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NEUTRAL SUBSTITUTED CARBONYL CLUSTERS OF IRIDIUM. SYNTHESIS AND X-RAY STRUCTURE OF μ_3-CARBONYLTRI-μ-CARBONYLOCTACARBONYLTETRAKIS(TRIPHENYLPHOSPHITE)-OCTAHEDRO-HEXAIRIDIUM

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Summary

The reaction of $Ir_6(CO)_{16}$ with $P(OPh)_3$ in toluene yields $Ir_6(CO)_{12}[P(OPh)_3]_4$ which has been shown by X-ray diffraction to contain an octahedral cluster bearing four terminal $P(OPh)_3$ ligands, one face-bridging, three edge-bridging and eight terminal carbonyl groups. The carbonyl arrangement is different from that found in the analogous rhodium complex.

In the course of the characterization of neutral substituted derivatives of $M_6(CO)_{16}$ (M = Rh, Ir) we previously reported the structures of $Rh_6(CO)_{12}$-$[P(OPh)_3]_4$ [1] and $Rh_6(CO)_{10}(DPM)_3$ (DPM = bis(diphenylphosphino)methane) [2]. We describe below the synthesis and X-ray characterization of the first neutral derivative of $Ir_6(CO)_{16}$, namely $Ir_6(CO)_{12}[P(OPh)_3]_4$, which was prepared by heating $Ir_6(CO)_{16}$ with $P(OPh)_3$ in the molar ratio 1/6 at 80°C for 2 h in toluene. Crystals suitable for X-ray investigation were obtained by slow diffusion of propan-2-ol into a THF solution of the compound.

Crystal data. $C_{84}H_{60}Ir_6O_{24}P_4$, $M = 2730.5$, orange-red orthorhombic crystals, space group *Pbca*, a 18.995(4), b 38.083(7), c 23.263(4) Å, V 16828 Å^3, D_c 2.155 gcm^{-3} for $Z = 8$, μ(Mo-K_α) 101.52 cm^{-1}, Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer, with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) in the θ range 3—25°. The structure was solved by conventional Patterson and Fourier methods and the refinement was carried out by full-matrix least-squares down to a current R value of 0.046 for 5606 absorption and decay corrected reflections, having $I \geqslant 3\sigma(I)$. Typical

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e.s.d.'s on single distances are Ir—Ir 0.001, Ir—P 0.005, Ir—C 0.02, C—O 0.02, P—O 0.017 Å.

The structure of $Ir_6(CO)_{12}[P(OPh)_3]_4$ consists of a slightly distorted octahedron of iridium atoms connected to four triphenylphosphite ligands, one face-bridging, three edge-bridging and eight terminal carbonyls. As a result of this ligand distribution, the molecule does not possess any symmetry element. The Ir—Ir bond lengths, in the range 2.776—2.825 Å, have a mean value of 2.795 Å, which is larger than the mean value found in the anionic octahedral cluster $[Ir_6(CO)_{15}]^{2-}$ (2.773 Å) [3]. The scattering of the Ir—Ir distances is probably due to the different bonding environment of each iridium atom. The four triphenylphosphite ligands are arranged alternately above and below the equatorial plane of the octahedron defined by atoms Ir(1), Ir(2), Ir(3), and Ir(4), in order to minimize the intramolecular non-bonding contacts. The average Ir—P distance is 2.232 Å. All the terminal CO's are almost linear (mean Ir—C—O angle 175.4°) with Ir—C and C—O bond lengths of 1.85 and 1.16 Å, respectively. These values are similar to those found, for instance, in $[Ir_6(CO)_{15}]^{2-}$ and $[Ir_6(CO)_{15}COEt]^-$ [4]. The edge-bridging CO's are quite

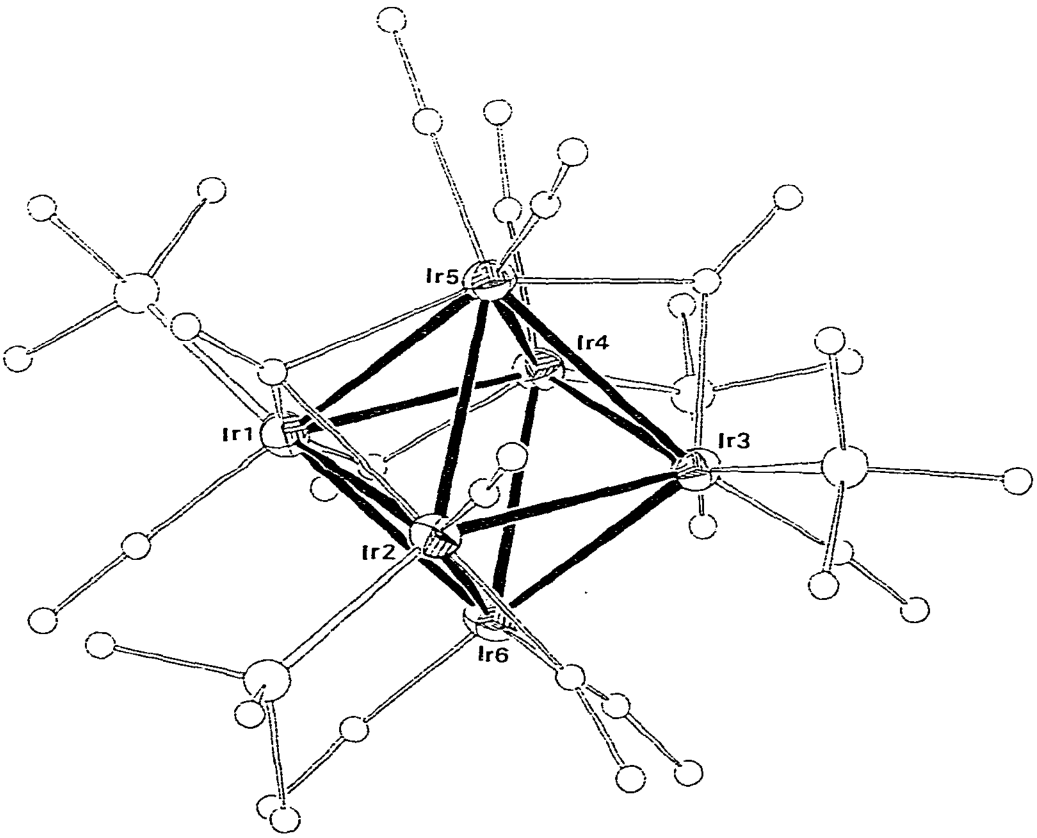

Fig. 1. ORTEP view of $Ir_6(CO)_{12}[P(OPh)_3]_4$ (phenyl groups of the triphenylphosphite ligands omitted for clarity). Ir—Ir bond lengths (Å) are: Ir(1)—Ir(2) 2.802(1), Ir(1)—Ir(4) 2.799(1), Ir(1)—Ir(5) 2.817(1), Ir(1)—Ir(6) 2.781(1), Ir(2)—Ir(3) 2.825(1), Ir(2)—Ir(5) 2.790(1), Ir(2)—Ir(6) 2.775(1), Ir(3)—Ir(4) 2.804(1), Ir(3)—Ir(5) 2.781(1), Ir(3)—Ir(6) 2.766(1), Ir(4)—Ir(5) 2.775(1), Ir(4)—Ir(6) 2.825(1).

asymmetric, with Ir—C distances spread over the range 2.02—2.30 Å, and an average C—O bond length of 1.18 Å. The face-bridging carbonyl is also asymmetric, with Ir—C distances of 2.24, 2.30 and 2.10 Å, and a C—O bond length of 1.19 Å.

A comparison of the structure of the compound with that of the analogous $Rh_6(CO)_{12}[P(OPh)_3]_4$, in which four CO ligands are face-bridging, confirms the lower tendency of iridium with respect to rhodium to form bridging bonds, a behaviour already observed, among the octahedral clusters, for $[Ir_6(CO)_{15}]^{2-}$ and $[Ir_6(CO)_{15}COEt]^-$.

It is of interest that the stereochemical arrangement of the four bridging carbonyl groups in the present compound is intermediate between those found in the two isomers of $Ir_6(CO)_{16}$, one of which is isostructural with $Rh_6(CO)_{16}$ [5] while the other bears twelve terminal and four edge-bridging carbonyl groups [6]. Several substituted derivatives of $Ir_6(CO)_{16}$ have also been prepared with various ligands such as triphenylphosphine, trimethylphosphite, 1,2-bis(diphenylphosphino)ethane. All the isolated compounds show IR bands in the range characteristic of the terminal and bridging CO ligands; IR bands (THF) for $Ir_6(CO)_{12}[P(OPh)_3]_4$: 2040vs, 2015vs, 1735s cm^{-1}.

Preliminary studies of $^{13}C\{H\}$ NMR of ^{13}CO enriched $Ir_6(CO)_{12}[P(OPh)_3]_4$ show a signal at around 220 ppm (downfield to TMS) due to the bridging CO's and a set of signals in the 172—178 ppm region due to the terminal CO's, with the intensity ratio expected for the $Ir_6(CO)_{12}L_4$ derivative.

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