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ISOMERIC OLEFIN COMPLEXES OF TRINUCLEAR OSMIUM

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Summary

$Os_3(CO)_{12}$ and $RR'C{=}CH_2$ react to give $H_2Os_3(CO)_9C_2RR'$ which exist in several isomeric forms. Evidence for structure is presented.

Several studies have demonstrated that $M_3(CO)_{12}$ (M = Ru, Os) readily abstract hydrogen from molecules capable of prior coordination. Thus, e.g. $M_3(CO)_{12}$ cleave C—H bonds in ethylene [1] in a stepwise manner [2] to give first $HOs_3(CO)_{10}CH{=}CH_2$ and then $1,1\text{-}H_2Os_3(CO)_9C{=}CH_2$ (I). We now report that higher olefins react similarly to yield complex mixtures from which molecules of type I have been isolated. In particular, we report useful structural information which derives from the use of prochiral olefins $RR'C{=}CH_2$.

$Os_3(CO)_{12}$ and 1-octene in n-octane under reflux yield $H_2Os_3(CO)_9(C_8H_{14})$ (II) in two separable isomeric forms which may be regarded as 1,1 (IIa) and 1,2 (IIb) disubstituted 1-octene derivatives (Fig. 1). The two olefin bonding modes are easily distinguished by their ^1H NMR spectra (40°C, $CDCl_3$). IIa shows H^a as a triplet (1 : 2 : 1, τ 3.13, $J(H{-}CH_2)$ 6.8 Hz) whereas H^a in IIb appears at lower field as an uncoupled singlet (τ 1.82). Evidence for the asymmetric hydride dispositions shown (Fig. 1) comes from lower temperature ^1H NMR data where, at least for IIa the dominant (1,1) isomer, two further isomeric forms [*] (IIa, IIa') are clearly resolved (Fig. 2). The H^a signal at —40°C consists of two triplets in the intensity ratio 10 : 1, also observed are separate hydride signals for each diastereoisomer at high field, in this same ratio (IIa: τ 3.08, t, H^a, $J(H{-}CH_2)$ 6.8 Hz, τ 28.28, d, τ 31.32, d, $H^b + H^c$, $J(H^bH^c)$ 1.0 Hz. IIa': τ 3.51, t, $H^{a'}$, $J(H{-}CH_2)$ 6.5 Hz, τ 27.96, d, τ 31.49, d, $H^{b'} + H^{c'}$, $J(H^{b'}H^{c'})$ 1.0 Hz). Diastereoisomerism is not possible with the obvious alternative structure (Fig. 3). Previously [3] we assigned this structure to the related but more symmetrical $1,2\text{-}H_2M_3(CO)_9C_8H_{12}$ (M = Ru, Os) complexes but now find the form

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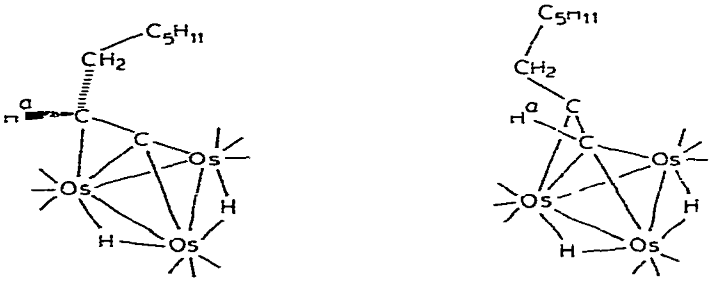
[*] The metal—olefin interaction viewed in the 'cyclopropane' form reveals two dissimilar chiral carbon centres leading to diastereoisomerism, and this provides an alternative view of the geometric isomerism clear from Fig. 2.



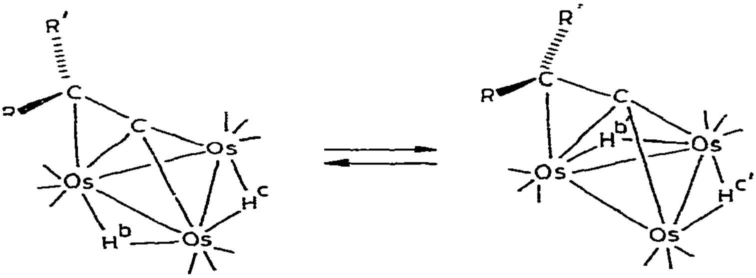
(IIa) (IIb)

Fig 1.

exemplified in Fig. 2b to be more consistent with ^{13}C and re-examined ^{1}H NMR data. Asymmetric hydride dispositions also provide a clear explanation for the hydride 'satellites' in the low temperature ^{1}H NMR of the unsymmetrical 1,2-$H_2Ru_3(CO)_9(C_8H_{10})$; previously these were attributed to impurity but probably represent the other possible diastereoisomer [3]. The hydride arrangement established here seems a general phenomenon amongst dihydrido-trinuclear metal carbonyl complexes.

$Os_3(CO)_{12}$ and propene give exclusively 1,1-$H_2Os_3(CO)_9C_3H_4$ (III), as found by others [1], but IIIa together with some 1,2 isomer (IIIb) are formed in an alternative preparative route from $H_2Os_3(CO)_{10}$ and $CH_3C{\equiv}CH$ [2] Isomer assignments again follow from chemical shift differences and H—H coupling (IIIa: τ 2.85, q, 1H, τ 7.83, d, 3H, $J(H{-}CH_3)$ 6.0 Hz, τ 28 28, s, 1H, τ 31 24, s, 1H, CD_2Cl_2, 35°C; IIIb: τ 1.05, s, 1H, τ 7 51, s, 3H, τ 26 46, s, 1H, τ 30.35, s, 1H, $CDCl_3$, 35°C) We did not resolve the expected diastereoisomerism in either IIIa, or IIIb. 1,1-$H_2Os_3(CO)_9C{=}C(H)CH_2CH_3$ (IVa) from $HOs_3(CO)_{10}CH{=}C(H)$-CH_2CH_3 [2] also shows no evidence of a second diastereoisomer ($CDCl_3$, 35°C τ 3.02, t, 1H, $J(H{-}CH_2)$ 5.5 Hz, τ 7 85, m, 2H, τ 8 75, t, 3H $J(CH_2CH_3)$ 7 0 Hz, τ 28.35, s, 1H, τ 31.41, s, 1H). We suggest one form predominates in solution (vide infra).

Other olefins examined, $Ph(CH_3)C{=}CH_2$, $(CH_3)_2CHCH_2(CH_3)C{=}CH_2$ and $(CH_3)_2CH(CH_3)C{=}CH_2$, gave as expected 1,1 olefin complexes only (Va, VIa and



(Ia) (IIa)

Fig 2.

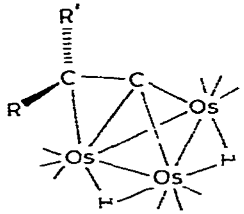


Fig 3

VIIa respectively). Va and VIa also provided firm evidence for the structures shown in Fig. 2, where each showed the expected diastereoisomerism This was clearest for IV where Ph, CH_3, and hydride signals at 40°C ($CDCl_3$, τ 2 60, br, m, 5H, τ 7 38, 5, 3H, τ 29 71, br, s, 2H) each doubled in the intensity ratio 3 · 1 (Va . Va') on cooling (—40°C), in addition, the inequivalent hydride sites in each of Va and Va' were clearly resolved as hydride-coupled doublets (Va τ 2.71, br, m, 5H, τ 7.51, s, 3H, τ 28 71, d, 1H, τ 31.06, d, 1H, J(HH) 1.5 Hz 5a' . τ 2 49, br, m, 5H, τ 7.24, s, 3H, τ 28 29, d, 1H, τ 30 50, d, 1H, J(HH) 1 3 Hz) VIa exists as a 1 . 1 mixture of diastereoisomers [4] The isomer ratio (a : a') found for III, IV, (>20 . 1), II (10 . 1). V (3 1) and VI (1 1) suggests that free energy differences are steric in origin, the more abundant form thus corresponds to that with the bulkier R group (Fig. 2) farther from the nearer hydride No significant temperature dependence of the diastereoisomer proportions was noted

Two distinct processes operate in the fluxional olefin complexes reported here, one leading to equilibration of the diastereoisomers and the other, effective hydride equivalence at a slower rate. Plausible mechanisms backed by direct experimental evidence have been suggested previously [4]

This work provides first examples of competitive 1,1 and 1,2 elimination of hydrogen from olefins using $Os_3(CO)_{12}$ As with 1,1 and 1,2-$H_2Ru_3(CO)_9C_2H_2$ [5], the isomers arising from the resultant two modes of olefin bonding (Fig. 1) are separable and not readily interconverted Thus the solution and solid state skeletal structures are the same It follows that $H_2Os_3(CO)_9C_2H_2$ (I), for which only one isomer is known and thought to be the 1,1 form from an X-ray study [1], retains the 1,1 arrangement in solution, as first suggested by the lack of *geminal* H-coupling in the ^1H NMR We have directly confirmed the 1,1 solution structure from its ^{13}C NMR The CH_2 group appears as a triplet (1 2 1, CH_2Cl_2, $J(C—H) = J(C{=}H^b) = 160$ Hz, —50 to +50) centred at 65 5 ppm downfield from TMS, this collapses to a singlet on selective olefin proton decoupling The quarternary carbon signal was not detected

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