Preparation and *X*-Ray Crystal and Molecular Structure of Di-μ-diphenylphosphido-bis(triphenylphosphinecarbonyliridium)

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Summary In the title compound, obtained from two different iridium hydrides in boiling DMF, the two metal atoms are connected by a formal double bond 2·551(1) Å long, and are bridged by two diphenylphosphido-ligands.

WHEN solutions of $Ir(CO)H(PPh_3)_3$ (A),[1] or $IrH_3(PPh_3)_3$ (B),[2] in dimethylformamide (DMF) are refluxed under nitrogen for 3 h, a brown diamagnetic compound (C) which is insoluble in all common solvents separates. The i.r. spectrum of (C) in Nujol shows no Ir–H band and shows CO stretching bands at 1920s and 1870sh cm^{-1}. Since the lack of solubility prevents a molecular weight determination and makes it impossible to record n.m.r. spectra, a crystallographic analysis was undertaken to elucidate the structural details. Results show that the novel species consists of the binuclear complex di-μ-diphenylphosphido-bis(triphenylphosphinecarbonyliridium), $[Ir(CO)(PPh_3)(\mu\text{-}PPh_2)]_2$. Satisfactory elemental analyses were obtained.

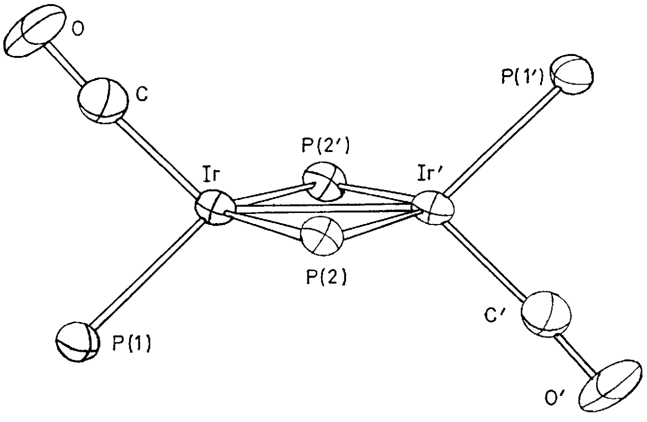

FIGURE. Perspective view of the inner co-ordination geometry in $[Ir(CO)(PPh_3)(\mu\text{-}PPh_2)]_2$. Ir–Ir′ 2·551(1), Ir–P(1) 2·277(3), Ir–P(2) 2·298(3), Ir–P(2′) 2·298(3), Ir–C 1·81(1), C–O 1·15(1), P(2) · · · P(2′) 3·824(4) Å; Ir–P(2)–Ir′ 67·4(1), P(2)–Ir–P(2′) 112·6(1), Ir–Ir′–P(2) 56·3(1), Ir′–Ir–P(2) 56·3(1), P(1)–Ir–P(2) 113·0(1), P(1)–Ir–P(2′) 113·5(1), P(2)–Ir–C 113·6(3), P(2′)–Ir–C 113·3(3), P(1)–Ir–C 88·9(3)°.

Crystal data: $C_{62}H_{50}Ir_2O_2P_4$, $M = 1335{\cdot}4$, monoclinic, $a = 11{\cdot}48(1)$, $b = 13{\cdot}73(1)$, $c = 16{\cdot}49(2)$ Å, $\beta = 96{\cdot}8(1)°$, $U = 2580$ Å^3, $D_m = 1{\cdot}70$ (by flotation), $D_c = 1{\cdot}72$ g cm^{-3} for $Z = 2$, $F(000) = 652$, space group $P2_1/n$ (No. 14) from systematic absences.

Three-dimensional X-ray data were collected on a Pailred linear diffractometer using a graphite monochromatized Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). Intensities were corrected for Lorentz, polarization, and absorption effects ($\mu = 56{\cdot}4$ cm^{-1}). The structure was solved by conventional Patterson and Fourier methods on the basis of 2357 independent structure amplitudes having $\sigma(I)/I \leqslant 0{\cdot}20$. In the full-matrix least-squares refinement the phenyl rings were treated as rigid bodies of known geometry (D_{6h} symmetry, C–C 1·392 Å), the phenyl carbon atoms were assigned individual isotropic thermal factors, and all the remaining atoms were allowed anisotropic vibration. The final R was 0·032.

The crystal structure consists of the packing of discrete centrosymmetric molecules of (C); the asymmetric unit thus consists of one half molecule. No unusual intermolecular contacts are present. In this complex, each metal atom is bonded to another metal atom, to two bridging diphenylphosphido-ions, to one carbonyl and one phosphine ligand (see Figure). The symmetry of the $[Ir(CO)P(\mu\text{-}P)]_2$ entity is strictly C_{2h} as shown by the distances and angles in the Figure caption; in the entire moleulce, the symmetry is lowered to C_i, owing to the presence of phenyl rings.

If the inert gas rule is assumed for the iridium atoms, then the Ir–Ir bond in (C) must be assigned an order of two. This is in agreement with the length of this bond, 2·551(1) Å, much shorter than the distances observed in the metal, 2·714 Å,[3] in $[Ir(NO)_2PPh_3]_2$, 2·717(1) Å,[4] in $Ir_4(CO)_{12}$, 2·68 Å,[5] and in the clusters $Ir_4(CO)_{12-n}(PPh_3)_n$ ($n = 2$ or 3), 2·73 Å.[6] The electronic configuration and the stereochemistry of the present complex are strictly parallel to those of $[Ru(NO)(PPh_3)(\mu\text{-}PPh_2)]_2$, a unique complex in which the Ru–Ru bond, 2·629(1) Å long, has also a formal order of two.[7]

When (C) is prepared from (A), the yield is 40%, and at least one other major product is obtained, which is soluble; its chemical characterization is presently under way. When (B) is used as starting product, the yield is 30%. In the latter case, the metal atom is carbonylated by DMF, and in this respect the reaction is similar to that involved in the synthesis of $Ir(CO)Cl(PPh_3)_2$ from $IrCl_3{\cdot}3H_2O$ and PPh_6 in the same solvent.[8]

The formation of bridging phosphido-ligands is a novel, unexpected feature of these solvolytic reactions. We are presently investigating how a number of transition metal hydrides behave in DMF. These complexes give bi- or poly-nuclear species containing μ-phosphido-groups.

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