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Preliminary Communication

Crystal structure and intramolecular dynamics of $[Ir_3Rh(CO)_8(\eta^4$-cycloocta-1,5-diene$)_2]$

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Abstract

The redox condensation of $[Ir(CO)_4]^-$, $[Ir(COD)(THF)_2]^+$ and $[Rh(COD)(THF)_2]^+$ (COD = cycloocta-1,5-diene) yields $[Ir_3Rh(CO)_8(\eta^4\text{-COD})_2]$ (**I**). X-ray diffraction shows that **I** contains three edge-bridging CO's defining a basal Ir_2Rh face of the metal tetrahedron, and two COD chelating the Rh atom and one basal Ir atom, respectively. In solution this structure is static on the NMR time scale up to *ca.* 220 K. Above that temperature CO scrambling occurs due to the rotation of three terminal CO's about a local C_3 axis on the apical Ir atom. The reaction of **I** with CO (1 atm) in THF affords the first synthetic route to pure $[Ir_3Rh(CO)_{12}]$.

Key words: Iridium; Rhodium; Carbonyl; Dynamics; Crystal structure

The tetrahedral carbonyl cluster compounds of mixed d^9 metals known to date are $[Co_xRh_{4-x}(CO)_{12}]$, $[Co_xIr_{4-x}(CO)_{12}]$ and $[Ir_xRh_{4-x}(CO)_{12}]$ ($x = 2$ or 3) [1–5]. $[Ir_3Rh(CO)_{12}]$ could not be obtained by the standard redox condensation of two monomeric complexes of Ir^{-I} and Rh^{III} nor by the reaction of $[Rh(CO)_4]^-$ with $[Ir_4(CO)_{12}]$. We have now found that a redox condensation of three monomeric units (eqn. (1)) yields $[Ir_3Rh(CO)_8(\eta^4\text{-COD})_2]$ (**I**) (COD = cycloocta-1,5-diene).

$$2\,[Ir(CO)_4]^- + [Ir(COD)(THF)_2]^+ + [Rh(COD)(THF)_2]^+ \longrightarrow [Ir_3Rh(CO)_8(COD)_2] + 4\,THF \qquad (1)$$

Diene displacement was later achieved by stirring **I** in THF under CO (1 atm) giving pure $[Ir_3Rh(CO)_{12}]$ (overall yield 21%). The orange-yellow crystals of $[Ir_3Rh(CO)_{12}]$ were found highly disordered and unfit for X-ray analysis. As no structural information exists on Ir_3Rh cluster compounds, the structure of **I** was established by single crystal X-ray diffraction.

Crystal data for $[Ir_3Rh(\mu_2\text{-CO})_3(CO)_5(1\text{-}2\text{-}\eta:5\text{-}6\text{-}\eta\text{-COD})_2]$ (**I**): M_r: 1120, orthorhombic space group *Pnma*, a 11.132(7), b 15.042(2), c 15.444(3) Å, U 2586.1 Å^3, $F(000) = 2032$, $Z = 4$, Mo-Kα radiation, λ 0.71069 Å, μ(Mo-Kα) 176.3 cm^{-1}. Intensity measurements: CAD 4 diffractometer, 2579 reflections collected by the ω–2θ method in the range $2.5 < \theta < 25°$, ω-scan width 0.7°, octants explored $+h$, $+k$, $+l$, 1995 independent reflections with $I_o > 2\sigma(I_o)$ corrected for absorption [6], yielding a final R value of 0.060 ($R_w = 0.064$). Disorder involving the Rh atom position was detected at the early stages of data treatment. As the crystallographically imposed m-symmetry was not compatible with an Ir : Rh ratio of 3 : 1, a statistical distribution of the Rh atom over the two basal sites related by mirror symmetry was assumed and dealt with by using an averaged analytical scattering factor (atoms M in Fig. 1) calculated from those of Ir and Rh. The correctness of this strategy was confirmed by successful refinement of the disordered structural model with least-squares calculations [7]. A similar kind of disorder involving the tetrahedron of metal atoms has been observed in $[Co_2Ir_2(CO)_{12}]$ [2], $[Co_2Ir_2(CO)_{10}(\eta^4\text{-COD})]$ and $[CoIr_3(CO)_{10}(\eta^4\text{-COD})]$ [8]. All non-hydrogen atoms were refined anisotropically, while single isotropic temperature factors were refined for the H atoms [0.05(2) Å^2]. H atoms were added in calculated positions [C–H = 1.08 Å] and not refined, although their contribution to the structure factors was taken into account. Residual electron density peaks [*ca.* 2 e/Å^3] were found in the proximity of the metal atoms *.

The average molecular symmetry (Fig. 1) is C_s (the mirror plane bisects the heteronuclear M–M bond and passes through the other two Ir atoms). The four metal atoms define an almost regular tetrahedron.

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* The atomic coordinates for this structure are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Any request should be accompanied by the full literature citation for this communication.

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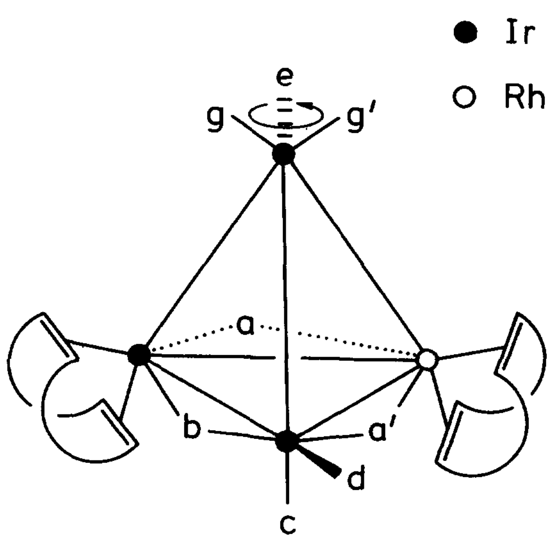
The overall ligand distribution is that common to the majority of substituted Ir_4 and Rh_4 clusters, with three edge-bridging CO-groups defining a basal plane of the metal polyhedron and with two bidentate diolefin ligands replacing both axial and radial terminal CO-groups on two metal atoms belonging to this face.

The Rh atom is disordered over the two COD-coordinated basal positions (50% occupancy). As a consequence, the interatomic metal–metal bond lengths (see caption of Fig. 1) must be regarded as average values of pure Ir–Ir and Ir–Rh interactions. This also applies to the metal–COD and metal–CO(bridging) interactions. The distance between the two COD-coordinated atoms (M–M) is the longest of the metal frame, as also found in $[Ir_2Rh_2(CO)_5(\mu_2\text{-}CO)_3(\eta^4\text{-norbornadiene})_2]$ [9]. No appreciable shortening of the CO-bridged intermetallic distances with respect to the unbridged ones was detected, consistent with the behaviour shown by most Ir_4 and Rh_4 substituted derivatives [10].



Scheme 1.

The geometry of I in solution is similar to that found in the solid state. Its IR spectrum has absorptions below 1900 cm^{-1}, indicating the presence of bridging CO's. The ^{13}C-NMR spectrum of a sample of I enriched in ^{13}CO (ca. 30%) in CD_2Cl_2 is blocked at 220 K and contains 8 CO-resonances of equal intensities at δ 234.4, 225.1 (2d, $J(C,Rh) = 27$ Hz, *a* and *a'*) (see Scheme 1); 214.4 (s, *b*); 175.4 (s, *d*); 164.7 (s, *g'*); 164.4 (br s, $^2J(C,Rh) < 7$ Hz, *g*); 158.7 (s, *e*); 157.6 ppm (s, *c*). The assignment of the two resonances at 234.4 and

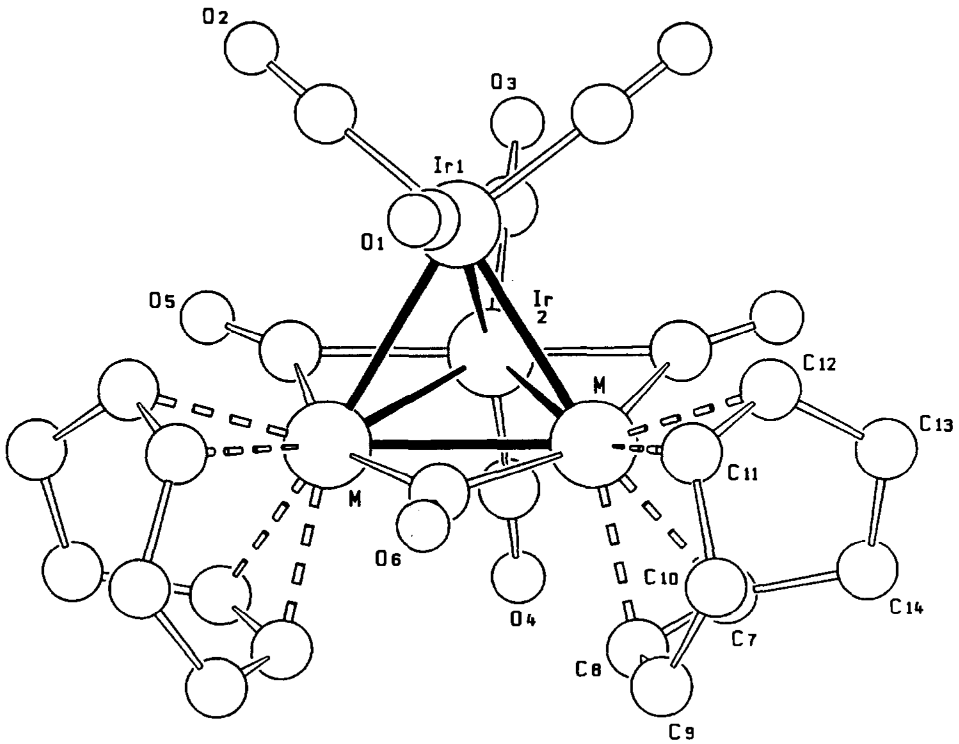


Fig. 1. The molecular structure of $[Ir_3Rh(\mu_2\text{-}CO)_3(CO)_5(1\text{-}2\text{-}\eta:5\text{-}6\text{-}\eta\text{-}COD)_2]$ (I). Bond lengths (Å) are: Ir(1)–Ir(2) 2.702(1), Ir(1)–M 2.707(1), Ir(2)–M 2.718(1), M–M 2.822(1), mean Ir(1)–C(terminal) and Ir(2)–C(terminal) 2.11(1), mean M–C(bridge) 2.10(2), mean M–C(olefin) 2.25(1) (axial), 2.21(1) (radial), mean C–O 1.12(2) (terminal), 1.13(2) (bridge), mean C=C 1.40(2), mean C–C 1.52(2).

225.1 ppm follows the general observation that in carbonyltetrairidium clusters the δ's decrease in the order: bridging > radial > axial ≈ apical [11]. The assignment of the signals in the terminal CO region was based on the C,C couplings observed in a 2D-COSY spectrum of I enriched in ^{13}CO (*ca.* 33%) at 220 K. The consequence of this assignment is that one COD-ligand is chelating the Rh atom and the other a basal Ir atom.

The variable-temperature ^{13}C-NMR spectra show that I is fluxional on the NMR time scale (Fig. 2). A 2D-NOESY (perhaps more accurately EXSY) spectrum (CD_2Cl_2, 280 K, mixing time 80 ms) shows the dynamic connectivity g, $g' \leftrightarrow e$ (Fig. 3). Therefore, the CO-scrambling is due to the rotation of 3 CO-groups about a local C_3 axis on the apical Ir atom, as shown in Scheme 1. Line-shape analysis [12] of the variable temperature ^{13}C NMR spectra (Fig. 2, right) was carried out using the following Kubo-Sack matrix elements: $(g, g) = (e, e) = (g', g') = -k$; $(g', g) = (g, e) = (e, g') = k$, where k = rate constant in s^{-1} for the three site exchange. A plot of ln k *vs.* $1/T$ gave a free enthalpy of activation of 59.9 ± 0.4 kJ mol^{-1} at 298 K. The fluxionality of most Ir_4, Ir_2Rh_2 and Rh_4 carbonyl clusters is owing to the merry-go-round of CO's around a triangular face or to changes of basal face [9,13–15]. Cluster I is an example of a CO scrambling process localised at one metal center.

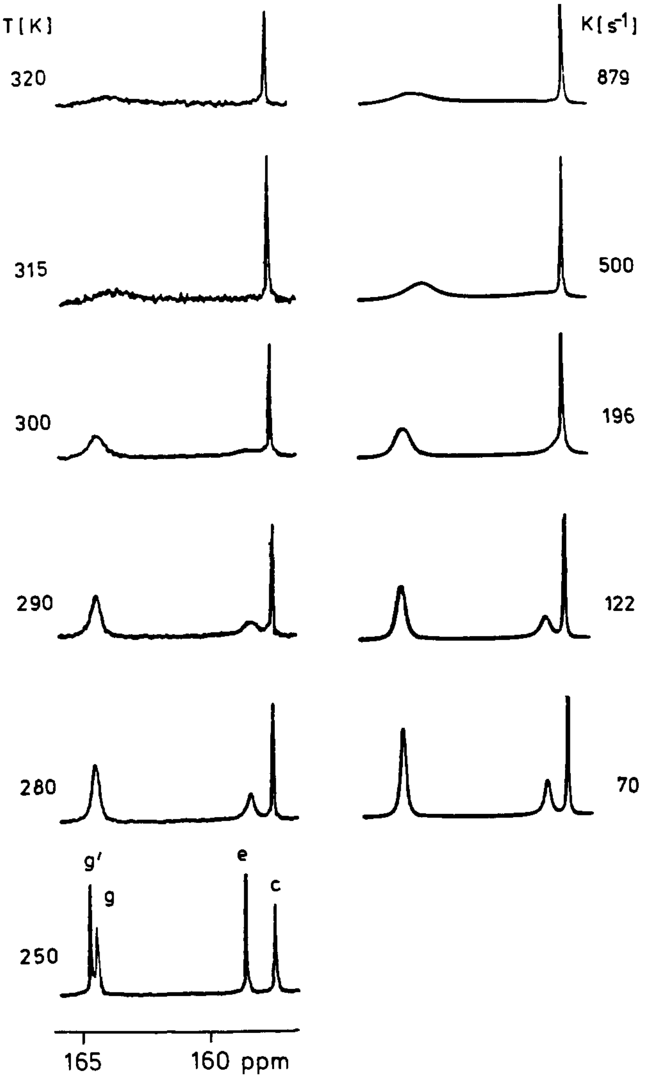


Fig. 2. Experimental and calculated VT ^{13}C NMR spectra of I in CD_2Cl_2.

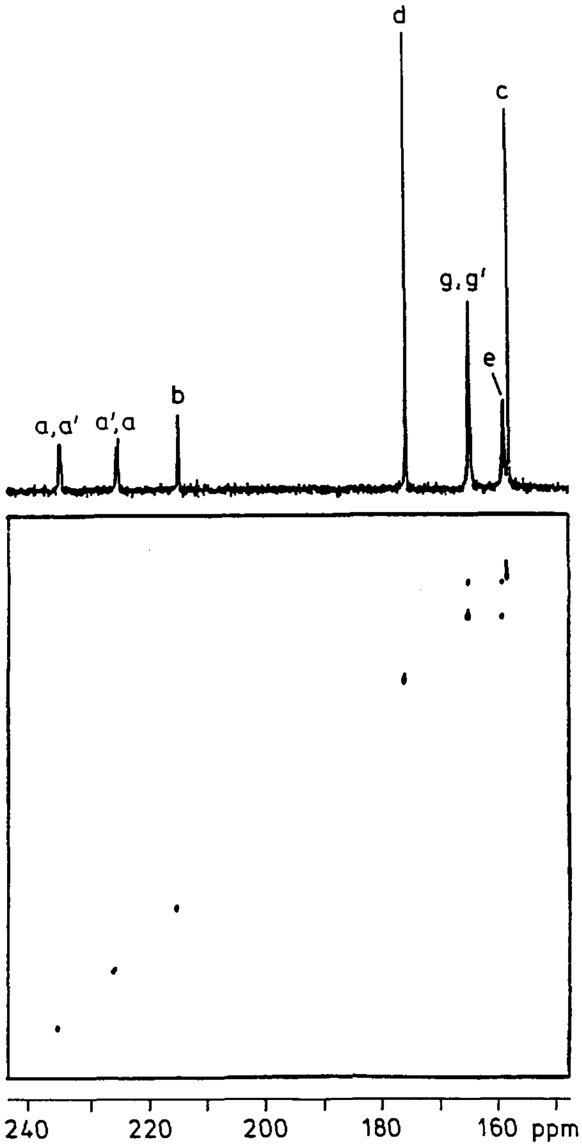


Fig. 3. 2D-NOESY spectrum of I in CD_2Cl_2 at 280 K (mixing time: 80 ms, F2 = 8771.9, F1 = 4385.9 Hz).

Acknowledgments

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