X-Ray Crystal Structure and Dynamic behaviour of $[Ir_4(CO)_{11}(CNBu^t)]$

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Summary $[Ir_4(CO)_{11}(CNBu^t)]$ has been prepared and shown (by *X*-ray crystallography and ^{13}C n.m.r. studies) to be the first example of a derivative of $Ir_4(CO)_{12}$ without bridging carbonyl groups; variable temperature ^{13}C n.m.r. spectra establish carbonyl scrambling *via* a triply bridged intermediate, *i.e.*, the formal inverse of the $C_{3v} \rightarrow T_d$ scrambling mechanism proposed for $[Rh_4(CO)_{12}]$.

Whereas $[Ir_4(CO)_{12}]$ has a structure of idealized T_d symmetry (containing only terminal carbonyl ligands),[1] all previously reported derivatives (*e.g.*, those in which one or more CO ligand is replaced by a phosphine,[2,3] cyclo-octa-1,5-diene,[4] or various anions[5]) possess structures in which there are three mutually adjacent bridging carbonyl ligands. These substituted species thus more closely resemble the C_{3v} configuration exemplified by $[Rh_4(CO)_{12}]$[6] and $[Co_4(CO)_{12}]$.[7] We now report the synthesis, structural characterization, and dynamic behaviour in solution of $[Ir_4(CO)_{11}(CNBu^t)]$; the first substituted derivative of $[Ir_4(CO)_{12}]$ containing no bridging carbonyl ligands.

Treatment of $Ir_4(CO)_{12}$ in tetrahydrofuran (THF) at 65 °C with $Me_3NO.2H_2O$ in the presence of a molar deficiency of Bu^tNC yields largely $[Ir_4(CO)_{11}(CNBu^t)]$,† which is isolated after separation as an air-stable, yellow crystalline solid. Spectral data suggest the presence of only terminal carbonyl ligands [i.r.: (ν_{CO}) 2094m, 2056vs, 2038s, 2016s, and 2008m cm^{-1}; (ν_{CN}) 2181 cm^{-1}]. The non-bridged structure has been confirmed by a single-crystal *X*-ray diffraction study.‡

Crystal data: $C_{16}H_9Ir_4NO_{11}$, $M = 1160{\cdot}13$, monoclinic, space group $P2_1/c$ (C_{2h}^5; No. 14), $a = 13{\cdot}5032(22)$, $b = 14{\cdot}3578(19)$, $c = 12{\cdot}4211(16)$ Å, $\beta = 97{\cdot}070(12)°$, $U = 2389{\cdot}8(6)$ Å^3, $D_c = 3{\cdot}22$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) = 236·0 cm^{-1}. Diffraction data were collected by the θ—2θ scan technique[8] using a Syntex $P2_1$ diffractometer. All

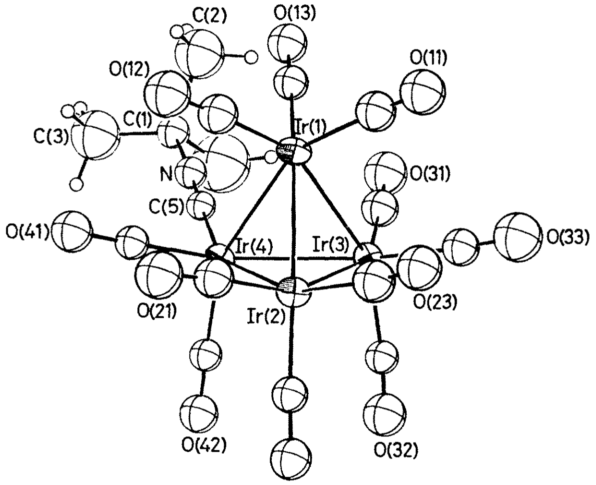

Figure 1. Stereochemistry of the $[Ir_4(CO)_{11}(CNBu^t)]$ molecule (ORTEP-II diagram, 30% ellipsoids).

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† Small amounts of $[Ir_4(CO)_{12-n}(CNBu^t)_n]$ (n = 2—4) are also isolated. I.r. spectroscopy indicated bridging carbonyl ligands for those species with $n \geqslant 3$. These species were separated by t.l.c..

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

non-hydrogen atoms were located and refined (anisotropically for Ir, isotropically for C, N, and O; H atoms fixed in idealized staggered locations), leading to $R = 5{\cdot}9\%$ for those 2798 reflections with $I > \sigma(I)$ and $3° < 2\theta < 45°$ (Mo-K_α). The resulting structure is shown in Figure 1.

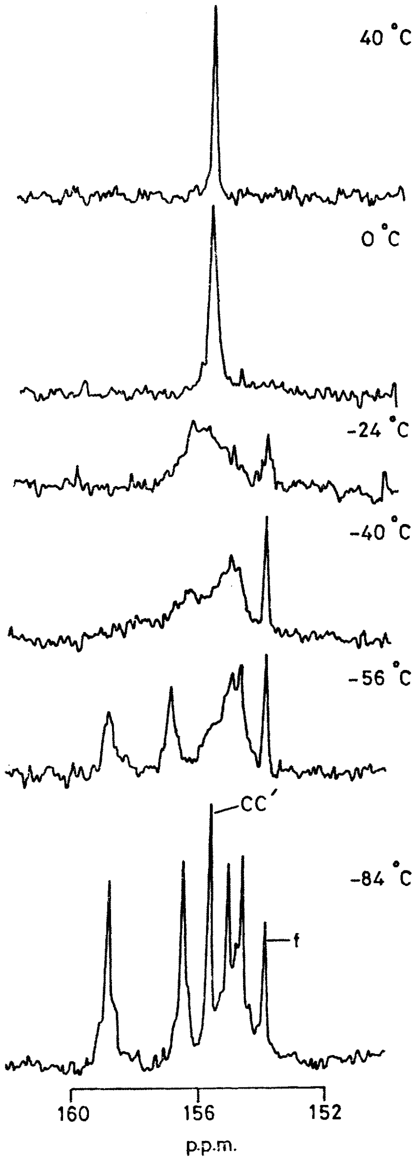
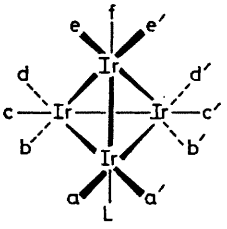


FIGURE 2. Variable temperature ^{13}C n.m.r. spectrum of $[\mathrm{Ir_4(CO)_{11}(CNBu^t)}]$.

The $\mathrm{Bu^tNC}$ ligand occupies a site on Ir(4), the Ir(4)–C(5) bond length being 1·976(19)Å as compared with the Ir–CO bond lengths of 1·800(30)—1·916(28) Å; the Ir(4)–C(5)–N and C(5)–N–C(1) angles are 179·2(18) and 176·3(20)°, respectively, with C(5)–N 1·150(25) and N–C(1) 1·461-(28) Å. There are some slight variations in Ir–Ir distances within the $\mathrm{Ir_4}$ tetrahedron. Distances involving the unique Ir(4) [Ir(1)–Ir(4) 2·682(1), Ir(2)–Ir(4) 2·678(1), and Ir(3)–Ir(4) 2·684(1) Å; average 2·681(3) Å] are slightly shorter than the other three distances [Ir(1)–Ir(2) 2·686(1), Ir(1)–Ir(3) 2·692(1), and Ir(2)–Ir(3) 2·689(1) Å; average 2·689(3) Å].

The limiting low temperature ^{13}C n.m.r. spectrum of $[\mathrm{Ir_4(CO)_{11}(CNBu^t)}]$ is entirely consistent with the solid state structure (Figure 2, −84 °C). Four of the two-carbon signals (159·9, 157·6, 156·2, and 155·8 p.p.m.) display an additional doublet arising from ^{13}C–^{13}C coupling (J 11·5 Hz). These can be assigned to the four pairs of carbonyls that are *trans*-related through Ir–Ir bonds: a,a′ : d,d′ and b,b′ : e,e′ (see **A**). The remaining two-carbon signal (156·8 p.p.m.) is due to c and c′; the one-carbon signal (155·0 p.p.m.) arises from the unique carbonyl f. At -40 °C, the five two-carbon signals have broadened and coalesced, whereas the one-carbon signal of f (*trans* to L = $\mathrm{CNBu^t}$) remains sharp. This preservation of *trans* relationships is characteristic of the $C_{3v} \rightarrow T_d$ rearrangement initially proposed for $[\mathrm{Rh_4(CO)_{12}}]$[9] and more recently demonstrated for $[\mathrm{Ir_4(CO)_{11}(PPh_2Me)}]$.[2] However, in these two cases the ground state is of C_{3v} (or pseudo C_{3v}) symmetry, *i.e.*, with three bridging carbonyl groups. In the present study the converse is true, the ground state is of pseudo T_d symmetry and carbonyl scrambling occurs *via* an intermediate of pseudo C_{3v} symmetry. At higher temperatures complete averaging of all carbonyls occurs by a different process.



(A)

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