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Organometallic 'Helicopters.' Characterisation of the Non-Rigid Triosmium Arene–Alkene Complexes $[Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, (R=H, Ph) and the *X*-Ray Crystal Structure of $[Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$

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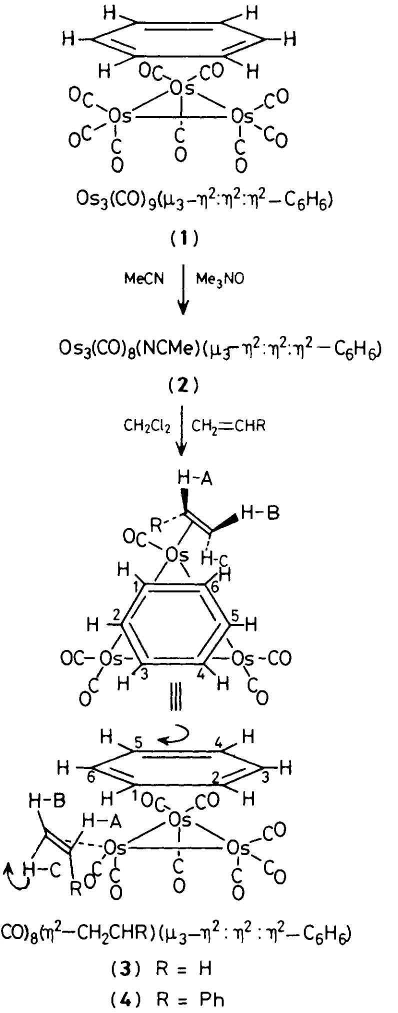
The cluster-alkene complexes $[Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (R=H, Ph) contain benzene ligands in a face-capping co-ordination mode, and the geometry of the ethylene derivative has been confirmed by a single-crystal *X*-ray analysis; the intramolecular dynamics of these complexes have been investigated in solution by n.m.r. spectroscopy and are discussed in terms of arene ring-whizzing and alkene rotation.

We have recently established a new face-capping bonding mode for benzene in the triosmium cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (**1**)[1] that bears a striking resemblance to the Kekulé type distortion found for benzene adsorbed on Rh(111)[2] and Os(0001)[3] single crystal surfaces. We now report the preparation of derivatives of (**1**) containing π-bound alkene ligands and a single crystal *X*-ray diffraction study on the prototype ethylene compound. Variable temperature n.m.r. studies (20 to −100 °C) on these arene–alkene triosmium complexes demonstrate organic-ligand mobility and we designate these intramolecular rearrangements 'helicopter-like' behaviour.

The reaction of equimolar quantities of (**1**) and anhydrous trimethylamine *N*-oxide in acetonitrile affords yellow, air-sensitive solutions of the lightly-ligated complex $[Os_3(CO)_8(NCMe)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (**2**).† Two-electron donor ligands L (*e.g.* L = CO, PR_3, C_5H_5N, alkenes) readily displace the labile MeCN ligand from (**2**) giving derivatives $[Os_3(CO)_8(L)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ which retain the face-capping benzene ligand. Specifically, room temperature reactions of (**2**) with ethylene and styrene afford the π-bound alkene complexes $[Os_3(CO)_8(\eta^2\text{-}CH_2{=}CHR)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ [R = H (**3**), R = Ph (**4**)], in high yield [*ca.* 85% from (**1**): see Scheme 1].



Scheme 1. The synthesis of $[Os_3(CO)_8$ $(\eta^2\text{-}CH_2CHR)$ $(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (R=H, Ph).

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† Spectroscopic data, (all $^3J_{HH}$ values are in Hz). (**2**) I.r.: ν_{CO}/cm^{-1} (CH_3CN), 2054(s), 2012(vs), 1985(vs), 1971(sh), 1912(w). ^1H N.m.r.: δ (CD_3CN) 4.60 (6H, s); MeCN resonance obscured by solvent. (**3**) I.r.: ν_{CO}/cm^{-1} (CH_2Cl_2), 2066 (s), 2027 (vs), 2003 (s), 1991 (sh), 1971 (m), 1959 (m). ^1H N.m.r.: 20 °C, δ (CD_2Cl_2) 3.96 (6H, br., s), 2.03 (4H, br., s); −96 °C, δ (CD_2Cl_2) 4.65 (H-2, t, ^3J 6.5), 4.60 (H-4, t, ^3J 5.9), 4.33 (H-1 or-5, t, ^3J 6.5), 4.31 (H-5 or -1, t, ^3J 6.4), 3.97 (H-3, t, ^3J 6.1), 2.56 (H-A, t, ^3J 9.7), 2.31 (H-C, t, ^3J 9.5), 2.04 (H-O, t, ^3J 9.9), 1.73 (H-6, t, ^3J 6.2), 0.72 (H-B, t, ^3J 9.8). (**4**) I.r.: ν_{CO}/cm^{-1} (CH_2Cl_2), 2066 (s), 2027 (vs), 2004 (s), 1972 (m), 1961 (m). ^1H n.m.r.: 20 °C, δ (CD_2Cl_2) 7.10—7.35 (5H, m, Ph), 4.03 (6H, br., s), 3.25 (H-A, t, ^3J 9.7), 3.01 (H-C, dd, $^3J_{AC}$ 11.6, $^3J_{BC}$ 2.5), 2.69 (H-B, dd, $^3J_{AC}$ 8.3, $^3J_{BC}$ 2.5); −85 °C, δ (CD_2Cl_2) 7.04—7.32 (5H, m, Ph), 4.69 (H-2, t, ^3J 6.0), 4.65 (H-4, t, ^3J 6.0), 4.52 (H-1, t, ^3J 5.7), 4.40 (H-5, t, ^3J 5.8), 3.97 (H-3, t, ^3J 6.2), 2.99 (H-B, d, ^3J 5.8), 2.79 (H-C, d, ^3J 11.1), 2.50 (H-A, t, ^3J 9.8), 2.08 (H-6, t, ^3J 5.1).

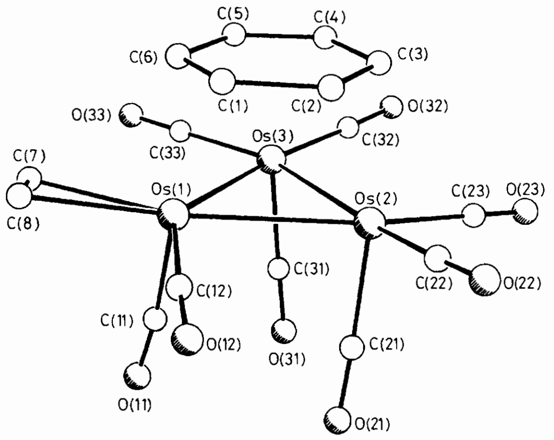

Figure 1. The molecular structure of [$Os_3(CO)_8(\eta^2$-$CH_2CH_2)(\mu_3$-$\eta^2:\eta^2:\eta^2$-$C_6H_6)$] (**3**). Bond lengths: Os(2)–Os(1), 2.843(1); Os(3)–Os(1), 2.858(1); Os(1)–C(1), 2.30(2); Os(1)–C(6), 2.30(2); Os(1)–C(7), 2.29(3); Os(1)–C(8), 2.27(3); Os(3)–Os(2), 2.839(1); Os(2)–C(2), 2.34(2), Os(2)–C(3), 2.32(2); Os(3)–C(4), 2.32(3); Os(3)–C(5), 2.31(2); C(2)–C(1), 1.50(3); C(6)–C(1). 1.41(3); C(3)–C(2), 1.44(3); C(4)–C(3), 1.46(3); C(5)–C(4), 1.38(3); C(6)–C(5), 1.44(4); C(8)–C(7), 1.39(4) Å. Bond angles: Os(3)–Os(1)–Os(2), 59.8(1); Os(3)–Os(2)–Os(1), 60.4(1); Os(2)–Os(3)–Os(1), 59.9(1); C(6)–C(1)–C(2), 119(2); C(3)–C(2)–C(1), 119(2); C(4)–C(3)–C(2), 119(2); C(5)–C(4)–C(3), 119(2); C(6)–C(5)–C(4), 124(2); C(5)–C(6)–C(1), 119(2); C(8)–C(7)–Os(1), 72(2); C(7)–C(8)–Os(1), 73(2)°.

The molecular structure‡ of (**3**) determined by *X*-ray diffraction is shown in Figure 1 together with some important bond parameters. The structure is derived from that of (**1**) with an equatorial carbonyl ligand on one metal atom being replaced by a π-bound ethylene ligand. The C_6 ring is strictly planar and adopts the μ_3-$\eta^2:\eta^2:\eta^2$-face-capping mode,[1] lying parallel to the metal triangle (tilt angle 0.8°) at a distance of 2.17 Å above the Os_3 plane. Although unambiguous assessment of the bonding within the ring is precluded by the high estimated standard deviations associated with the C–C distances, the apparent alternation of 'long' and 'short' bonds is consistent with Kekulé-type distortion of the benzene ligand. Mean 'co-ordinated' and 'unco-ordinated' C–C bond lengths of 1.41(3) and 1.46(3) Å for (**3**) may be compared with the corresponding distances 1.41 and 1.51 Å in the parent complex (**1**).[1] We propose that the nature of the face-capping C_6H_6 ligand may be best understood within a continuum defined by the limiting descriptions of a highly localised, μ_3-cyclohexatriene moiety and a completely delocalised μ_3-arene.

The ethylene group is symmetrically co-ordinated in (**3**) and is displaced slightly from the Os_3 plane towards the benzene ring [deviations: C(7), 0.18; C(8), 0.46 Å]. The C(7)–C(8) vector is twisted by some 14° with respect to the triosmium plane, minimising unfavourable interactions between the proximal ethylene and benzene protons H-B and H-6 (see Scheme 1).

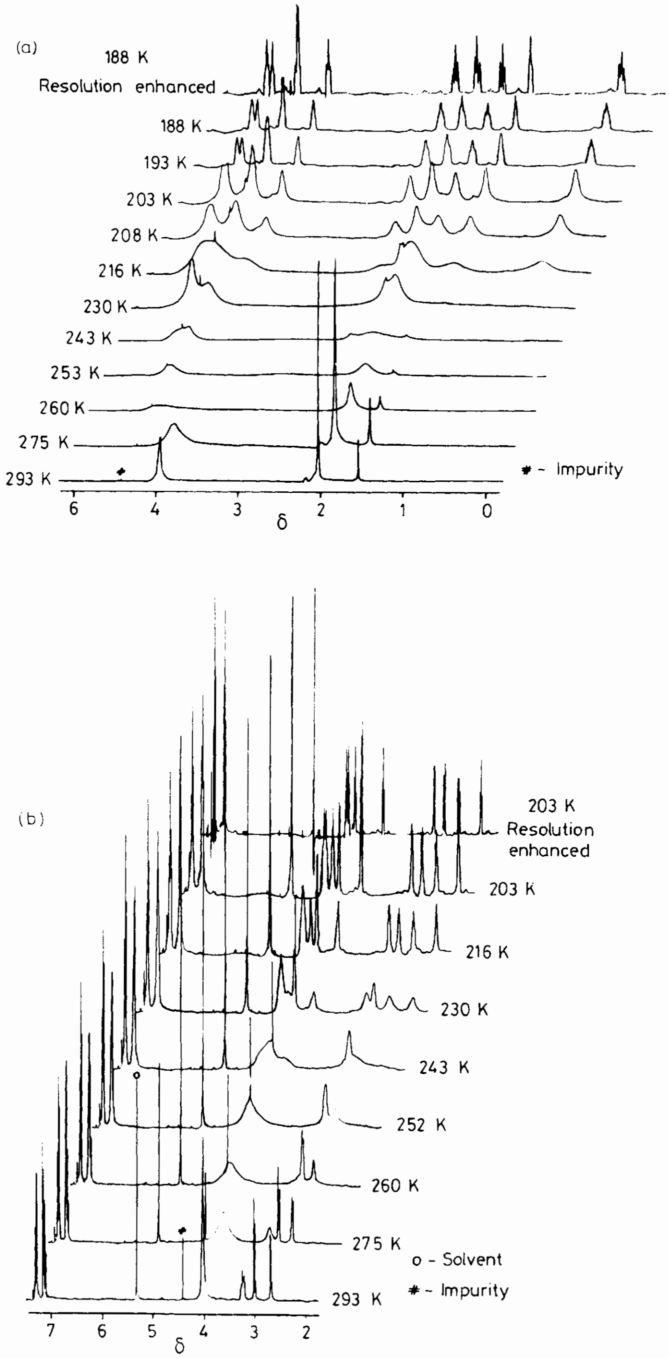

Figure 2. The variable temperature ^1H n.m.r. spectra of (a) (**3**) and (b) (**4**).

Variable-temperature ^1H n.m.r. spectra for complexes (**3**) and (**4**) (Figure 2) clearly demonstrate that these molecules undergo fluxional behaviour in solution. At ambient temperature the six inequivalent ring protons of both (**3**) and (**4**) see time-averaged environments and broadened, singlet resonances are observed at δ 3.92 and 4.03 respectively. The four ethylene protons in (**3**) give rise to a single resonance at δ 2.03 while three olefinic styrene proton signals may be clearly

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‡ *Crystal data* for (**3**): $C_{16}H_{10}O_8Os_3$, M = 900.84, monoclinic, space group $P2_1/n$ (alt. setting of $P2_1/c$, No. 14), a = 8.876(1), b = 14.665(2), c = 14.178(2) Å, β = 92.56(2)°, U = 1843.7 Å^3, D_c = 3.24 g cm^{-3}, Z = 4, $F(000)$ = 1592, Mo-K_α radiation, λ = 0.71069 Å, μ = 206.59 cm^{-1}. Stoe-Siemens 4-circle diffractometer, 2720 measured reflections, 2θ range 5—45°, numerical absorption correction, 1890 unique observed reflections, $F > 4\sigma(F)$. Structure solved by Σ_2 sign expansion and subsequent Fourier difference techniques. Refined by blocked full-matrix least-squares with non-hydrogen atoms anisotropic, converged R = 0.048, R_w = 0.047. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

identified in the spectrum of (**4**) at 20 °C. These resonances broaden and collapse on cooling until sharp, low-temperature limiting spectra are obtained at *ca.* −90 °C.

Consistent with the solid-state structure, ten distinct proton resonances are seen in the limiting spectrum of (**3**) and its assignment has been greatly facilitated by the use of two-dimensional homonuclear correlation (COSY) and nuclear Overhauser effect (n.O.e.) spectroscopy.[4] Strong n.O.e. enhancements between proximal benzene and ethylene protons H-6 and H-B effectively label the resonances at δ 1.73 and 0.72 respectively, and form the basis for the remaining assignments. The proximal proton of the face-capping ligand in (**4**) also suffers a substantial upfield shift (*ca.* 2 p.p.m.) reflecting, perhaps, a slight bending back of the C-6–H-6 bond in response to steric pressure from the alkene ligand.

Significantly, only one set of olefinic resonances is found in the limiting spectrum of styrene complex (**4**). A single conformation of the styrene ligand is therefore particularly favoured in the static limit, and n.O.e. measurements establish the geometry of the preferred rotamer to be as shown in Scheme 1. The limiting ring-proton resonances in (**3**) and (**4**) are pseudo-triplets with $^3J_{HH} \simeq 6$ Hz, suggesting that the μ_3-cyclohexatriene description of the face-capping ligand over-estimates the extent of double bond localisation in the ring.

We propose that the intramolecular rearrangements of clusters (**3**) and (**4**) may be thought of in terms of helicopter-like motion of the component organic 'rotors'. Several possible ring-whizzing mechanisms may be envisaged for equilibrating the benzene protons, with preliminary studies by two-dimensional exchange spectroscopy favouring rearrangement by a sequence of (1,2) shifts of the C_6H_6 moiety relative to the basal Os_3 triangle.[4] Straightforward rotation about the Os/CH_2CH_2 axis alone cannot account for the collapse of the four ethylene resonances to a single line in (**3**). Preliminary studies suggest that alkene rotation is coupled with an additional process localised at the unique osmium that simultaneously exchanges axial and equatorial carbonyl ligands, and transfers the alkene between the two equatorial co-ordination sites. We plan to determine kinetic and activation parameters for these fluxional processes and to examine the possibility that the benzene and olefin ligand motions are correlated (or geared) in these 'helicopter' clusters.

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