Preliminary communication

A TRI-COORDINATE HYDROGEN LIGAND IN A TRINUCLEAR IRIDIUM CLUSTER

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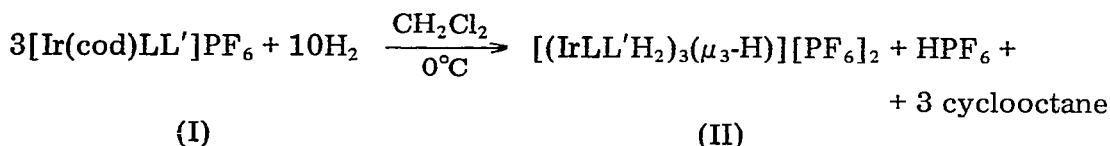
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Summary

The novel complex [{IrH$_2$(PCy$_3$)(C$_5$H$_5$N)}$_3$(μ_3-H)][PF$_6$]$_2$ has been characterized by X-ray crystallography, IR and ^{1}H NMR spectroscopy. It contains a tri-coordinate hydrogen ligand within a triangle of iridium atoms.

Tri-coordination of a hydrogen ligand was first suggested for Cp$_4$Rh$_3$H [1] and Ru$_6$H$_2$(CO)$_{18}$ [2] and has recently been demonstrated unequivocally for a number of carbonyl and cyclopentadienyl complexes, such as Re$_4$H$_4$(CO)$_{12}$ [3], FeCo$_3$H(CO)$_9${P(OMe)$_3$}$_3$ [4,5], Cp$_4$Co$_4$H$_4$ [6], and Cp$_4$Ni$_4$H$_3$ [5,7]. We now provide evidence for a tri-coordinate hydrogen in the first example of a trinuclear iridium cluster.

We have previously described [8] highly active olefin hydrogenation catalysts formed in non-coordinating solvents from [Ir(cod)LL′]PF$_6$ (I, cod = 1,5-cyclooctadiene; L = tertiary phosphine; L′ = L or pyridine). In the absence of the substrate olefin, the catalyst irreversibly deactivates to give yellow solutions. From these solutions (where L = L′ = PPh$_3$), the complex [Ir$_2$H$_2$(μ-H)$_3$L$_4$]PF$_6$ [8] has been isolated.

We now find that the complexes [(IrLL′H$_2$)$_3$(μ_3-H)][PF$_6$]$_2$(II) can be isolated as yellow crystals in 30% yield from solutions formed by the action of H$_2$ on the catalyst precursors I (L = PCy$_3$ or P-i-Pr$_3$, L′ = pyridine).

$$3[\text{Ir(cod)LL}']\text{PF}_6 + 10\text{H}_2 \xrightarrow[\text{0°C}]{\text{CH}_2\text{Cl}_2} [(\text{IrLL}'\text{H}_2)_3(\mu_3\text{-H})][\text{PF}_6]_2 + \text{HPF}_6 +$$

$$+ \text{ 3 cyclooctane}$$

$$(\text{I}) \qquad\qquad\qquad (\text{II})$$

$$(\text{L} = \text{PCy}_3, \text{a; P-i-Pr}_3, \text{b})$$

The manometric hydrogen absorption curve for Ib (L = P-i-Pr$_3$) at 0°C showed that the reaction was completed after 3.5 h, when 3.1 mol (theor: 3.3 mol) of H$_2$ had been absorbed and 0.98 mol (theor: 1.0 mol) of cyclooctane had been formed per mol of Ib (GLC). The complexes were recrystallized from acetone/ethanol and then twice from CH$_2$Cl$_2$/octane by liquid diffusion to give yellow crystals. The complexes were both thermally- and air-stable at room temperature in the solid state and in solution.

The crystallographic data for IIa (CH$_2$Cl$_2$ solvate) are: space group $P\bar{1}$, a 14.279(4), b 14.515(5), c 23.173(9) Å, α 76.05(3)°, β 80.61(3)°, γ 72.74(3)°, Z = 2. A total of 8963 reflections were recorded with Mo-K_α radiation over the range 0° < 2θ < 40° of which 6324 conformed to $F^2 > 3\sigma(F^2)$; these were used to solve the structure by heavy atoms methods. All non-hydrogen atoms were located. Anisotropic refinement was possible only for iridium, phosphorus and nitrogen atoms, due to computational constraints. The final R factor was 0.058*.

Figure 1 shows the heavy atoms in the immediate coordination spheres of the metal atoms. Three iridium atoms are located at the vertices of a very nearly equilateral triangle and are separated by distances ranging from 2.755(1) to 2.775(1) Å. To each metal is bound a tricyclohexylphosphine phosphorus atom and a pyridine nitrogen atom. The center of the P$_3$ plane is 1.17 Å above, and the N$_3$ plane 1.35 Å below the Ir$_3$ plane in Fig. 1. All three planes are nearly parallel; no dihedral angle between them exceeds 3°. Furthermore, the X-ray data indicate the presence of one CH$_2$Cl$_2$ molecule of solvation, equally dis-ordered over three sites, and of two PF$_6$ anions per trinuclear unit. A difference-Fourier map failed to reveal the locations of the hydrogen ligands.

The assignment that we propose for the hydrogen ligands in the coordination environment of the cluster is shown in Fig. 2. A bridging hydrogen, H$_A$, is equi-distant from the three iridium atoms. Assuming reasonable Ir—H distances (ca. 1.7 Å) [4,5], this hydrogen is probably 0.6—0.8 Å above or below the Ir$_3$ plane. In addition, each metal atom bears two terminal hydrogens, H$_B$ and H$_C$, *cis* to the tertiary phosphine ligand. The bonding of the unique hydrogen atom seems to involve a 4-center, 2-electron interaction.

The PMR spectra of IIa and IIb in CD$_2$Cl$_2$ at 20°C are very similar and show three types of hydrido ligand. For example, for IIa, a quartet at δ −3.9 ppm (relative to TMS) is assigned to H$_A$. The coupling constant, ^2J(P,H,*trans*), is 50 Hz, or about one third of the values usually observed in mononuclear com-plexes [9] (130—160 Hz). This reduction in coupling constant seems to be related to the fractional bond orders of Ir—H bonds in Ir$_n$(μ_n-H) clusters, since we found [8] values of ^2J(P,H,*trans*) of 60—85 Hz, or half the normal value, in the complexes [Ir$_2$H$_5$L$_4$]PF$_6$, where the hydride ligands in question are 2-coor-dinate. In view of the magnitude of ^2J(P,H$_A$), we tend to prefer a structure for II in which H$_A$ is *trans* with respect to the tertiary phosphine groups and so lies on the opposite side of the Ir$_3$ plane from them (Fig. 2).

A doublet at δ −20 ppm [^2J(P,H,*cis*) 25 Hz] and another doublet at δ −22
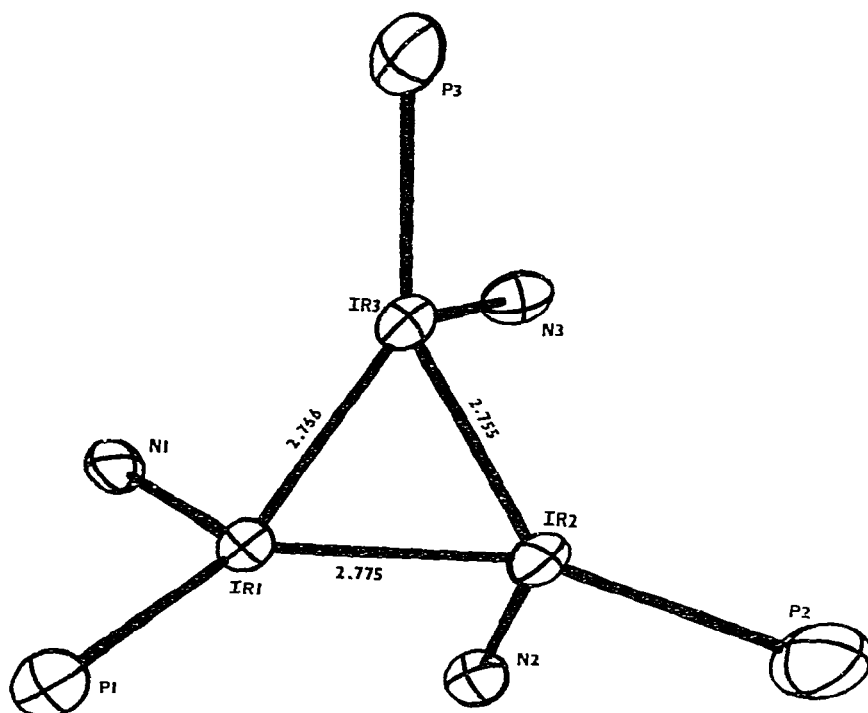
Fig. 1. An ORTEP diagram of the heavy atom environment of the iridium coordination sphere. Atoms are represented by 50% probability ellipsoids. Important bond distances (Å), angles and esd's not mentioned above are: Ir(1)—P(1), 2.286(3); Ir(2)—P(2), 2.291(3); Ir(3)—P(3), 2.281(3); Ir(1)—N(1), 2.140(8); Ir(2)—N(2), 2.134(8); Ir(3)—N(3), 2.144(9); Ir(1)—Ir(2)—Ir(3), 60.01(1)°; Ir(2)—Ir(3)—Ir(1), 60.35(1)°; Ir(3)—Ir(1)—Ir(2) , 59.64(1); P(1)—Ir(1)—N(1), 95.7(2)°; P(2)—Ir(2)—N(2), 96.9(2)°; P(3)—Ir(3)—N(3), 94.9(2)°; Ir(2)—Ir(1)—P(1), 129.42(7)°;Ir(3)—Ir(1)—P(1), 142.92(8)°; Ir(2)—Ir(1)—N(1), 134.2(2)°; Ir(3)—Ir(1)—N(1), 90.0(2)°. The corresponding bond angles around Ir(2) and Ir(3) are within 2.5° of those given above (except Ir(3)—Ir(2)—N(2), 127.7(2)°).
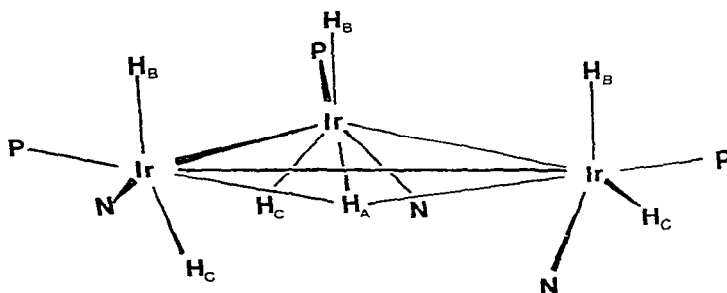

Fig. 2. Our assignment of the full coordination environment of the cluster.

ppm [^2J(P,H,cis) 10 Hz], each having three times the intensity of the quartet resonance, are assigned to H_B and H_C. No sign of fluxional behavior was observed; possibly the large size of the tertiary phosphines involved fix the structure in one conformation. The unusual chemical shift of the H_A resonance may result from the bridging arrangement. In the case of [$Ir_2H_5L_4$]PF_6, the bridging hydrides also resonate ca. 15 ppm downfield from the terminal resonances.

The IR spectrum shows only the terminal Ir—H vibrations at 2240 and 1770 cm^{-1}, together with bands characteristic of the ligands and the PF$_6$ anions.

The hydrogen atoms H$_B$ and H$_C$ seem most likely to be in or near the equatorial plane of a pseudo-trigonal bipyramid having H$_A$—Ir—P as its axis. They are each bound only to a single metal center, each of the pair is inequivalent and each is *cis* to the PCy$_3$ ligand, as required by the PMR data.

The Ir—Ir distances of about 2.76 Å are consistent [10] with bond orders of unity. The tertiary phosphine and pyridine ligands are normal and there are no unusually close contacts in any part of the structure.

The possibility that H$_A$ is mono- or bi-coordinate and fluxional, which would be consistent with the PMR spectra, was rejected on the basis of the close approach of the cluster to 3 fold symmetry in the solid state and the absence of any abnormal thermal parameters or, indeed, of any reasonable alternative structure. In addition, a mono- or bi-coordinate H$_A$ would be expected to be more nearly *cis* than *trans* to the PCy$_3$ groups, leading to a $^2J(P,H)$ coupling constant in the PMR spectrum closer to 10 than to 50 Hz [9].

Acknowledgements

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