Inorganica Chimica Acta, 20 (1976) 141 – 143

Cleavage of Carbon–Hydrogen Bonds in Reactions of Dodecacarbonyltriosmium with Pentenes and Hexenes

R. P. FERRARI and G. A. VAGLIO

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy

Received April 1, 1976

*Homogeneous isomerisation of 1-pentene to 2-*cis-*and 2-*trans-*pentene occurs in presence of dodecacarbonyltriosmium. A contemporaneous formation of compounds of molecular formula* $HOs_3(CO)_{10}C_5H_9$ *and* $H_2Os_3(CO)_9C_5H_8$ *can be observed. The structures of these complexes are discussed. An analogous behaviour is shown by dodecacarbonyltriosmium in its reactions with hexenes.*

Introduction

Cleavage of carbon–hydrogen bonds of unsaturated molecules is accomplished by dodecacarbonyltriosmium and the resulting species are present as ligands in hydridocarbonyl complexes [1–5]. We now report some related work on the reactions of $Os_3(CO)_{12}$ with linear alkenes, such as pentenes and hexenes, where the formation both of isomers of the starting molecules and of hydridocarbonyl complexes takes place. So far the reactions of $Os_3(CO)_{12}$ and alkenes, such as ethylene and propene, have been described [2].

Experimental

I.r. spectra were recorded on a Beckman model IR 12 double-beam spectrophotometer with KBr optics. Proton n.m.r. spectra were obtained with a Jeol 60 HL spectrometer and mass spectra with a Hitachi RMU 6H mass spectrometer, using an ionising energy of 75 eV. Gaschromatographic analyses were performed at 55 °C by a C. Erba Fractovap model B, using a 4m column of 20% silicon oil 720 on chromosorb P 60/80 mesh. Helium was used as carrier gas at 50 ml/min.

All reactions were carried on under nitrogen, unless stated otherwise. The reaction products were separated by TLC, using as absorbent kieselgel $PF_{254+356}$. The petroleum ether used in elutions had b.p. 60–70 °C. All the products were crystallised from n-heptane at 0 °C.

Reaction of Dodecacarbonyltriosmium with 1-Pentene

A solution of $Os_3(CO)_{12}$ (0.300 g) and 1-pentene (2.0 ml) was heated in refluxing toluene (500 ml) for 15 hours. The yellow solution was dried under vacuum and the residue, extracted with carbon tetrachloride, was separated by TLC (eluent petroleum ether and 3% diethyl ether) to give two main bands, the first containing a yellow compound (I) (0.006 g) and a colourless compound (II) (0.006 g), and the second a large amount of unreacted $Os_3(CO)_{12}$. Subsequently the mixture of (I) and (II) was separated by TLC, eluent petroleum ether. (I), ν(n-heptane): 2108w, 2063vs, 2055s, 2024vs, 2015s, 1999m, 1995m, 1990w, 1983m cm^{-1}; mass spectrum, m/e 926 [M$^+$], followed by the loss of ten carbonyl groups; ^{1}H. n.m.r. spectrum (CCl_4): τ 2.91d (1), 5.65t (1), 8.08dt (2), 8.45s′ (2), 9.01t (3), 28.9s (1). (II), ν(n-heptane): 2106w, 2081vs, 2057vs, 2030s, 2020s, 2015s, 2007m, 1993w, 1984m cm^{-1}; mass spectrum, m/e 898 [M$^+$], followed by the loss of nine carbonyl groups; ^{1}H n.m.r. spectrum (CCl_4): τ 3.09d (1), 7.93dt (2), 8.37s′ (2), 8.96t (3), 28.3s (1), 31.3s (1).

*Reaction of Dodecacarbonyltriosmium with 2-*cis-*Pentene and 2-*trans-*Pentene*

The reactions, carried out under analogous conditions, gave two complexes, (I′) and (II′), separated as above. When the ligand used was 2-*trans*-pentene, (I′) (0.002g) and (II′) (0.004g), subsequently purified by TLC (eluent petroleum ether) were characterised as follows. (I′), ν(n-heptane): 2106w, 2062vs, 2054s, 2023vs, 2014s, 2005m, 1992w, 1981m cm^{-1}; mass spectrum, m/e 926 [M$^+$], followed by the loss of ten carbonyl groups; ^{1}H n.m.r. spectrum (CCl_4): hydrido singlet at τ 28.9. (II′), ν(n-heptane): 2106w, 2079vs, 2055vs, 2028s, 2018s, 2014s, 2005s, 1990w, 1981m cm^{-1}; mass spectrum, m/e 898 [M$^+$], followed by the loss of nine carbonyl groups; ^{1}H n.m.r. spectrum (CCl_4): τ 3.08q (1), 6.34q (1), 8.15d (3), 8.66d (3), 28.3s (1), 31.4s (1).

Reaction of Dodecacarbonyltriosmium with 3-trans-Hexene

A solution of $Os_3(CO)_{12}$ (0.300g) and 3-*trans*-hexene (2.0 ml) was heated in refluxing toluene (500 ml) for 15 hours. The cooled solution was filtered, the solvent removed under vacuum and the residue dissolved in carbon tetrachloride. Separation by TLC, eluent as above, gave one main band containing a yellow compound (I″) (0.006 g) and a colourless compound (II″) (0.006 g). (I″) and (II″) were further separated by TLC, eluent petroleum ether. (I″), ν(n-heptane): 2106w, 2061vs, 2053s, 2023vs, 2013m, 1998m, 1995m, 1990w, 1983m cm^{-1}; mass spectrum, m/e 940 $[M^+]$, followed by the loss of ten carbonyl groups; ^1H n.m.r. spectrum (CCl_4): hydrido singlet at τ 28.9. (II″), ν(n-heptane): 2106w, 2079vs, 2056vs, 2029s, 2019ms, 2014s, 2006m, 1992w, 1983m cm^{-1}; mass spectrum, m/e 912 $[M^+]$, followed by the loss of nine carbonyl groups; ^1H n.m.r. spectrum (CCl_4): hydrido singlets at τ 28.3 and 31.4 in the ratio 1:1.

Thermal Decomposition of (I)

A toluene solution (100 ml) of (I) (0.025 g) was refluxed for 3 hours. The cooled solution was filtered and the solvent removed under vacuum. The residue was dissolved in carbontetrachloride and separated by TLC, eluent petroleum ether, to give (II) (0.015g) and traces of unreacted (I).

Reaction of (II) with Carbon monoxide

A stream of carbon monoxide was bubbled through a solution (100 ml) of (II) (0.020 g) in refluxing petroleum ether (b.p. 60–70 °C) for 8 hours. Then the solution was dried under reduced pressure and the residue, extracted with carbon tetrachloride, was separated by TLC, eluent petroleum ether. $Os_3(CO)_{12}$ (0.010 g) was obtained as main product with traces of unreacted (II).

Hydrogenation of $HOs_3(CO)_9C_5H_7$ with H_2

A slow stream of H_2 was bubbled through a solution of $HOs_3(CO)_9C_5H_7$ (0.030 g) in toluene under reflux for 24 hours. After cooling the filtered solution was dried under reduced pressure and the residue was extracted with carbon tetrachloride and separated by TLC (eluent petroleum ether and 2% diethyl ether) to give (III′) and unreacted $HOs_3(CO)_9C_5H_7$. (III′), ν(n-heptane): 2105m, 2077s, 2054vs, 2029s, 2020m, 2009s, 1998m, 1983m cm^{-1}; mass spectrum, m/e 898 $[M^+]$, followed by the loss of nine carbonyl groups; ^1H n.m.r. spectrum (CCl_4): hydrido broad singlet at τ 29.0.

$HOs_3(CO)_9C_5H_7$ was prepared from $Os_3(CO)_{12}$ and 2-pentyne, under conditions completely analogous to those used for $HOs_3(CO)_9C_6H_9$ [5].

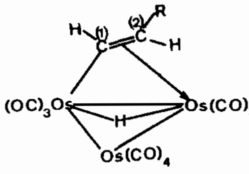
Isomerisation of 1-Pentene catalysed by Dodecacarbonyltriosmium

10.0 ml of 2.5 × 10^{-4} *M* toluene solution of $Os_3(CO)_{12}$ were sealed under nitrogen in a 70 ml tube equipped with a gc septum to add 50 μl of 1-pentene and to remove known amounts of solution by a liquid syringe. The ampoules were placed in a thermostatic tank at 120 °C. The extent of the isomerisation reaction was checked by gc analyses of solution samples.

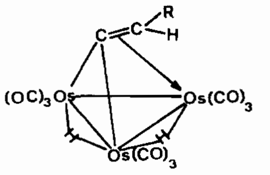
Results and Discussion

Dodecacarbonyltriosmium in toluene solution shows catalytic activity in the isomerisation of linear monoolefins, such as pentenes and hexenes, at temperatures of 110–120 °C. Conversion of 1-pentene gives 2-*cis*- and 2-*trans*-pentene in an initial ratio 0.4–0.5. Reliable values of the initial isomerisation rate cannot be obtained, because the formation of carbonyl complexes occurs since the 1-pentene conversion begins to be detectable.

The first product of the reaction between $Os_3(CO)_{12}$ and 1-pentene is a compound of molecular formula $Os_3(CO)_{10}C_5H_{10}$ (I) which gives $Os_3(CO)_9C_5H_{10}$ (II) by loss of carbon monoxide. Most of the starting $Os_3(CO)_{12}$ remains unreacted and no other products can be detected. At longer reaction times the amounts of (I) and (II) decrease while traces of a number of other compounds, not identified, are formed. Chemical reactivity and analogous i.r. and n.m.r. spectra indicate for (I), reformulated as $HOs_3(CO)_{10}C_5H_9$, a structure shown below, similar to that of $HOs_3(CO)_{10}CR^1CHR^2$ (R^1 = H, R^2 = H, CH_3), obtained from $H_2Os_3(CO)_{10}$ and acetylene or propyne [6].



(I)



(II)

In addition to the singlet at τ 28.9, the proton n.m.r. spectrum of (I) shows a doublet at τ 2.91 assignable to H–C(1) coupled (J = 13.4 Hz) with a doublet–triplet at τ 5.65 due to H–C(2) and signals from the $-CH_2-CH_2-CH_3$ (R) unit linked to C(2). As shown in the reaction scheme, (I) gives (II) in refluxing toluene under nitrogen, while a stream of carbon monoxide converts (II) to $Os_3(CO)_{12}$ directly, without evidence of intermediate formation of (I).

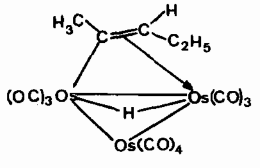
$\rightarrow Os_3(CO)_{12}$ + 1-pentene $\longrightarrow HOs_3(CO)_{10}C_5H_9$ (I)

$\xrightarrow[-CO]{} H_2Os_3(CO)_9C_5H_8$ (II)

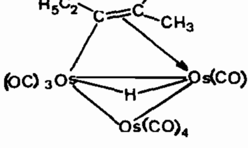
+CO

The proton n.m.r. spectrum of (II) exhibits two singlets at τ 28.3 and 31.4, a triplet at τ 3.09 coupled (J = 6.8 Hz) with a doublet–triplet at τ 7.93, a sextet and a triplet at τ 8.37 and 8.98 respectively. Therefore the structure of (II) is analogous to that of the complexes of the type $H_2Os_3(CO)_9CCHR$, prepared from $H_2Os_3(CO)_{10}$ and terminal alkynes [6] and of $H_2Os_3(CO)_9CCH(CH_3)$, obtained from $Os_3(CO)_{12}$ and propene [2]. In this case 1,1 elimination of hydrogen from the alkene occurs. Indeed the proton n.m.r. spectrum of (II) displays a singlet at τ 1.74, which suggests the presence of a little amount (~5%) of an isomer of (II), where the ligand arrangement is $HC{=}C{-}CH_2{-}CH_2{-}CH_3$.

Treatment of $Os_3(CO)_{12}$ and 2-*cis*-pentene or 2-*trans*-pentene gives two complexes of molecular formula $HOs_3(CO)_{10}C_5H_9$ (I′) and $H_2Os_3(CO)_9C_5H_8$ (II′). The yields of these compounds, in particular of (I′), are rather low, so that a full characterisation was achieved only for (II′). For (I′), obtained from 2-*trans*-pentene, the proton n.m.r. spectrum (which shows the hydrido signal at τ 28.9 and overlapped patterns in the τ 0–10 region) and the i.r. and mass spectra (similar to those of (I)) suggest the formation of the two isomers (I′a) and (I′b).

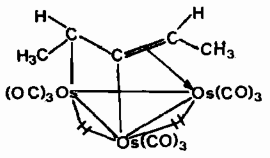


(I′a)



(I′b)

In addition to two singlets in the high field region, two $CH_3{-}CH$ units are present in the hydrocarbon chain of (II′). The quartet at τ 3.08 coupled with the doublet at τ 8.15 (J = 5.8 Hz) suggests that one $CH_3{-}CH$ group is linked by a double bond to the central carbon of the ligand. 3,4 elimination of hydrogen from the alkene takes place as can be seen from the structure of (II′).



(II′)

In the reaction of $Os_3(CO)_{12}$ with 1-pentene complexes of type (I′) and (II′) were not observed. When the reaction is stopped about 90% 1-pentene is, in fact, still present.

Hydrogenation of $HOs_3(CO)_9C_5H_7$, prepared from $Os_3(CO)_{12}$ and 2-pentyne, isostructural with $HRu_3(CO)_9C_6H_9$ [7, 8], gave a yellow complex (III′), isomer of (II′), which exhibits a broad hydrido absorption and an i.r. spectrum strictly related to that of $H_2Os_3(CO)_8CHCCH_3$ [6].

A similar behaviour is shown by $Os_3(CO)_{12}$ in its reaction with hexenes. However, these reactions were not examined in detail, because the number of hexene isomers and possibly of the trinuclear complexes made more difficult the separation and the analysis of the products.

When alkenes are reacted with $Os_3(CO)_{12}$, cleavage of C–H bonds occurs with transfer of hydrogen to the cluster and formation of hydridocarbonyl complexes. A parallel decomplexation process of the organic molecule gives a mixture of alkene isomers. This reaction trend is strictly related to that reported for $Ru_3(CO)_{12}$ [7] and the weaker catalytic activity of $Os_3(CO)_{12}$ in the olefin isomerisation is likely to be ascribed to the higher bond energy of the Os–CO bond. In the case of $Ru_3(CO)_{12}$, however, the formation of hydrido complexes takes place after the equilibrium between the pentene isomers has been reached, whilst the formation of the hydrido complexes from $Os_3(CO)_{12}$ proceeds at a rate similar to the isomerisation rate and gives as first step hydride–vinyl species of the type $HOs_3(CO)_9$(vinyl), as was proposed in the reaction of $Os_3(CO)_{12}$ with ethylene and propene [2].

References

1 A. J. Canty, A. J. P. Domingos, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. Dalton,* 2056 (1973).

2 A. J. Deeming and M. Underhill, *J. Chem. Soc. Dalton,* 1415 (1974).

3 A. J. Deeming and M. Underhill, *J. Chem. Soc. Dalton,* 2727 (1973).

4 O. Gambino, R. P. Ferrari, M. Chinone and G. A.Vaglio, *Inorg. Chim. Acta, 12,* 155 (1975).

5 R. P. Ferrari and G. A. Vaglio, *Gazz. Chim. It., 105,* 939 (1975).

6 A. J. Deeming, S. Hasso and M. Underhill, *J. Chem. Soc. Dalton,* 1614 (1975).

7 M. Castiglioni, L. Milone, D. Osella, G. A. Vaglio and M. Valle, *Inorg. Chem., 15,* 394 (1976).

8 G. Gervasio, D. Osella and M. Valle, private communication.