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PRODUCTS OF THE REACTION OF $H_2Os_3(CO)_{10}$ WITH CYCLONONA-1,2-DIENE

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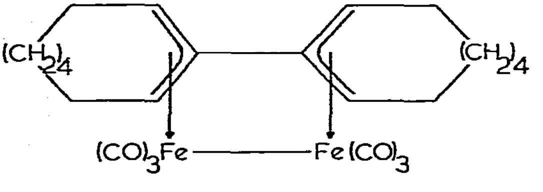
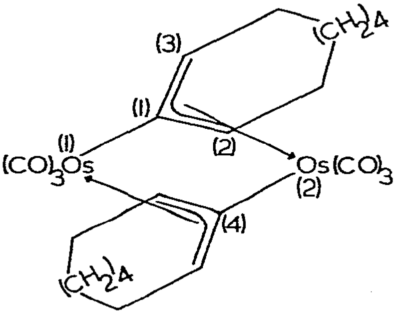
Summary

Treatment of $H_2Os_3(CO)_{10}$ with cyclonona-1,2-diene produced $HOs_3(CO)_9C_9H_{13}$ and $Os_2(CO)_6(C_9H_{14})_2$. Single crystal X ray analysis has shown that the latter is not isostructural with $Fe_2(CO)_6(C_9H_{14})_2$.

Recently it was found that the reaction of cyclonona-1,2-diene, the smallest stable cyclic allene, with $Fe_2(CO)_9$, proceeded with dimerisation of the allene ligand to give the bis(π-allylene)$Fe_2(CO)_6$ complex (1) [1]. The structure of this complex was elucidated by single crystal X ray analysis, which showed the allene dimer to be coordinated unsymmetrically to the $Fe_2(CO)_6$ moeity. Variable temperature ^{13}C NMR studies showed this molecule was involved in rapid *cis—trans* isomerisation which rendered the two sets of outer allyl positions equivalent at room temperature.



(I)



(II)

We now report a reaction between $H_2Os_3(CO)_{10}$ [2] and cyclonona-1,2-diene which proceeds at 25°C to give two products, identified analytically and spectroscopically (see Table 1) as $Os_2(CO)_6(C_9H_{14})_2$ (II) and $HOs_3(CO)_9C_9H_{13}$ (III). Initial evidence pointed toward compound II being isostructural with its iron

TABLE 1

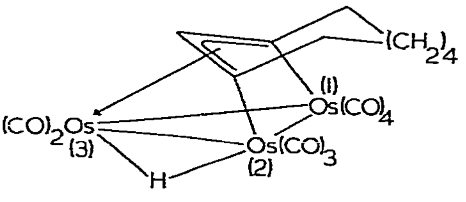
SPECTROSCOPIC DATA FOR COMPOUNDS I, II AND III

COMPOUND	INFRA RED SPECTRUM †	^{1}H N.M.R. SPECTRUM ††	MASS SPECTRUM	ANALYSIS †††
$Os_2(CO)_6(C_9H_{14})_2$	2060s, 1989s, 1986s	6.12τ(t; 1H; J = 8Hz) 8.50τ(m; 6H)	M^+=796 $M-(CO)_n$ n=0→6	C=36.20(36.18) H=3.61(3.52)
$HOs_3(CO)_9C_9H_{13}$	2095m, 2066s, 2040s, 2020s, 2009m, 1993s, 1986m, 1979m, 1972m	6.75τ(m; 1H) 7.25τ(m; 12H) 31.00τ(s; 1H)	M^+=950 $M-(CO)_n$ n=0→9	C=22.69(22.73) H=1.40(1.47)
$Fe_2(CO)_6(C_9H_{14})_2$ [1]	2055, 2013, 1985, 1961	6.74τ(t; 1H; J = 9Hz) 8.15τ(m; 6H)	M^+=524	

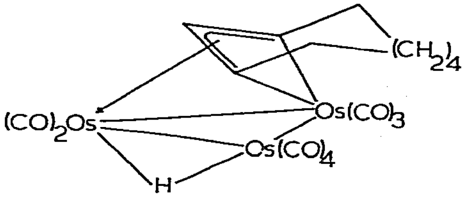
† s=strong; m=medium

†† s=singlet; t=triplet; m=multiplet

††† calculated values in parentheses



(IIIa)



(IIIb)

analogue I, but a closer examination of the spectroscopic data for the two complexes (see Table 1) revealed disimilarities, which prompted examination of the product by single crystal X ray analysis [3].

Crystals of II are monoclinic, space group $P2_1/c$, with a = 7.174(3), b = 8.850 (4), c = 19.17(1) Å, β = 103.1°, U = 1185 Å^3, Z = 2 [3]. The two cyclononaallyl rings are bound in a symmetrical fashion with an approximate, though not crystallographic, plane of symmetry through Os(1), Os(2), C(1), C(4). Thus the angle Os(1)—C(1)—C(2) is 120(1)° whereas Os(1)—C(1)—C(3) is 118(1)°. The distances Os(1)—C(1) (2.16(1) Å), Os(2)—C(1) (2.25(1) Å), Os(2)—C(3) (2.30(1)-Å) and Os(2)—C(2) (2.30(1) Å) reflect the nature of the bonding of the cyclononaallyl ring to the two osmium atoms. The distance Os(1)—Os(2) (3.629(1) Å) indicates the absence of a metal—metal bond which is consistent with the eighteen valence electron rule. Both C(1)—C(3) and C(1)—C(2) are 1.47(2) Å and the angle C(2)—C(1)—C(3) is 120(1)°.

Variable temperature ^{13}C NMR studies of complex II also indicate the equivalence of the outer allyl positions, even at −95°C. The ^{1}H-decoupled ^{13}C NMR spectrum (CD_2Cl_2, 0.05 M $Cr(acac)_3$) showed C(2), C(3) as a singlet at 111.4, C(1) as a singlet at 145.0 and the methylene carbons as a multiplet centered at 28.9 ppm. (This contrasts markedly with compound I in which the inner allylic carbon atoms appear at 84.4 and the outer allylic carbon atoms at 66.6 ppm.) Two carbonyl resonances in the ratio 1 : 2 were observed at 177.9 and 180.7 ppm. These data are not only in agreement with the crystal structure determination of an approximate plane of symmetry but also show that localised carbonyl exchange between different sites on the same metal atom was not occuring.

Compound III was shown by a variety of spectroscopic methods (see Table 1) to be $HOs_3(CO)_9C_9H_{13}$. In contrast to other trinuclear osmium clusters [4—6] for which a structural model displaying a bridging carbonyl appears satisfactory, the apparent absence of a bridging carbonyl band in the IR spectrum of compound III indicates that, if the structure is of type IIIa, only Os(3) has the optimum eighteen valence electrons, whereas Os(1) and Os(2) have nineteen and seventeen valence electrons respectively. However conformity to the eighteen electron rule can be achieved by considering the Os(1)—Os(2) interaction as a donor acceptor bond of a type recently proposed for $Os_3(CO)_{10}C_2(C_6H_5)_2$ [7]. Less formally this would require the six electrons donated by the organic ligand and the metal hydride to be delocalised over the metal triangle. An alternative structure must be considered (IIIb) in which the allylic fragment is coordinated to one osmium atom only. This structure satisfies the eighteen electron rule. A low temperature ^{13}C NMR limiting spectrum of the compound could not be obtained and no suitable samples were prepared for single crystal X ray analysis. It was therefore not possible to distinguish between these two proposed structures.

Experimental

^{13}C NMR spectra were recorded on a Varian Associates XL 100 spectrometer operating in the Fourier Transfer mode at 25.2 MHz. All ^{13}C NMR spectra were ^1H decoupled. Chemical shifts relative to TMS. ^1H NMR spectra were recorded on a Varian Associates CFT 20 spectrometer operating in the Fourier Transform mode at 80 MHz. Mass spectral data were recorded on an AEI MS 12 spectrometer and IR data on a Perkin Elmer 257 spectrophotometer. Cyclonona-1,2-diene was used as purchased.

Preparation of $Os_2(CO)_6(C_9H_{14})_2$ and $HOs_3(CO)_9C_9H_{13}$: $H_2Os_3(CO)_{10}$ (50 mg) was stirred with cyclonona-1,2-diene (0.1 ml) in hexane (50 ml) for eight h at 25°C. After removal of the solvent and excess diene under reduced pressure the residue was chromatographed (using hexane) on TLC plates (silica) to give two bands. The first yielded $Os_2(CO)_6(C_9H_{14})_2$ as colourless crystals (from hexane; 40 mg). The second $HOs_3(CO)_9C_9H_{13}$ as dark red crystals (from hexane; 30 mg).

Acknowledgements

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