; H, 3.8; Cl, 13.4; P, 7.7; mol wt ($CHCl_3$), 787. The complex is insoluble in benzene, ether, and acetone, but slowly dissolves in chloroform, from which addition of ether precipitates yellow crystals, having the same analytical composition but different X-ray powder photograph. Bands (cm^{-1}) due to ν(Ir–Cl) in the far-ir are the following: orange form, 326 s, 281 s, 256 ms, and 232 m; yellow form, 331 s, 266 s, and 230 w. The purple filtrate was chromatographed on silica gel in benzene and the product precipitated as dark purple crystals (0.08 g, 19%) by slowly adding petroleum ether (bp 40–60°): mp 150° (darkening at 120°). *Anal.* Calcd for $C_{36}H_{30}Cl_4P_2Ir$: C, 50.4; H, 3.5; Cl, 16.5; P, 7.3; mol wt, 859. Found: C, 49.7; H, 3.4; Cl, 16.2; P, 7.1; mol wt ($CHCl_3$), 820. The molar conductance is 0.4 ohm^{-1} cm^2; the band in the ir at 329 cm^{-1} is due to ν(Ir–Cl).

Preparation of $IrCl_3(Ph_3P)_2$ and *trans*-$IrCl_4(Ph_3P)_2$ from $IrHCl_2(Ph_3P)_3$. The complex $IrHCl_2(Ph_3P)_3$ (6.7 g) was suspended in benzene (200 ml), saturated with chlorine, and left at room temperature for 5 days. The yellow-orange precipitate of $IrCl_3(Ph_3P)_2$ (2.6 g, 50%) was filtered from the purple solution. Crystals of $IrCl_4(Ph_3P)_2$ (1.2 g, 21%) were isolated by chromatography as above.

Reaction of $IrCl(Ph_3P)_3$ with Nitrosyl Chloride to Give *trans*-$IrCl_4(Ph_3P)_2$. To 20 ml of deoxygenated benzene was added 0.3 g of $IrCl(Ph_3P)_3$. Nitrosyl chloride was passed for 1 hr at 25° and the purple solution left overnight. Slow addition of 20 ml of petroleum ether (bp 60–80°) gave purple crystals (0.16 g, 62%), isomorphous with *trans*-$IrCl_4(Ph_3P)_2$ obtained above.

Reaction of $IrCl_3(Ph_3P)_2$ with Chlorine to Give *trans*-$IrCl_4(Ph_3P)_2$. A suspension of 0.1 g of $IrCl_3(Ph_3P)_2$ in 10 ml of benzene was saturated with chlorine. After 2 days the purple solution was filtered and the product (0.09 g, 87%) isolated by addition of petroleum ether.

Reaction of $IrCl(Ph_3As)_3$ with Chlorine to Give *trans*-Tetrachlorobis(triphenylarsine)iridium(IV). The reaction was carried out as described above for the chlorination of $IrCl(Ph_3P)_3$. No orange intermediate $IrCl_3(Ph_3As)_2$ was observed. From 0.5 g of $IrCl(Ph_3As)_3$ was obtained 0.21 g (47%) of *trans*-$IrCl_4(Ph_3As)_2$, mp 165° dec. *Anal.* Calcd for $C_{36}H_{30}As_2Cl_4Ir$: C, 45.5; H, 3.2; Cl, 15.0; mol wt, 949. Found: C, 44.2; H, 3.2; Cl, 16.5; mol wt ($CHCl_3$), 820.

Reactions of Trichlorobis(triphenylphosphine)iridium(III). (a) Carbon Monoxide. Carbon monoxide was bubbled through a solution of $IrCl_3(Ph_3P)_2$ (0.2 g) in 20 ml of chloroform for 1 hr. The pale yellow solution was evaporated to dryness at 25° (15 mm) and the residue was recrystallized from benzene–petroleum ether (bp 60–80°) to give 0.16 g (77%) of pale yellow crystalline trichlorocarbonylbis(triphenylphosphine)iridium(III) (phosphines *cis*). *Anal.* Calcd for $C_{36}H_{30}Cl_3OP_2Ir$: C, 52.3; H, 3.6; Cl, 12.5; mol wt, 851. Found: C, 53.2; H, 3.7; Cl, 13.5; mol wt ($CHCl_3$), 819. Bands (cm^{-1}) in the far-ir due to ν(Ir–Cl) occurred at 324 s and 275 s. In Nujol, ν(CO) was at 2100 cm^{-1}.

(b) Pyridine. To $IrCl_3(Ph_3P)_2$ (0.2 g) in benzene (20 ml) was added pyridine (0.5 ml) and the mixture refluxed for 1 hr. The yellow solid which precipitated on cooling was filtered, washed with ether, and recrystallized from benzene to give yellow crystalline trichloropyridinebis(triphenylphosphine)iridium(III), mp 264–266° dec. *Anal.* Calcd for $C_{41}H_{35}Cl_3NP_2Ir$: C, 54.6; H, 3.9; Cl, 11.8; N, 1.3; P, 6.9; mol wt, 901. Found: C, 54.4; H, 4.0; Cl, 12.1; N, 1.6; P, 7.2; mol wt ($CHCl_3$), 790. Bands (cm^{-1}) in the far-ir are at 328 s, 302 m, 282 m br, and 245 w.

(c) Triphenylphosphine. Triphenylphosphine (0.63 g) and $IrCl_3(Ph_3P)_2$ (0.2 g) were heated in 20 ml of benzene under reflux for 1 hr. Slow addition of 30 ml of petroleum ether (bp 40–60°) to the cold solution gave 0.21 g (57%) of yellow crystalline $IrCl_3(Ph_3P)_3$, possibly contaminated with a small amount of $IrCl_3(Ph_3P)_2$. *Anal.* Calcd for $C_{54}H_{45}Cl_3P_3Ir$: C, 59.7; H, 4.2; Cl, 9.8; mol wt, 1087. Found: C, 56.6; H, 4.3; Cl, 10.3; mol wt ($CHCl_3$), 810. Bands (cm^{-1}) in the far-ir are at 325 s, 303 w, and 278 s.

Reaction of *trans*-$IrCl_4(Ph_3P)_2$ with Carbon Monoxide. To 20 ml of benzene saturated with CO at 25° (1 atm) was added *trans*-$IrCl_4(Ph_3P)_2$ (0.1 g) and the mixture left under CO overnight. Addition of 40 ml of petroleum ether (bp 40–60°) to the yellow solution and recrystallization of the resulting precipitate from 1:1 benzene–petroleum ether (bp 60–80°) gave 0.08 g (81%) of yellow crystalline trichlorocarbonylbis(triphenylphosphine)iridium(III) (phosphines *trans*). *Anal.* Found: C, 51.7; H, 3.9; Cl, 12.8. Bands (cm^{-1}) in the far-ir due to ν(Ir–Cl) are at 326 vs, 302 s.

Hydrogen Abstraction Reactions. The complex $IrCl(Ph_3P)_3$ (0.5 g) was refluxed in deoxygenated benzene (10 ml) under nitrogen for 1 hr. The red-brown solution had become yellow before the benzene boiled. The solution was allowed to cool, 20 ml of petroleum ether (bp 80–100°) added, and the solution evaporated to $\sim$15 ml at 25° (15 mm). The cream product was filtered and recrystallized from benzene to give colorless crystals (0.39 g, 78%), mp 250° (darkening at 212°). The same product was obtained in 92% yield by refluxing $IrCl(Ph_3P)_3$ in cyclohexane for 2 hr, or by dissolving $IrCl(Ph_3P)_3$ in chloroform, benzene, or acetone and allowing the mixture to stand under nitrogen for 24 hr. The molar conductance is 0.7 ohm^{-1} cm^2.

The corresponding hydrides derived from $IrClL_3$ [L = $(C_6D_5)_3P$, $(o\text{-}DC_6H_4)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(p\text{-}CH_3OC_6H_4)_3P$, $(p\text{-}FC_6H_4)_3P$, $(C_6H_5)_3As$, and $(C_6H_5)_3Sb$] were made by heating $IrClL_3$ (prepared *in situ* from $IrCl(C_8H_{14})_2$ and the ligand) in benzene or cyclohexane under nitrogen. The duration of heating was 2 hr in the case of the phosphine complexes (yield 90%), and 6 hr in the case of the triphenylarsine and triphenylstibine complexes (yields 59 and 52%, respectively). Analytical data are in Table IV.

Reactions of $IrHCl[(o\text{-}C_6H_4)Ph_2P](Ph_3P)_2$. (a) Carbon Monoxide. Benzene (20 ml) was saturated with CO at 25° (1 atm) and 0.2 g of "$IrHCl(Ph_3P)_3$" added. There was no reaction at 25°. On heating, the color changed from pale to lemon yellow after $\sim$10 min. After refluxing for 1 hr, the solution was cooled. The product was precipitated by adding petroleum ether (bp 60–80°) (40 ml) and recrystallized from benzene–ethanol (1:1). The complex was isomorphous with *trans*-$IrCl(CO)(Ph_3P)_2$.

(b) Ethanol. The complex "$IrHCl(Ph_3P)_3$" (0.15 g) was heated in deoxygenated ethanol (30 ml) for 1 hr. A slow stream of nitrogen was passed continuously through the mixture and into 10 ml of Brady's reagent. The initial suspension gave an orange solution after $\sim$1 min, a colorless solution after 5 min, and deposited colorless crystals on further heating. After 20 min, a precipitate formed in the Brady's reagent and was identified as the 2,4-dinitrophenylhydrazone of acetaldehyde (mp and mmp 166°). The colorless

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(65) Reference 61, p 334.

crystals, mp 208° dec, were isomorphous with an authentic sample of $IrH_2Cl(Ph_3P)_3$. *Anal.* Calcd for $C_{54}H_{47}ClP_3Ir$: C, 63.8; H, 4.7; Cl, 3.5. Found: C, 62.6; H, 5.2; Cl, 2.9.

(c) **Hydrogen.** There was no change in the infrared spectrum of the solution when hydrogen was passed at 25° (1 atm) through a solution of "$IrHCl(Ph_3P)_3$" (0.2 g) in 30 ml of benzene. Refluxing for 1 hr and slow addition of petroleum ether (bp 60–80°) gave colorless, light-sensitive crystals (0.17 g, 85%) isomorphous with $IrH_2Cl(Ph_3P)_3$. *Anal.* Found: C, 64.1; H, 4.6; Cl, 3.8.

(d) **Deuterium.** The reaction was carried out as under (c) to give a complex isomorphous with $IrH_2Cl(Ph_3P)_3$. From 0.25 g of "$IrHCl(Ph_3P)_3$" was obtained 0.14 g (70%) of $IrH(D)H(D)Cl(Ph_3P)_3$ (see text).

(e) **Hydrogen Chloride.** Dry hydrogen chloride was passed into a refluxing solution of "$IrHCl(Ph_3P)_3$" (0.3 g) in benzene (20 ml) for 30 min. The color changed from pale yellow to yellow. After 40 ml of petroleum ether (bp 80–100°) had been added, the solution was evaporated to $\sim$30 ml at 15 mm; the solid was filtered off and recrystallized from benzene–petroleum ether (bp 60–80°) to give 0.22 g (71%) of pale yellow $IrHCl_2(Ph_3P)_3$. *Anal.* Calcd for $C_{54}H_{46}Cl_2P_3Ir$: C, 61.7; H, 4.4; Cl, 6.7. Found: C, 61.4; H, 4.6; Cl, 6.4.

(f) **Deuterium Chloride.** Reaction of DCl with 0.3 g of "$IrHCl(Ph_3P)_3$" as under (e) gave 0.19 g (62%) of $IrDCl_2(Ph_3P)_3$, isomorphous with $IrHCl_2(Ph_3P)_3$.

Kinetic Measurements. The rates of hydrogen abstraction for the phosphine complexes were measured by following the appearance of the band due to ν(Ir–H) at *ca.* 2200 cm^{-1}. Only one concentration of each complex was used (1.44×10^{-3} *M*), this being near the limit of solubility of the $(p\text{-}FC_6H_4)_3P$ complex. Lower concentrations would have made the initial stages of reaction difficult to follow. The complexes were dissolved in degassed benzene; the solution was placed in a 1-mm cell having sodium chloride windows and quickly transferred to the sample beam of the Perkin-Elmer 225 spectrophotometer. With a 1-mm cell containing pure benzene in the reference beam, the spectrum was scanned continuously between 2500 and 1800 cm^{-1}. The temperature in the sample beam was 39.5 ± 0.5°. The infinity reading was taken as six half-lives (some decomposition being evident thereafter), and the reproducibility was within experimental error.

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Oxygen Complexes of Nickel and Palladium. Formation, Structure, and Reactivities

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Abstract: Novel oxygen complexes of formula $M(O_2)(RNC)_2$ (R = *t*-butyl and cyclohexyl for M = Ni; R = *t*-butyl for M = Pd) were prepared by oxygenation of the corresponding zerovalent isocyanide complexes, $M(RNC)_4$ or $M(RNC)_2$. These diamagnetic, thermally relatively unstable oxygen complexes are intermediates in the catalytic oxygenation of alkyl isocyanides. They are insoluble in nonpolar solvents and not monomeric in the solid state. The ir, nmr, and electronic spectra and magnetic data were collected to deduce essentially square-planar structures with an intermolecular axial interaction through the O_2 ligand. The chemical behaviors toward reagents of varying donor–acceptor properties were studied to show that reagents of strong electron affinities release oxygen while electron donor reagents, *e.g.*, PR_3 and RNC, cause oxygen-atom transfer. The reaction of $Ni(O_2)(t\text{-}BuNC)_2$ with CH_3NC involves incipient formation of $Ni(O_2)(t\text{-}BuNC)_2(CH_3NC)_2$ and $Ni(O_2)(t\text{-}BuNC)(CH_3NC)_2$ prior to the oxygen-atom transfer. Ligation of RNCO to Ni(O) was confirmed by isolation of $Ni(RNCO)(RNC)_2$, a product of oxygen-atom transfer. The isocyanate ligand was shown to be quite susceptible to substitution with RNC as required for the catalytic oxygenation of RNC.

Recently it was found[1] that alkyl isocyanides can be catalytically oxygenated with molecular oxygen into the corresponding alkyl isocyanates in the presence of a low-valent nickel complex such as bis(1,5-cyclooctadiene)nickel or tetrakis(isocyanide)nickel. Eventually a peroxo complex, $Ni(O_2)(t\text{-}BuNC)_2$, was isolated as pale green crystals. Closely related peroxophosphine complexes, $M(O)_2(PPh_3)_2$(M = Ni, Pd, and Pt), have been reported[2,3] to be formed from $M(PPh_3)_{3\sim4}$ and an oxygen molecule. Analogous oxidative additions of ligands (L), *e.g.*, tetracyanoethylene, carbon disulfide, and others, to $M(PPh_3)_{3\sim4}$ giving $ML(PPh_3)_2$ have been extensively surveyed.[4-15] The per-

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(1) S. Otsuka, A. Nakamura, and Y. Tatsuno, *Chem. Commun.*, 836 (1967).

(2) S. Takahashi, K. Sonogashira, and N. Hagihara, *J. Chem. Soc. Jap.*, **87**, 610 (1966).

(3) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, **79**, 62 (1967).

(4) S. Takahashi, K. Sonogashira, and N. Hagihara, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 23, 69 (1966).

(5) C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Commun.*, 407 (1967).

(6) M. C. Baird and G. Wilkinson, *ibid.*, 514 (1966); *J. Chem. Soc.*, 865 (1967).

(7) J. J. Levison and S. D. Robinson, *Chem. Commun.*, 198 (1967).

(8) T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41**, 296 (1968).

(9) S. Cenini, R. Ugo, F. Bonati, and G. Lamonica, *Inorg. Nucl. Chem. Lett.*, **3**, 191 (1967).

(10) S. Takahashi and N. Hagihara, *J. Chem. Soc. Jap.*, *Pure Chem. Sect.*, **88**, 1306 (1967).