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Preliminary communication

$[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]^+ PF_6^-$, A NOVEL IRIDIUM COMPLEX CONTAINING A METAL—METAL TRIPLE BOND

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Summary

The new complex $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]^+ PF_6^-$ contains a metal—metal triple bond. Its structure was determined by X-ray crystallography, IR, and ^{31}P and NMR spectroscopy.

Recent interest [1] in complexes containing metal—metal multiple bonds prompts us to report a novel example, $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]^+ PF_6^-$, having the shortest Ir—Ir bond yet observed, to which we assign the bond order three.

The complex [2] $[Ir(cod)(PPh_3)_2]^+ PF_6^-$ (cod = 1,5-cyclooctadiene) in toluene suspension was treated with dihydrogen. A light yellow oil was deposited on the walls of the vessel. The oil was washed with ether and recrystallised from CH_2Cl_2/hexane to give light yellow needles of $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]^+ PF_6^- \cdot CH_2Cl_2$ (yield 50%). Satisfactory analyses for C, H and Cl were obtained for this complex. An unsolvated material may be obtained from acetone/ether. Both these materials are air-stable.

The crystallographic data for the dichloromethane solvate are: space group $P2_1/c$, $a = 16.505$, $b = 17.260$, $c = 22.213$ Å, $\alpha = \gamma = 90°$, $\beta = 91.546°$, $Z = 4$. A total of 11 724 independent reflections were recorded with Mo-K_α radiation over the range $0° < \theta < 25°$. The structure was solved by standard methods. Disorder in the PF_6 group and in the phenyl groups of the PPh_3 ligands precluded a full analysis of the structure; nevertheless a final R value of 0.1291 was obtained omitting the carbon atoms other than those directly bonded to phosphorus.

The structure, shown in Fig. 1, although incomplete, is quite adequate to show the significant feature, namely the presence of a dimeric cation having a remarkably short Ir—Ir bond (2.518 Å). Each iridium atom coordinates two PPh_3 groups. Furthermore, the crystal structure shows the presence of one hexafluorophosphate anion and one dichloromethane of solvation per dimeric cation.

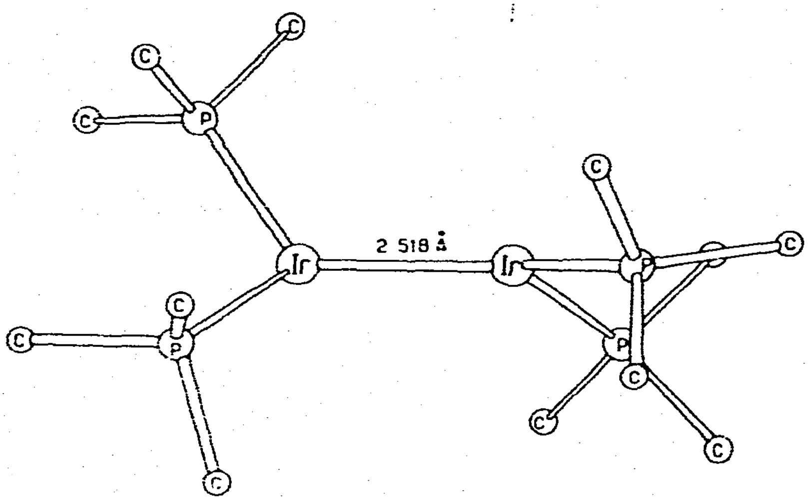

Fig. 1.

Fig. 2 shows our assignment of the structure of the coordination environment of the dimeric cation. Each H_A is *trans* to a single phosphorus atom, while H_B is *trans* to two phosphorus atoms. The P- and H-ligands are in a distorted octahedral arrangement around each iridium, with the second iridium atom capping one face.

The assignment of the hydrido ligands follows from the IR and PMR measurements. Only the terminal Ir—H vibrations at 2200 cm^{-1} appear in the IR spectrum (confirmed by deuteriation ν(Ir—D) 1555 cm^{-1}). The high field region of the PMR spectrum in deuterioacetone at −90°C shows the following sets of broad peaks: (reported as: position, multiplicity, $|{}^2J(PH)|$, relative intensity, assignment) τ 16.9 ppm, doublet, 86 Hz, 2, H_A : τ 18.4 ppm, triplet, 65 Hz, 1, H_B: τ 33.9 ppm, singlet, —, 2, H_C.

In neutral mononuclear iridium(III) hydrido complexes [3], $|{}^2J(PH)|$ (*cis*) is of the order of 10—30 Hz, while $|{}^2J(PH)|$ (*trans*) is 130—180 Hz. In the present case only the *trans* coupling constants are observed and the values are less than those characteristic of the neutral mononuclear complexes. Finally, at much higher field, appropriate for a terminal hydride ligand, appears the resonance of the H_C protons. At room temperature, the resonances of the H_A and H_B ligands coalesce to give a single broad resonance indicating that an exchange process occurs.

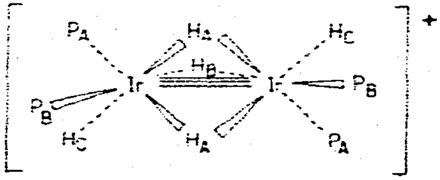

Fig. 2.

The proton-decoupled ^{31}P NMR spectrum at 36.4 MHz in deuterioacetone at 25°C shows a broad peak of intensity 4 due to the PPh_3 phosphorus nuclei and a septet of intensity ca. 0.8 characteristic of the PF_6^- anion. The spectrum at −80°C shows that the two sets of phosphorus nuclei of the PPh_3 groups, shown as P_A and P_B in Fig. 2, resonate at slightly different magnetic fields (δ(P) +15.3 and +18.5 ppm relative to external H_3PO_4, $^2J(P_AP_B)$ 95 Hz) as expected for the proposed structure.

The bridging hydrido ligand can only contribute one electron to the complex as a whole. In contrast, nearly all other anionic bridging ligands can use a lone pair of electrons to complete the bridge bond and so contribute 3 electrons to the complex as a whole (e.g., μ-Cl, μ-PPh_2). In the present case the 18 electron rule requires an iridium—iridium bond order of three. The Ir—Ir distance (2.518 Å) is indeed very short, and may be compared with the Ir—Ir double bond [4] in $[Ir_2(CO)_2(\mu\text{-}PPh_2)_2(PPh_3)_2]$ (2.551 Å)

It seems likely that in the analogous triply bridged cations $[M_2(\mu\text{-}H)_n(\mu\text{-}Y)_{3-n}(XL)_2]^+$ (where XL_2 is a five-electron donor group such as η^5-C_5Me_5 or set of groups such as $H(PPh_3)_2$; M = Rh or Ir; and Y is a 3-electron bridging group such as Cl, SPh or OH), of which many examples have been prepared by Maitlis [5], a metal—metal bond of order *n* will be found to be present. The structure of only one other member of this series is known, that of the cation [6] $[Ir_2(\mu\text{-}Cl)(\mu\text{-}SPh)_2H_2(PPh_3)_4]^+$, which has three 3-electron bridging groups; accordingly this cation has a very long metal—metal distance (3.37 Å), implying a zero Ir—Ir bond order.

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