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Preliminary communication

NEUTRAL SUBSTITUTED CARBONYL CLUSTERS OF IRIDIUM. SYNTHESIS AND X-RAY CHARACTERIZATION OF TRI-μ_3-CARBONYL-μ-CARBONYLHEPTACARBONYLPENTAKIS(TRIMETHYLPHOSPHITE)-*octahedro*-HEXAIRIDIUM

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Summary

The reaction of $Ir_6(CO)_{16}$ with $P(OMe)_3$ in toluene yields $Ir_6(CO)_{11}[P(OMe)_3]_5$ which has been shown by X-ray diffraction to contain an octahedral cluster of iridium atoms bearing five terminal trimethylphosphite ligands, three face-bridging, one edge-bridging and seven terminal carbonyl groups.

A few neutral substituted octahedral carbonyl clusters of rhodium and iridium are known [1,2]. We previously reported the synthesis and X-ray characterization of the tetrasubstituted cluster $Ir_6(CO)_{12}[P(OPh)_3]_4$ [2], but all attempts to obtain a degree of substitution greater than four using $P(OPh)_3$ were unsuccessful even under forcing conditions. However, use of the less bulky trimethylphosphite ligand [3] has now given the penta-substituted cluster $Ir_6(CO)_{11}[P(OMe)_3]_5$ (I); this was obtained by refluxing $Ir_6(CO)_{16}$ with trimethylphosphite in a molar ratio 1/8 for 9 h in toluene. Crystals suitable for X-ray structure analysis were grown by slow evaporation of a clear solution in toluene (50 cm^3)/isopropanol (30 cm^3). IR (in tetrahydrofuran): 2032m, 1991vs, 1961w, 1714m cm^{-1}.

Crystal data. $C_{26}H_{45}Ir_6O_{26}P_5$, M = 2081.7, orange-red orthorhombic prisms, space group *Pbcm* (no. 57), after refinement, a 11.681(2), b 20.060(3), c 20.674(3) Å, U 4844.3 Å^3, D_c 2.854 g cm^{-3} for Z = 4, μ(Mo-K_α) 166.02 cm^{-1}. Intensity data, obtained with monochromated Mo-K_α radiation (λ 0.71073 Å) on an Enraf—Nonius CAD-4 automatic diffractometer were collected by the ω-scan technique, in the 2θ range 6—50°. The structure solution and refinement are based upon 1783 independent reflections, corrected for Lorentz polarization and

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absorption, having $I \geqslant 3\sigma(I)$. Metal atoms were located by means of MULTAN. Subsequent Fourier syntheses and refinements revealed the positions of all the remaining non-hydrogen atoms and showed a disordered situation for the carbon atoms and for one oxygen atom of the trimethylphosphite ligands. The present values for R and R_W are 0.052 and 0.066 respectively. Typical e.s.d.'s are: Ir—Ir 0.002, Ir—P 0.01, Ir—C 0.04 and C—O 0.04 Å*.

Compound I, which contains a slightly distorted octahedral cluster of iridium atoms, displays crystallographic C_s symmetry with the mirror plane passing through atoms O(1), P(1), Ir(1), C(244′), O(244′), Ir(2), C(33′), O(33′). The five trimethylphosphite ligands are terminally bonded to five different iridium atoms, whereas the carbonyl stereochemistry is very close to that of $Rh_6(CO)_{16}$ [4] and the corresponding $Ir_6(CO)_{16}$ isomer [5]; the only difference involves the bonding mode of CO(33′) (see Fig. 1) which behaves as a two-way instead of three-way

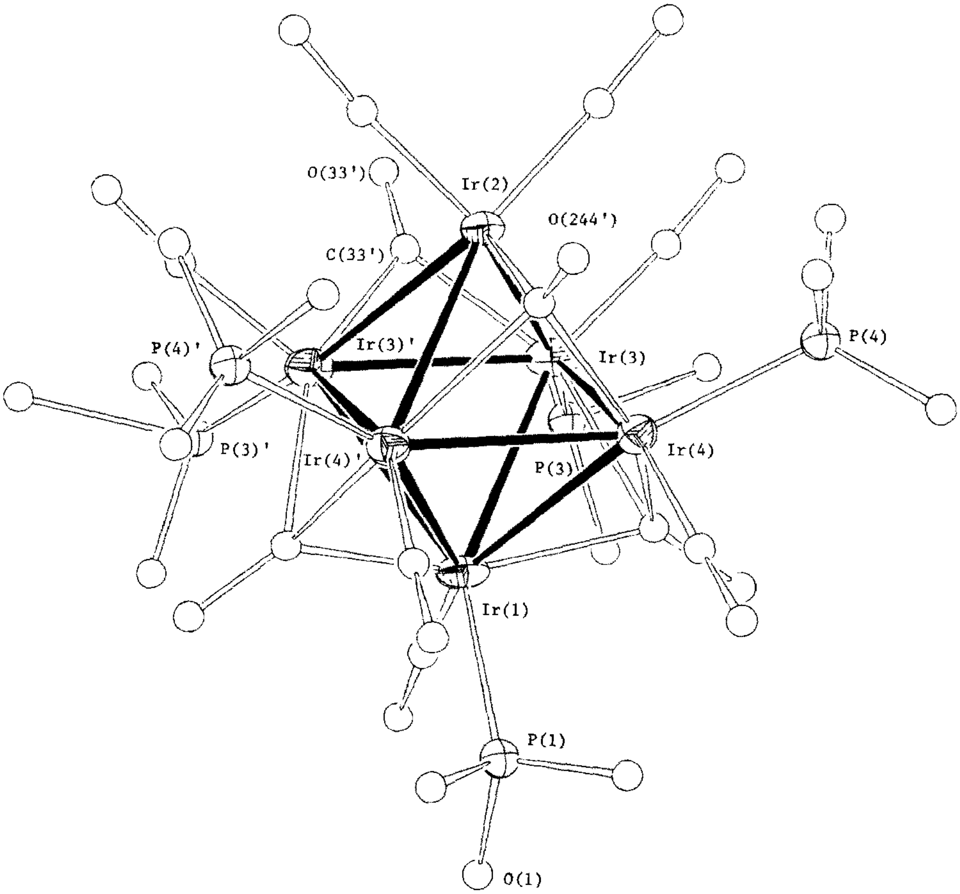

Fig. 1. ORTEP view of the $Ir_6(CO)_{11}[P(OMe)_3]_5$ compound (carbon atoms of the trimethylphosphite ligands omitted for clarity). Metal—Metal bond lengths are: Ir(1)—Ir(3) 2.814(2), Ir(1)—Ir(4) 2.800(2), Ir(2)—Ir(3) 2.815(2), Ir(2)—Ir(4) 2.777(2), Ir(3)—Ir(3)′ 2.816(3), Ir(3)—Ir(4) 2.828(1), Ir(4)—Ir(4)′ 2.787(2) Å.

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*Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full literature citation for this communication.

bridging ligand (Ir(2)···C(33′) 2.77(4) Å). The Ir—Ir distance vary over the range 2.777(2)—2.828(2) Å, with a mean value of 2.806 Å, and the average Ir—P distance is 2.224 Å; both of these average bond lengths are very similar to those found in $Ir_6(CO)_{11}[P(OPh)_3]_5$ 2.795 and 2.232 Å, respectively. The existence of disorder in the $P(OMe)_3$ ligands results in a rather low overall precision in the structure determination, as shown by the estimated standard deviations for the bonding parameters reported above. As a consequence, the Ir—C and C—O bond lengths are rather scattered, although the average values for chemically equivalent interactions are comparable to those found in other hexanuclear iridium clusters [6,7]: $Ir-C_{(term)}$ 1.84, $Ir-C_{(double\ bridg.)}$ 2.06(3), $Ir-C_{(triple\ bridg.)}$ 2.17, $C-O_{(term.)}$ 1.16, $C-O_{(bridg.)}$ 1.23 Å. It is of interest to compare the coordination mode of the phosphite ligands in this compound with that in $M_6(CO)_{12}$-$[P(OPh)_3]_4$ (M = Rh, Ir) [1,2]. In both of these tetrasubstituted species the $P(OPh)_3$ ligands are bonded to the metal atoms defining an equatorial plane of the metal cluster and are alternately directed above and below this plane. In compound I, on the contrary, the presence of a fifth $P(OMe)_3$ ligand coordinated to Ir(1) (see Fig. 1) determines a different orientation of the four remaining phosphites, whose arrangement is such that an adjacent pair of phosphites, P(4) and P(4)′, is directed above the equatorial plane defined by atoms Ir(3), Ir(3)′, Ir(4) and Ir(4)′, and the other, P(3) and P(3)′, below it. This results in relief of the non-bonded repulsions between phosphites 1, 4, and 4′ but conversely in severe strain for phosphites 3 and 3′, suggesting that in the case of monodentate phosphorus ligands penta-substitution may be considered to be the upper limit.

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