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Preliminary communication

SIMPLE SYNTHESES OF SOME ISOMERIC TRINUCLEAR OSMIUM CARBONYL CLUSTERS CONTAINING A CYCLOOSMAHEXADIENONE FRAGMENT

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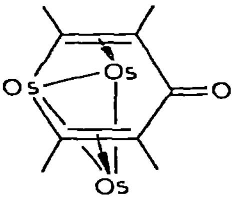
Summary

The reactions between acetylenes and $H_2Os_3(CO)_{10}$ have given novel complexes of stoichiometry $Os_3(CO)_{10}(RC_2R')_2$.

Current interest in reactions between trinuclear osmium carbonyls and acetylenes [1,2] prompts us to report the isolation and properties of several complexes of stoichiometry $Os_3(CO)_{10}(RC_2R')_2$ (I)*, which we believe to have the novel structure shown in Fig. 1.

Reaction between $H_2Os_3(CO)_{10}$ and an excess of RC≡CR′ yield I under mild conditions (n-hexane solution, 20°C, 3 h); when R or R′ = H, yields are substantial (20-50%).

The intensely coloured I shows ν(CO) at 1640^{-1}, suggesting the presence of a conjugated cyclic ketone and leads to the formulation of I as



(I)

Fig.1.

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*The parent ions in the mass spectra of I are clearly seen with the more volatile alkyl derivatives. Stepwise loss of ten CO groups, H, C, CH_n and acetylene fragments are observed. The ring ketone (see text) is not distinguished from the metal carbonyls.

$Os_3(CO)_9(RC_2R'CORC_2R')$. For the complexes derived from unsymmetrical acetylenes, e.g. R = Me, R' = H (see Table 1) three isomeric forms have been obtained; these were readily separated by TLC and show very similar IR spectra. These results suggest that isomerism arises from a simple permutation of substituents within the same basic structure, the ^1H NMR data confirm this, and the chemical shifts, proton integration and multiplicities in the isomers are fully consistent with the proposed structural features (Fig. 1). A possible alternative shown in Fig. 2, which more closely resembles the structurally related [3] $Os_3(CO)_9(RC_2R')_2$ complex II (Fig. 3), can be ruled out largely on the basis of IR data. Thus the spectra of complexes I are quite different from II and simpler suggesting a higher symmetry (Fig. 1). These conclusions are further supported by comparison with the IR data of other $Os_3(CO)_{12}$ derivatives having the same carbonyl arrangement and symmetry.

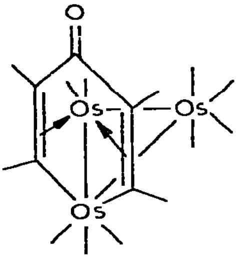


Fig.2.

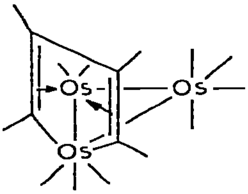


Fig.3.

Use of the NMR shift reagent $Eu(fod)_3$ [4] confirms the presence of the unique, symmetrically inserted ketone grouping. Large downfield shifts (up to ~10 ppm) are observed for the ring substituents (CH_3, H) both α and β ($\alpha > \beta$) to the ketone. For the PhC≡CH derivatives, large splittings and unusual upfield shifts are observed for the Ph groups. The Eu shift results confirm the ^1H NMR assignment of isomers for complex I (R = Me, R' = H) (see Table 1).

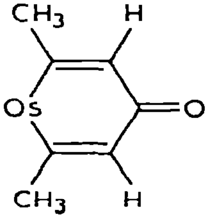
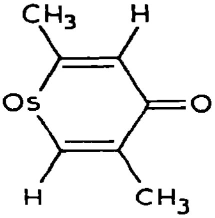
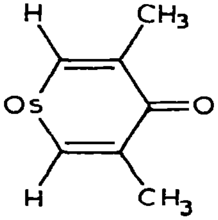
The formation of I from $H_2Os_3(CO)_{10}$ requires a dehydrogenation step which is effected by the excess of acetylene. Compounds I appear to be formed directly, since the relative yields of I and other monoacetylene products [5] are essentially independent of reaction time and acetylene concentration, and we have shown independently that none of the observed monoacetylene derivatives react further with RC≡CR' to give I. This precludes a convenient route to mixed acetylene—I derivatives similar to that found for dinuclear iron [6].

It is noteworthy that whereas the monosubstituted RC≡CH (R = CH_3, CH_3CH_2, $(CH_3)_3C$, Ph) give 20-50% yields of I disubstituted acetylenes RC≡CR' (R = Ph, R' = CH_3, CH_3CH_2), give very low yields (≤3%). Surprisingly $CH_3OCH_2C{\equiv}CCH_2OCH_3$ gives a yield of 90% of I. The formation of I is not stereospecific; three isomers are normally obtained in similar yields, but PhC≡CH yields only two, $Os_3(CO)_9$(PhC=CHCOCH=CPh) and $Os(CO)_9$-(PhC=CHCOC(Ph)=CH).

The subtle kinetic control in these systems is further evidenced with PhC≡CPh in which II (~10%) (Fig. 3) is obtained rather than I. Possibly is the precursor of II, CO, being extruded from the ring. Indeed, $Os_3(CO)_{10}(PhC_2H)_2$

TABLE 1

PHYSICAL DATA FOR $Os_3(CO)_{10}(CH_3C_2H)_2$ ISOMERS

Ring structure			
Colour	Pink-red	Orange-red	Orange
M^+ [a]	936	936	936
R_F [b]	0.1	0.2	0.3
IR, ν(CO) (cm^{-1}) [c]	2093m 2057s 2050s 2023s 2004(sh) 2000sm 1980m 1952w 1638wm	2094m 2058s 2051s 2023s 2009w 2000sm 1981m 1953w 1631wm	2094m 2059s 2051s 2022s 2009(sh) 2001sm 1982m 1955w 1628wm
^1H NMR (τ, ppm) [d]	6.85(s, 3H) 4.24(s, 1H)	6.85(s, 3H), 7.67(s, 3H) 4.12(s, 1H), —0.08(s, 1H)	7.65 (s, 3H) —0.11 (s, 1H)
Eu shift ratio [e] CH_3/H	0.108 [f]	2.40 [f], 0.055 [f], 0.642 [g]	2.19 [f]

[a] Parent ion, $^{192}Os_3$ peak. [b] Silica, CH_2Cl_2. [c] Cyclohexane. [d] $CDCl_3$, 40°. [e] Relative shifts, $Eu(fod)_3$. [f] Groups same side of ring. [g] Groups opposite side of ring.

(I) is converted rapidly in n-octane under reflux (10 min) into $Os_3(CO)_8$-$(PhC_2H)_2$ (III), $Os_2(CO)_6(PhC_2H)_2$ (IV) and another unidentified product. The formation of III instead of II is not surprising, since for PhC≡CPh, II on heating rapidly undergoes *ortho*-metallation with CO loss to give III. Consistently these more vigorous conditions correspond to those under which III and IV, the dinuclear analogue of II, were originally obtained [1,3] from PhC≡CPh and the markedly less reactive $Os_3(CO)_{12}$ (cf. $H_2Os_3(CO)_{10}$). The *ortho*-metallation of II to give III can be reversed with CO but on further reaction the cluster III breaks down (20 °C) to give IV [1,3]. Clearly *ortho*-metallation is an important feature in these reaction sequences, for we note that the $Os_3(CO)_{10}(CH_3C_2H)_2$ complexes of type I which cannot give III are significantly more thermally stable than the phenyl-substituted complexes, and are essentially unchanged after 3 h reflux in n-heptane[*].

Finally, we note that dinuclear Fe [7], Ru [8] and Os [1,3,9] analogues of II are known, and indeed dinuclear Fe complexes very similar to I [6,10][**]. An unusual *ortho*-metallated Fe_2 complex derived from PhC≡CPh also exists [11].

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[*] No *ortho*-metallated analogues of I have been obtained.

[**] Note that the dinuclear Fe complexes show structural differences similar to those found for I and II [6,7,10].

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