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REACTIONS OF DODECACARBONYLTRIOSMIUM WITH DIENIC LIGANDS

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Summary

Dodecacabonyltriosmium reacts with diene ligands (D) such as 2,4-*trans*, *trans*- and 2,4-*cis,trans*-hexadiene and 1,6- and 1,5-heptadiene to give $H_2Os_3D(CO)_9$, $H_4Os_4(CO)_{12}$ and two isomers of molecular formula $HOs_3(D - H)(CO)_9$ in addition to $Os_2(D - 2H)(CO)_6$ and $OsD(CO)_3$. The structures of the trimetal complexes show that dehydrogenation, isomerization and rearrangement of the organic substrates occur before the coordination to the metal cluster. 2,3-Dimethyl-1,3-butadiene and dodecacabonyltriosmium give only the well known bi- and mono-metal complexes. The results are compared with those obtained in the reactions of the some organic molecules with dodecacabonyltriruthenium.

Introduction

Dodecacabonyltriosmium has been shown to cause cleavage of C—H bonds in a variety of unsaturated organic molecules. In particular alkenes and alkynes give hydrido-carbonyltriosmium complexes containing rearranged ligands [1—5]. We describe below a study of the reactions of diene ligands with dodecacabonyltroismium indicating a comparison with the corresponding reaction of $Ru_3(Co)_{12}$ [6].

Results and discussion

The reaction of dodecacabonyltriosmium with 2,4-*trans,trans*-hexadiene (L) in refluxing toluene under nitrogen gives, after 8 h, three triosmium complexes (I), (III), (IV), with traces of $H_4Os_4(CO)_{12}$ (II). After longer times $Os_2(L - 2H)(CO)_6$ (V) and $OsL(CO)_3$ (VI) are also obtained in quite good yields.

The mass spectrum of I shows a molecular formula of $Os_3C_6H_{12}(CO)_9$, while the pattern of the IR absorption bands and the position of the high field signals in the ^{1}H NMR spectrum suggest that I should be formulated as $H_2Os_3C_6H_{10}(CO)_9$, having a structure similar to that of the compound $H_2Os_3C_5H_8(CO)_9$

obtained from $Os_3(CO)_{12}$ and 2-*trans*-pentene [5].

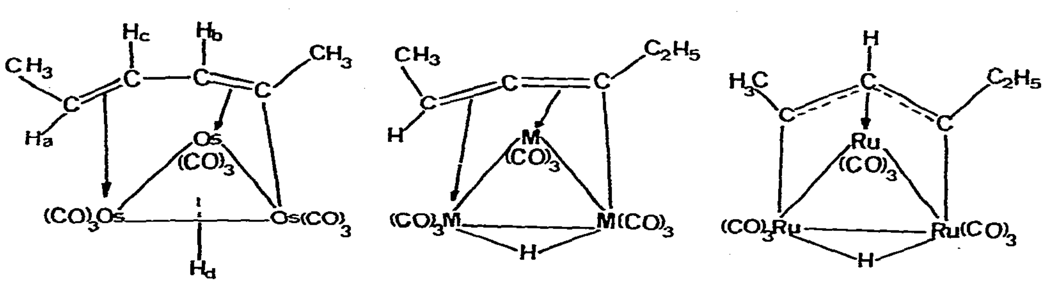
The formation of I and of $H_4Os_4(CO)_{12}$ can be ascribed to partial dehydrogenation of the substrate by the metal cluster. A reaction of $Os_3(CO)_{12}$ with 2,4-*trans,trans*-hexadiene under the same conditions but in the presence of molecular hydrogen gave I and $H_4Os_4(CO)_{12}$ after only 2 h.

Compounds III and IV have the same molecular formula and show the same successive loss of nine carbonyl groups in their mass spectra. The IR and NMR spectra show that the isomer III is identical to the $HOs_3C_6H_9(CO)_9$ obtained from $Os_3(CO)_{12}$ and 3-hexyne [1] and therefore, contains a ligand arrangement similar to that in $HRu_3C_5H_7(CO)_9$ [6]. The isomer IV, which is obtained in good yield compared with III, displays an IR spectrum in the C—O stretching region very similar to that of III, whereas the ^1H NMR spectrum shows at τ 28.30 a singlet H_d, at τ 8.0—7.6 a multiplet due to overlapped patterns H_a and CH_3CH_a, at τ 7.35 a singlet CH_3COs, at τ 4.85—4.70 a complex multiplet H_c, and at τ 2.55 a double doublet H_b. This pattern suggests a ligand arrangement of the type shown in Fig. 1(a), where the ligand behaves as a 5 electron donor. The shift of the CH_3COs and H_b signals to low fields is probably due to the σ—π bond of the organic moiety to the metal cluster [2,6,7].

The complex $Os_2(L - 2H)(CO)_6$ (V) shows the structure containing an osmacyclopentadiene ring coordinated by an $Os(CO)_3$ group, which has been previously identified [8]. Similarly $OsL(CO)_3$ (VI) exhibits the same structure as the monometal compounds obtained from $Ru_3(CO)_{12}$ and several dienes [6].

The reaction of $Os_3(CO)_{12}$ and 2,4-*cis,trans*-hexadiene under similar conditions gave the same products.

1,6-Heptadiene and 1,5-heptadiene (L') react with $Os_3(CO)_{12}$ in toluene under reflux to give the analogous complexes: the IR and mass spectra indicate that the skeletons are similar to those in I, III and IV. We could not obtain information about the fractions isolated in the reactions with heptadiene from the ^1H NMR spectra because of the complexity in the 0—10 τ range. The presence of very close resonances at high fields, such as at τ 32.04 and 32.12 in the NMR spectra of the III' fraction suggests the formation of isomers differing in the side-chains of the organic ligand. Thus it can be assumed that a prior isomerisation of the substrates occurs, to make possible the same type of coordi-



(a) (b) (c)

Fig. 1. (a) Suggested structure of $HOs_3C_6H_9(CO)_9$ (IV) (b) Structure of $HM_3C_6H_9(CO)_9$, M = Os (III), Ru [6b] (c) Structure of $HRu_3C_6H_9(CO)_9$ [6a].

nation as is observed with the hexadienes. Bi- and mono-metal complexes of formula $Os_2(L' - 2H)(CO)_6$ and $OsL'(CO)_3$ were also isolated in the reaction of $Os_3(CO)_{12}$ with heptadienes, and this supports the suggestion of an initial isomerisation of the substrates to give species containing conjugated double bonds.

The reaction of dodecacabonyltriosmium with 2,3-dimethyl-1,3-butadiene (L″) under similar conditions does not give tri-metal complexes, but only $Os_2(L'' - 2H)(CO)_6$ and $OsL''(CO)_3$. This indicates that the presence of at least one hydrogen atom α to a double bond is essential for the ligand to give the rearrangements responsible for III and IV. Very similar behaviour was observed in the reaction of dodecacabonyltriruthenium with the same dienes, including similar isomerisations and formation of complexes from rearranged diene. On the other hand, when the structures of the organic units present in the tri-metal complexes obtained from $Ru_3(CO)_{12}$ are compared with those from $Os_3(CO)_{12}$, the nature of the metal is seen to a role in the rearrangement of the dienic skeleton. Thus the type III structure is formed for both Ru and Os, whereas an isomer containing a pseudo-π-allyl moiety is obtained only from $Ru_3(CO)_{12}$. Moreover, the reaction of $Os_3(CO)_{12}$ with L gives a third isomer (IV), in which the coordinated ligand is only slightly changed compared to the free diene. This suggests that IV is the first stage in the interaction of dienic molecules with $Os_3(CO)_{12}$.

Experimental

IR spectra were recorded on a Beckman model IR 12 doublebeam spectrophotometer with KBr optics. ^1H NMR spectra were obtained with a Jeol 60 HL spectrometer and mass spectra with a Hitachi RMU 6H mass spectrometer, at an ionising energy of 70 eV.

All reactions were carried out under nitrogen. The products were separated by TLC, using Kieselgel $PF_{254+356}$ as absorbent. The petroleum ether used for elution had b.p. 60—70°C.

All the products were crystallised from n-heptane at 0°C.

Reaction of $Os_3(CO)_{12}$ with 2,4-trans,trans-hexadiene and 2,4-cis,trans-hexadiene.

A solution of $Os_3(CO)_{12}$ (0.200 g) and hexadiene (1.25 cm^3) in toluene (300 cm^3) was refluxed for 24 h. The solution was evaporated under vacuum and the residue was extracted with $CHCl_3$. The extract was separated by TLC (eluent petroleum ether, and 2% diethyl ether) to give six main bands, the first containing a yellow compound (I) (0.004 g), the second a mixture of II (0.002 g) and unreacted $Os_3(CO)_{12}$, the third a colourless compound (III) (0.002 g), the fourth a yellow compound (IV) (0.006 g), the fifth a white compound (V) (0.005 g), and the sixth a colourless compound (VI) (0.004 g). The mixture of II and $Os_3(CO)_{12}$ was subsequently separated by TLC (eluent petroleum ether).

I, $H_2Os_3(C_6H_{10})(CO)_9$, $\nu(CO)$ (n-heptane): 2106w, 2081vs, 2057vs, 2030s, 2020s, 2015s, 2007m, 1993w, 1984m cm^{-1}; mass spectrum: M^+ at m/e 912, followed by the loss of nine carbonyl groups; ^1H NMR spectrum (CCl_4):

τ 28.3 s (1), 31.3 s (1) and overlapping complex patterns in the 0—10 τ range.

II and III were identified as $H_4Os_4(CO)_{12}$ and $HOs_3(C_6H_9)(CO)_9$, respectively [1].

IV, $HOs_3(C_6H_9)(CO)_9$, ν(CO) (n-heptane): 2092s, 2063vs, 2041vs, 2020s, 2006s, 1994s, 1984s cm^{-1}; mass spectrum: M^+ at m/e 910, followed by the loss of nine carbonyl groups; ^{1}H NMR spectrum (CCl_4): τ 2.55dd (J_{bc} 4.5 Hz, J_{ba} 0.75 Hz) H_b; τ 4.70—4.85m, H_c, τ 7.35s CH_3COs, τ 7.6—8.0m H_a and CH_3CH_a, τ 28.30s H_d.

V was identified as $Os_2(C_6H_8)(CO)_6$ [8].

VI, $Os(C_6H_{10})(CO)_3$, ν(CO) (n-heptane): 2060s, 1986vs, 1973s cm^{-1}; mass spectrum: M^+ at m/e 358, followed by the loss of three carbonyl groups [6].

Reaction of $Os_3(CO)_{12}$ with 2,4-trans,trans-hexadiene carried out under hydrogen

A solution of $Os_3(CO)_{12}$ (0.200 g) and 2,4-*trans,trans*-hexadiene (1.25 cm^3) in toluene (300 cm^3) was refluxed for 2 h. Work up as before, culminating in separation by TLC (eluent petroleum ether, and 2% diethyl ether) gave two main bands, the first containing I (0.004 g) and the second a mixture of II (0.002 g) and unchanged $Os_3(CO)_{12}$.

I and II were identified as $H_2Os_3(C_6H_{10})(CO)_9$ and $H_4Os_4(CO)_{12}$, respectively.

Reaction of $Os_3(CO)_{12}$ with 1,6-heptadiene and 1,5-heptadienes

The reactions were carried out as described for the hexadienes. Six main fractions were separated, as above.

I′, $H_2Os_3(C_7H_{12})(CO)_9$, ν(CO) (n-heptadiene): 2106w, 2079vs, 2057vs, 2029s, 2019s, 2014s, 2006m, 1992w, 1983w cm^{-1}; mass spectrum: M^+ at m/e 1010, followed by the loss of nine carbonyl groups.

II′ was identified as $H_4Os_4(CO)_{12}$.

III′, $HOs_3(C_7H_{11})(CO)_9$, ν(CO) (n-heptane): 2097m, 2068vs, 2043vs, 2023s, 2012m, 1998s, 1991(sh)m, 1986(sh)w, 1974w, 1942w cm^{-1}; mass spectrum: M^+ at m/e 1008, followed by the loss of nine carbonyl groups; ^{1}H NMR spectrum (CCl_4): τ 32.04 s (1), 32.12 s (1).

IV′ $HOs_3(C_7H_{11})(CO)_9$, ν(CO) (n-heptane): 2092s, 2063vs, 2041vs, 2020s, 2008s, 1994s, 1988m, 1974m cm^{-1}; mass spectrum: M^+ at m/e 1008, followed by the loss of nine carbonyl groups.

V′ $Os_2(C_7H_{10})(CO)_6$, ν(CO) (n-heptane): 2082s, 2049vs, 2011vs, 2003vs, 1982s, 1972vs cm^{-1}; mass spectrum: M^+ at m/e 732, followed by the loss of six carbonyl groups [8].

VI′, $Os(C_7C_{12})(CO)_3$, ν(CO) (n-heptane): 2058s, 1985vs, 1980s cm^{-1}; mass spectrum: M^+ at m/e 372, followed by the loss of three carbonyl groups [6].

Reaction of $Os_3(CO)_{12}$ with 2,3-dimethyl-1,3-butadiene

A solution of $Os_3(CO)_{12}$ (0.200 g) and 2,3-dimethyl-1,3-butadiene (1.00 cm^3) in toluene was refluxed for 24 h. Work up as before, culmination in separation by TLC (eluent petroleum ether, and 5% diethyl ether) gave two main bands, the first containing a white compound (V″) (0.006 g) and the second a colourless compound (VI″) (0.005 g).

V″ was identified as $Os_2(C_6H_8)(CO)_6$ [8].

VI″, $Os(C_6H_{10})(CO)_3$, ν(CO) (n-heptane): 2063s, 1987vs, 1975s cm^{-1}; mass spectrum: M^+ at *m/e* 358, followed by the loss of three carbonyl groups [6].

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