Chlorotris(triphenylphosphine)iridium(I): an Example of Hydrogen Transfer to a Metal from a Co-ordinated Ligand

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ETHANOLIC rhodium(III) chloride is reduced by an excess (> 4 moles) of triphenylphosphine to the rhodium(I) complex $Rh(PPh_3)_3Cl$.[1] Under similar preparative conditions, iridium(III) chloride forms the octahedral hydrides, $Ir(PPh_3)_3HCl_2$ and $Ir(PPh_3)_3H_2Cl$,[2] which can be regarded as adducts of $Ir(PPh_3)_3Cl$ with HCl and H_2 respectively. It has recently been suggested[3] that this parent iridium(I) compound may be formed in solution when the nitrogen complex, $Ir(PPh_3)_2N_2Cl$, is treated with triphenylphosphine.

We now report that the complex $Ir(PPh_3)_3Cl$ can be isolated by treating either of the cyclo-octa-1,5-diene complexes $(C_8H_{12}IrCl)_2$ or $C_8H_{12}Ir(PPh_3)Cl$[4] with an excess of triphenylphosphine in ligroin under reflux. The corresponding bromide, $Ir(PPh_3)_3Br$, can be obtained by a similar procedure starting from $C_8H_{12}Ir(PPh_3)Br$. The orange, crystalline complexes $Ir(PPh_3)_3X$ (X=Cl,Br) are isomorphous with each other, with $Rh(PPh_3)_3Br$, and with the unstable orange modification of $Rh(PPh_3)_3Cl$, but they are not isomorphous with the stable red modification of $Rh(PPh_3)_3Cl$.[1] A square-planar arrangement of ligands about the metal is assumed for all these compounds. The low-frequency infrared spectrum of $Ir(PPh_3)_3Cl$ shows a band at 276 cm.$^{-1}$ which is absent from the spectrum of $Ir(PPh_3)_3Br$, and is assigned to ν(Ir–Cl). This may be compared with ν(Rh–Cl) at 296 cm.$^{-1}$ in $Rh(PPh_3)_3Cl$ and ν(Ir–Cl) at 317 cm.$^{-1}$ in $Ir(PPh_3)_2(CO)Cl$.[5]

Many of the reactions of $Ir(PPh_3)_3Cl$ resemble those of $Rh(PPh_3)_3Cl$ in that one molecule of triphenylphosphine is readily displaced by other ligands. For example, reaction with CO at 25°/1 atm. gives the known complex $Ir(PPh_3)_2(CO)Cl$,[6] and reaction with PF_3 similarly gives yellow $Ir(PPh_3)_2(PF_3)Cl$, which is isomorphous with the corresponding rhodium(I) compound prepared from $Rh(PPh_3)_3Cl$ and PF_3.[7] Methyl iodide reacts with $Ir(PPh_3)_3Cl$ to give deep green crystals of formula $IrICl(CH_3)(PPh_3)_2(ICH_3)$ which are isomorphous with the corresponding rhodium complex.[8] However, unlike $Rh(PPh_3)_3Cl$, the iridium(I) complex is only partly dissociated in organic solvents; the molecular weights observed in approximately 0·02M-solutions in benzene and chloroform are 800—850 and 700—750 respectively [calc. for $Ir(PPh_3)_3Cl$: 1015]. The iridium(I) complex also loses co-ordinated triphenylphosphine on heating *in vacuo* far less readily than does the rhodium(I) complex.

The reactions of the new complex testify to the high affinity of iridium(III) for hydrogen. Reaction of $Ir(PPh_3)_3Cl$ with hydrogen chloride gas (25°, 1 atm.) gives the yellow hydride $Ir(PPh_3)_3HCl_2$ [ν(M–H) 2230 cm.$^{-1}$ (Nujol)], which is apparently isomeric with the known complex of this formula prepared by Vaska[2] [ν(M–H) 2200 cm.$^{-1}$]. Similar reactions with hydrogen or deuterium give the known[2] colourless dihydrido-complex $Ir(PPh_3)_3H_2Cl$ [ν(M–H) 2116, 2204 cm.$^{-1}$ (Nujol)] and its dideuterio-analogue [ν(M–D) 1580, 1520 cm.$^{-1}$ (Nujol)], respectively. The dihydride is also obtained, together with acetaldehyde, when $Ir(PPh_3)_3Cl$ is heated with ethanol. The hydrogen addition reaction is not reversible, and, unlike the rhodium(I) anologue,[1b] the iridium(I) complex is not a good catalyst for the homogeneous hydrogenation of olefins, presumably owing to the stability of the dihydride complex.†

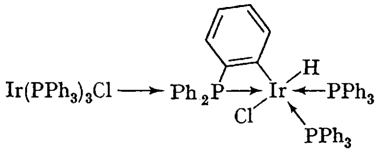
More remarkably, a colourless iridium(III) hydride of empirical formula $Ir(PPh_3)_3H_xCl$ is formed when $Ir(PPh_3)_3Cl$ is heated in cyclohexane, benzene, acetone, C_6D_6, and $(CD_3)_2CO$. The infrared spectrum shows a single strong band due to ν(M–H) at *ca.* 2190 cm.$^{-1}$ (C_6H_6) or 2240 cm.$^{-1}$ (Nujol). In the case of the cyclohexane reaction, a small amount of benzene is formed, presumably by a hydrogen abstraction reaction from the solvent, but no deuteride is formed on heating in the deuterated solvents. When the fully deuterated complex $Ir[P(C_6D_5)_3]_3Cl$ is heated in C_6H_6, the resulting complex shows strong bands due to ν(M–D) at 1600 cm.$^{-1}$ and 1540 cm.$^{-1}$, but no ν(M–H) bands are evident, showing that hydrogen (or deuterium) has been extracted from co-ordinated triphenylphosphine. An intense band in the infrared spectrum of the hydride at 728 cm.$^{-1}$, which is absent from the spectra of triphenylphosphine and its complexes, can be assigned to the C–H out of plane deformation mode of an *ortho*-disubstituted benzene,[9] and we therefore suggest the metal–carbon σ-bonded structure (I) (or possible isomers) for the hydride.

The loss of hydrogen from the *ortho*-position of the aromatic ring of a ligand with the concomitant formation of a metal–carbon σ-bond has been observed previously in the reaction of azobenzene with platinum and palladium salts,[10] although in this case the hydrogen did not migrate to the metal. Hydrogen to metal migration has also been observed in tautomeric equilibria involving complexes of ruthenium(0) and hydrido-alkyl complexes of ruthenium(II),[11] *e.g.*,

$$C_{10}H_8Ru(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2 \rightleftharpoons cis\text{-}RuH(C_{10}H_7)(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2 \quad (C_{10}H_8 = \text{naphthalene}).$$

In our case, however, the equilibrium lies entirely on the side of the hydride species.

Preliminary studies indicate that the iridium(I) complexes of other tertiary phosphines, such as Ph_2EtP, can be prepared by a similar method, and that they undergo a similar transformation even more readily than the triphenylphosphine complex.



(I)

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