Journal of Organometallic Chemistry, 320 (1987) 385–390
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DOUBLE BOND SHIFTS INDUCED BY REACTION OF HEX-5-EN-2-ONE WITH TRIOSMIUM CLUSTERS

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(Received September 10th, 1986)

Summary

Carbon–hydrogen bond cleavage at the terminal 6-position occurs when hex-5-en-2-one ($CH_2=CHCH_2CH_2COMe$) oxidatively adds to $[Os_3(CO)_{10}(MeCN)_2]$ to give $[Os_3H(\mu\text{-}CH=CHCH_2CH_2COMe)(CO)_{10}]$, which is completely analogous to the simple vinyl complex $[Os_3H(\mu\text{-}CH=CH_2)(CO)_{10}]$. A minor product from the reaction is $[Os_3(CH_3CH=CHCH_2COMe)(CO)_{10}]$, an isomer in which double-bond migration has occurred to give the $\beta\gamma$-unsaturated ketone; stabilisation occurs through chelation and ketone coordination. $[Os_3H_2(CO)_{10}]$ reacts with $CH_2=CHCH_2CH_2COMe$ in refluxing cyclohexane to give a third isomer, $[Os_3H(CH_3CH_2C=CHCOMe)(CO)_{10}]$, in which further double bond migration has occurred to give the $\alpha\beta$-unsaturated ketone. Metallation at the β-site gives an Os–C bond as part of a 5-membered chelate ring. Thermolysis of each of the three isomeric decarbonyl species in refluxing cyclohexane or heptane leads to the elimination of an $Os(CO)_4$ group to give the dinuclear compound $[Os_2H(EtC=CHCOMe)(CO)_6]$ in varying yield. Pathways from $\gamma\delta$ to the $\beta\gamma$ and finally the $\alpha\beta$ unsaturated ketones may be mapped out.

Introduction

We have previously shown that organic ligands readily coordinate through an oxygen atom when involved in chelation or bridging in triosmium clusters. For example, in the formation of $[Os_3H_2(C_6H_4O)(CO)_9]$ from phenol the ligand is trapped in the dienone form with the keto function coordinated [1,2]. Similarly the oxidative addition product of cyclohex-2-enone, $[Os_3H(C_6H_7O)(CO)_{10}]$, involves coordination through the keto-function [3]. We also reported that the interaction of straight chain $\alpha\beta$-unsaturated enones $RCH=CHCOCH_3$ (R = Me, Ph, or H) gives Os_3 clusters with coordinated oxygen atoms [4]. Corresponding aldehydes behave similarly except that oxidative addition of the aldehydic C–H occurs competitively with vinylic C–H cleavage [6]. Even coordination of an ether function occurs readily

0022-328X/87/$03.50

to stabilize a methoxyethyl complex [$Os_3H(CH_3CHOCH_3)(CO)_{10}$] formed by insertion of methyl vinyl ether into [$Os_3H_2(CO)_{10}$] [6].

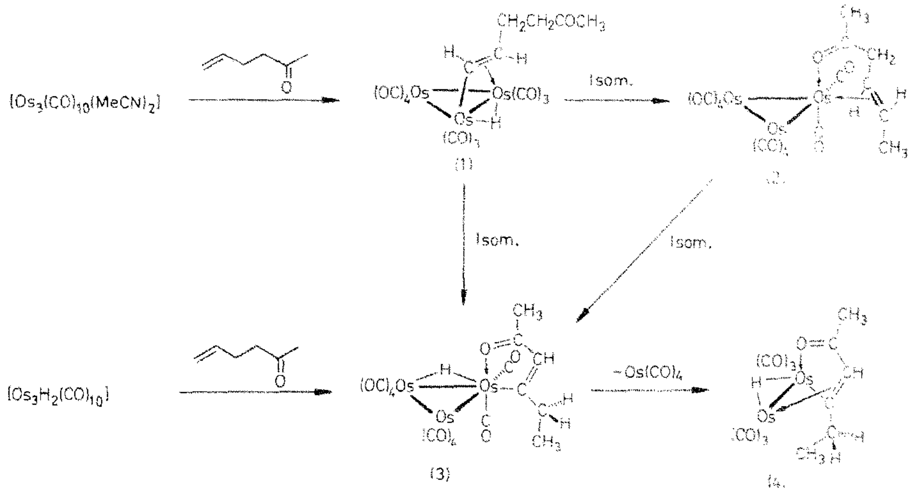
By using the $\gamma\delta$-unsaturated ketone hex-5-en-2-one in which the unsaturated C=C bond is far removed from the keto-function, we have examined the tendency for ketone coordination in this case. We assumed that the alkene group would coordinate initially and that chelation or bridging through the ketone would be much less likely. The overriding chemistry is hydrogen-transfer to shift the double bond in stages through to the $\alpha\beta$-unsaturated ketone.

Brief details of the reaction of [$Os_3(CO)_{10}(MeCN)_2$] with hex-5-en-2-one have already been given but here we will describe three isomers with the formula [$Os_3(C_6H_{10}O)(CO)_{10}$] and their interconversions [7].

Results and discussion

The reaction of hex-5-en-2-one with [$Os_3(CO)_{10}(MeCN)_2$] occurs with oxidative addition at the terminal vinyl group to give [Os_3H(μ-*trans*-$CH{=}CHCH_2CH_2COCH_3$)$(CO)_{10}$] (**1**) with the organic ligand bound only through the vinyl carbon atoms (ν(CO) 1726 cm^{-1}, characteristic of free ketone). The proton–proton coupling constant for the *trans* hydrogen atoms (J 13.7 Hz) may be compared with the corresponding value for [Os_3H(μ-$CH{=}CH_2$)$(CO)_{10}$] of 14.9 Hz [8]. In principle the ketonic function in **1** could coordinate but the large ring size necessary for this makes this unfavourable and an η^2-alkene interaction is prefered. Cluster **1** is directly comparable in every important respect with the $CH{=}CH_2$ analogue.

A minor product [$Os_3(CH_3CH{=}CHCH_2COCH_3)(CO)_{10}$] (**2**) (5%) is formed by double-bond migration from $\gamma\delta$ to $\beta\gamma$ positions and in **2** the ketone is coordinated [ν(CO) 1640 cm^{-1}]. The IR spectrum of **2** compares directly, almost indistinguishably, with those of [$Os_3(CH_2{=}CHOCOCH_3)(CO)_{10}$] or [$Os_3(CH_2{=}CMeCH_2COCH_3)(CO)_{10}$] [7]. The vinyl acetate complex has been structurally characterised so we can be very sure that the structure given for **2** in Scheme 1 is correct. ν(CO)



SCHEME 1

TABLE 1

SPECTROSCOPIC DATA FOR THE $CH_2=CHCH_2CH_2COCH_3$ DERIVATIVES

Compound	ν(CO) ^{a} (cm^{-1})	^{1}H NMR ^{b}		
$[Os_3H^A(CH^B=CH^CCH_2^DCH_2^ECOCH_3^F)(CO)_{10}]$ (1)	2103w, 2058s,	7.10(dd)	B	J_{BC} 13.7
	2050s, 2020vs,	4.29(dt)	C	J_{CD} 6.2
	2010s, 2000sh,	2.68(t)	E	J_{ED} 7.2
	1992m, 1984w,	2.19(dt)	D	
	1978w, 1954vw,	2.18(s)	F	
	1726m	−18.96(d)	A	J_{AB} 1.6
$[Os_3(CH_3^ACH^B=CH^CCH_2^{D,E}COCH_3^F)(CO)_{10}]$ (2)	2102w, 2052s,	3.81(d)	D	J_{DE} 20.8
	2021vs, 2013s,	3.35(dd)	C	J_{CD} 0
	2000m, 1981w,	3.01(dd)	E	J_{CE} 5.7
	1969w, 1936w,	2.32(s)	F	
	1640w	2.20(dq)	B	J_{CB} 9.4
		2.02(d)	A	J_{AB} 5.8
$[Os_3H^A(CH_3^BCH_2^{C,D}C=CH^ECOCH_3^F)(CO)_{10}]$ (3)	2126w, 2069m,	6.64(s)	E	
	2050vs, 2020s,	3.30(m)	C	
	2005m, 1996m,	3.29(m)	D	J_{BC} 7.4
	1981w, 1935w,	2.40(s)	F	
	1526m	1.29(t)	B	J_{BD} 7.4
		−15.32(s)	A	
$[Os_2H^A(CH_3^BCH_2^{C,D}C=CH^ECOCH_3^F)(CO)_6]$ (4)	2094s, 2056vs,	4.06(s)	E	
	2016s, 2003vs,	3.57(m)	C	
	1990s, 1974m,	3.10(m)	D	J_{BC} 7.3
	1486m	2.03(s)	F	
		1.37(t)	B	J_{BD} 7.3
		−11.42(s)	A	

^{a} Cyclohexane solution. ^{b} In $CDCl_3$, 200 MHz, 27°C; δ (ppm). J (Hz).

absorptions around 2000 cm^{-1} (Table 1) for these compounds are essentially the same and a very weak absorption at 1640 cm^{-1} may be assigned to the coordinated ketone.

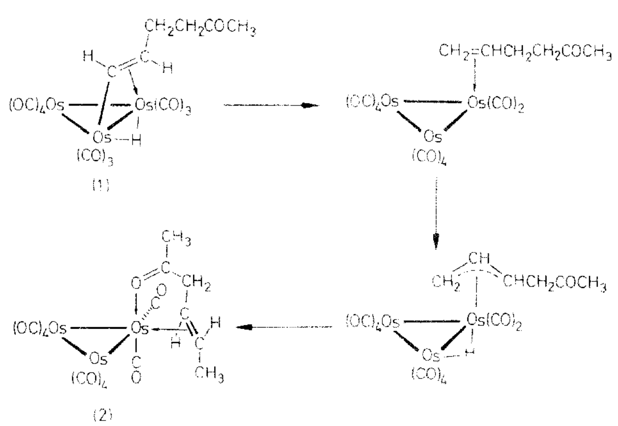
Thermal treatment of either compound **1** or **2** in refluxing cyclohexane (5 h) causes further double bond shift to give the compound $[Os_3H(CH_3CH_2C=CHCOCH_3)(CO)_{10}]$ (**3**). Compound **3** can be assigned to the structure shown in Scheme 1 by comparison with $[Os_3H(CH_3C=CHCOCH_3)(CO)_{10}]$ which is of known X-ray structure [4]. Although we have shown that **1** and **2** both give **3** on heating, it is likely that **1** transforms to **3** via **2**.

No organometallic products are obtained from the room temperature reaction of hex-5-en-2-one with $[Os_3H_2(CO)_{10}]$; the IR spectrum shows that the dihydride persists under these conditions. However, the ^{1}H NMR spectrum shows significant isomerisation of the enone. The dihydride $[Os_3H_2(CO)_{10}]$ is an effective catalyst for the isomerisation of terminal to internal alkenes [9–11], and presumably isomerisation to the $\beta\gamma$-enone occurs. Prolonged reflux of $[Os_3H_2(CO)_{10}]$ with the enone in cyclohexane (12.5 h) gave two Os_3 products: the major is $[Os_3H(CH_3CH_2C=CHCOCH_3)(CO)_{10}]$ (**3**) (53%) and a minor one is $[Os_2H(CH_3CH_2C=CHCOCH_3)(CO)_6]$ (**4**) (8%). Some unreacted $[Os_3H_2(CO)_{10}]$ (3.8%) was also isolated. Compound **3** is also obtained by thermal treatment of **1** or **2**, but this itself decomposes thermally to the dinuclear compound **4**.

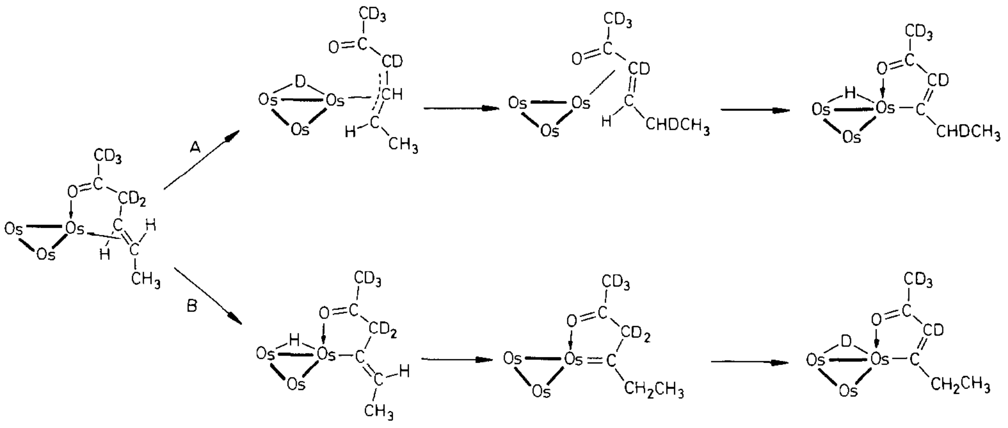
The stoichiometry of compound **4** as $[Os_2H(CH_3CH_2C{=}CHCOCH_3)(CO)_6]$ was established by elemental analysis and the parent molecular ion was observed in the EI mass spectrum (*m/e* corresponding to $^{192}Os_2$ at 650). The ^1H NMR spectrum (Table 1) clearly identifies the ligand as shown. Previously we reported that $[Os_3H(CH{=}CHCOCH_3)(CO)_{10}]$ loses CO on heating to give $[Os_3H(CH{=}CHCOCH_3)(CO)_9]$ which was only obtained as an oil so characterised only by its IR and NMR spectra [4]. This compound compares so closely spectroscopically with **4** that both must be dinuclear and our original report in error. In terms of electron counting the loss of CO from $[Os_3H(RC{=}CHCOCH_3)(CO)_{10}]$ (R = H or Et) is directly analogous to the loss of $Os(CO)_4$, although the latter is much less often encountered. In **4** the $CH_3CH_2C{=}CHCOCH_3$ is a five-electron donating ligand but only a three-electron donor in **3**. In accord with this the H^E signal shifts from $\delta 6.64$ to $\delta 4.06$ on coordination of the C=C bond in going from **3** to **4**. The structure shown for **4** in Scheme 1 is the most likely. The compound $[Ru_2H(PhC{=}CHCOCH_3)(CO)_6]$ and its X-ray structure [12] corresponds directly with that depicted for **4** in Scheme 1. No IR spectrum was reported for the Ru_2 compound but the ^1H NMR spectra compares well with that of **4** in important respects. The appearance of diastereotopic protons for the methylene group of **4** in the ^1H NMR spectrum at room temperature indicates that rapid oscillation of the organic ligand between the Os atoms does not occur.

Scheme 2 is a proposal for the mechanism of isomerisation of **1** to **2**. The oxidative addition whereby **1** is formed is reversed and the allylic C–H bond is then cleaved leading to **2**. Usually vinylic C–H cleavages are more facile than allylic ones in Os_3 clusters, contrary to the norm. As a consequence **1** is formed as the kinetic product of oxidative addition of hex-5-en-2-one to $[Os_3(CO)_{10}(MeCN)_2]$. On thermolysis, the product of oxidative addition at the allylic sites, cluster **2**, is obtained, probably via the route in Scheme 2.

To examine the mechanisms of isomerisation of clusters **1** and **2** to **3**, we prepared $CH_2{=}CHCH_2CD_2COCD_3$ (> 98% deuteration at the indicated sites) by exchange of hex-5-en-2-one with a CH_3OD/D_2O mixture in the presence of $NaOCH_3$ as catalyst. The deuterated enone was used to synthesise compounds **1** to



SCHEME 2



SCHEME 3

3 as in Scheme 1. The deuterium-distributions in these products were established by both ^1H and ^2H NMR spectra. We conclude that compounds **1** and **2** formed from CH_2=$CHCH_2CD_2COCD_3$ are $[Os_3H(CH{=}CHCH_2CD_2COCD_3)(CO)_{10}]$ and $[Os_3(CH_3CH{=}CHCD_2COCD_3)(CO)_{10}]$ respectively and that there has been no scrambling of hydrogen atoms involving the sites α to the ketone. The subsequent isomerisation of these deuterated compounds to **3** gave a 50/50 mixture of diastereomers of $[Os_3H(CH_3CHDC{=}CDCOCD_3)(CO)_{10}]$. In one diastereomer H is in one and D in the other diastereotopic site of the CH_3CHD group but these occupancies reversed in the other. In the ^1H NMR spectrum each diastereomer gives a 1/3/3/1 quartet for the respective $C\mathit{H}DCH_3$ protons at δ3.29 and 3.30. None of the CH_3CH_2 or CH_3CD_2 species are present and no D is in the hydride site.

The conversion of **2** to **3** requires a hydrogen atom shift from the 3- to the 5-position and an oxidative addition (C–H cleavage) at the 4-position. Our deuteration results favour a D-shift from the 3- to 5-position prior to the oxidative addition at the 4-position (process A, Scheme 3). Other mechanisms, such as B in which the oxidative addition occurs first, would lead to deuterium in the hydride site.

Experimental

The starting clusters $[Os_3H_2(CO)_{10}]$ [14] and $[Os_3(CO)_{10}(MeCN)_2]$ [15] were prepared as described previously. Hex-5-en-2-one was used as purchased (Aldrich). All reactions were carried out under nitrogen. Parent molecular ions were observed in the EI mass spectra of compounds **1** to **4**.

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with hex-5-en-2-one

A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.16 g) and hex-5-en-2-one (1 cm^3) in dichloromethane (20 cm^3) was stirred at room temperature for 8 h. Removal of the solvent and TLC (SiO_2; eluant: dichloromethane/petroleum ether (b.p. 30–40°C), 1/4 V/V) gave several bands. The two main ones were extracted with CH_2Cl_2 and gave yellow crystals characterised as $[Os_3H(CH{=}CHCH_2CH_2COCH_3)(CO)_{10}]$ (**1**) (0.050 g, 30%) (Found: C, 21.45; H, 1.3. $C_{16}H_{10}O_{11}Os_3$ calc: C, 20.6; H, 1.1%) and $[Os_3(CH_3CH{=}CHCH_2COCH_3)(CO)_{10}]$ (**2**) (0.008 g, 5%).

Reaction of [$Os_3H_2(CO)_{10}$] with hex-5-en-2-one

No reaction of the dihydride occurred on stirring a solution of it (0.16 g) and hex-5-en-2-one (0.1 cm^3) in cyclohexane (15 cm^3) at room temperature for 2 h (IR evidence). Even after 12.5 h under reflux the solution still contained some [$Os_3H_2CO)_{10}$] but most had reacted. Work-up by TLC [SiO_2; eluant: petroleum ether (b.p. 30–40°C)] gave [$Os_3H_2(CO)_{10}$] (0.006 g, 3.8%) and two yellow crystalline compounds characterised as [$Os_3H(CH_3CH_2C{=}CHCOCH_3)(CO)_{10}$] (**3**) (0.095 g, 53%) (Found: C, 20.4; H, 1.0. $C_{16}H_{10}O_{11}Os$ calc: C, 20.6; H. 1.1%) and [$Os_2H(CH_3CH_2C{=}CHCOCH_3)(CO)_6$] (**4**) (0.015 g, 8%) (Found: C, 23.05; H, 1.8; O, 17.2. $C_{12}H_{10}O_7Os$ calc: C, 22.4; H, 1.55; O, 17.3%).

*Thermolysis of [$Os_3H(CH{=}CHCH_2CH_2COCH_3)(CO)_{10}$] (**1**) in cyclohexane*

A solution of compound **1** (0.010 g) in cyclohexane (15 cm^3) was refluxed for 5 h. TLC work-up as above gave two yellow crystalline compounds: unreacted **1** (0.0028 g 28%) and [$Os_3H(CH_3CH_2C{=}CHCOCH_3)(CO)_{10}$] (**3**) (0.0025 g, 25%).

Thermolysis of [$Os_3(CH_3CH{=}CHCH_2COCH_3)(CO)_{10}$] (2) in cyclohexane

A solution of compound **2**, (0.05 g) in cyclohexane (15 cm^3) was heated under reflux for 4 h. The IR spectrum showed complete conversion to [$Os_3H(CH_3CH_2C{=}CHCOCH_3)(CO)_{10}$] (**3**).

Thermolysis of [$Os_3H(CH_3CH_2C{=}CHCOCH_3)(CO)_{10}$] (3) in cyclohexane

A solution of compound **3** (0.050 g) in cyclohexane (15 cm^3) was refluxed for 15 h. Removal of the solvent and TLC work-up gave several yellow bands. The two major bands gave compound **3** (0.020 g, 43%) and [$Os_2H(CH_3CH_2C{=}CHCOCH_3)(CO)_6$] (**4**) (0.014 g, 28%) as yellow solids.

Acknowledgements

We thank the S.E.R.C. for support.

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