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Preliminary communication

STABILISATION OF ALKYL COMPOUNDS OF THE TYPE $Os_3H(alkyl)(CO)_{10}$ FORMED BY ALKENE INSERTION INTO $Os_3H_2(CO)_{10}$

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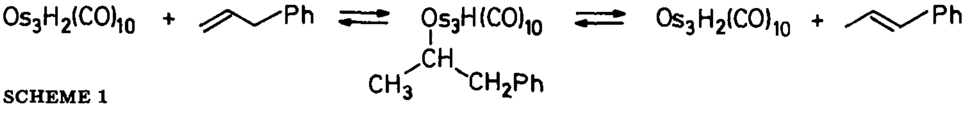
Summary

The hydrido cluster $Os_3H_2(CO)_{10}$ reacts with neat methyl vinyl ether to give two isomers of the insertion product $Os_3H(\mu\text{-}MeCHOMe)(CO)_{10}$ which are stabilised by ether coordination in the 1-methoxyethyl bridge but slowly revert to the dihydride on standing in solution. The clusters $Os_3H(CH{=}CH_2)(CO)_{10}$, $Os_3(CH{\equiv}CH)(CO)_{10}$, $Os_3H_2(C{=}CH_2)(CO)_9$ and $Os_3H_3(CCH_3)(CO)_9$ are formed as minor products from C—O ether cleavage at room temperature or on thermolysis. One product from heating the 1-methoxyethyl compound in refluxing n-heptane, the 1-methoxyethylidene compound $Os_3H_2(\mu_3\text{-}MeCOMe)(CO)_9$, retains the C—O bond.

Alkene isomerisation catalysed by $Os_3H_2(CO)_{10}$ is believed to occur by the insertion of the alkene into an Os—H bond followed by β-elimination of the intermediate alkyl compound [1—3]. For example, Scheme 1 shows a simplified picture for a particular alkene isomerisation; other probable intermediates such as $Os_3H_2(CH_2{=}CHCH_2Ph)(CO)_{10}$ are omitted. Alkyl intermediates of type $Os_3H(alkyl)(CO)_{10}$ such as that shown are unstable with respect to β-elimination and are not observed in the isomerisation. The methyl

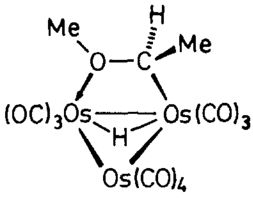


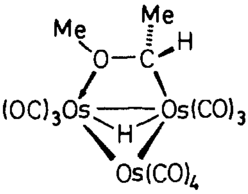
SCHEME 1

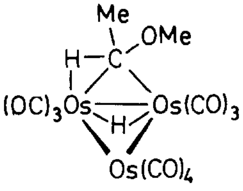
0022-328X/84/$03.00

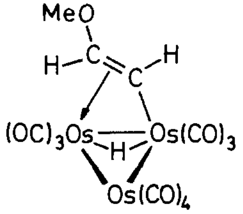
analogue with no β-hydrogen atoms undergoes slower reversible α-elimination to give $Os_3H_2(CH_2)(CO)_{10}$ in equilibrium with it [4]. α- or β-elimination or agostic C—H—Os bonding as in the methyl compound (and probably all simple alkyls of this sort) are ways that bonding C—H electrons may be used by the metal to avoid coordinative unsaturation.

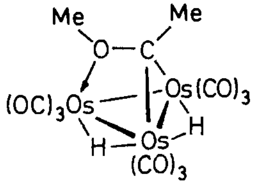
We now report that an ether function in the inserted alkene may coordinate in the alkyl compound preventing agostic bonding and considerably reducing the rate of β-elimination. Purple $Os_3H_2(CO)_{10}$ dissolves in neat methyl vinyl ether in a closed vessel to give a deep purple solution which becomes yellow over a week at room temperature. Removal of solvent gave a separable mixture of the 1-methoxyethyl compound $Os_3H(MeCHOMe)(CO)_{10}$ (1) (44%), the oxidative addition product $Os_2H(\mu$-*trans*-$CH{=}CHOMe)(CO)_{10}$ (2) (6%) as well as small amounts of products of C—O bond cleavage: $Os_3H(\mu\text{-}CH{=}CH_2)(CO)_{10}$ [5] and $Os_3(C_2H_2)(CO)_{10}$ [5] (8% together). The reaction of $CH_2{=}CHOMe$ with $Os_3H_2(CO)_{10}$ in THF in a sealed glass tube at 90°C gave


(1a)


(1b)


(1c)


(2)


(3)

$Os_3H_2(\mu_3\text{-}C{=}CH_2)(CO)_9$ as the major product; it is known that the vinyl ($CH{=}CH_2$) complex readily gives the vinylidene ($C{=}CH_2$) one on heating [6] and hence it is a reasonable product from the higher temperature reaction if $Os_3H(\mu\text{-}CH{=}CH_2)(CO)_{10}$ is formed at room temperature. The μ-ethyne compound $Os_3(C_2H_2)(CO)_{10}$ is difficult to account for, but is formed from $Os_3H(CH{=}CH_2)(CO)_{10}$ in 55% yield by reaction with neat $CH_2{=}CHOMe$ at room temperature for 5 days. The mechanisms of all these secondary reactions remain obscure.

The 1-methoxyethyl compound **1** exists as two isomers **1a** and **1b** in mol ratio 3/1 which are inseparable by chromatography and which give similar but non-overlapping sets of ^1H NMR signals consistent with the structures shown (see Fig. 1). The agostically bonded form **1c** would give the MeC*H*OMe

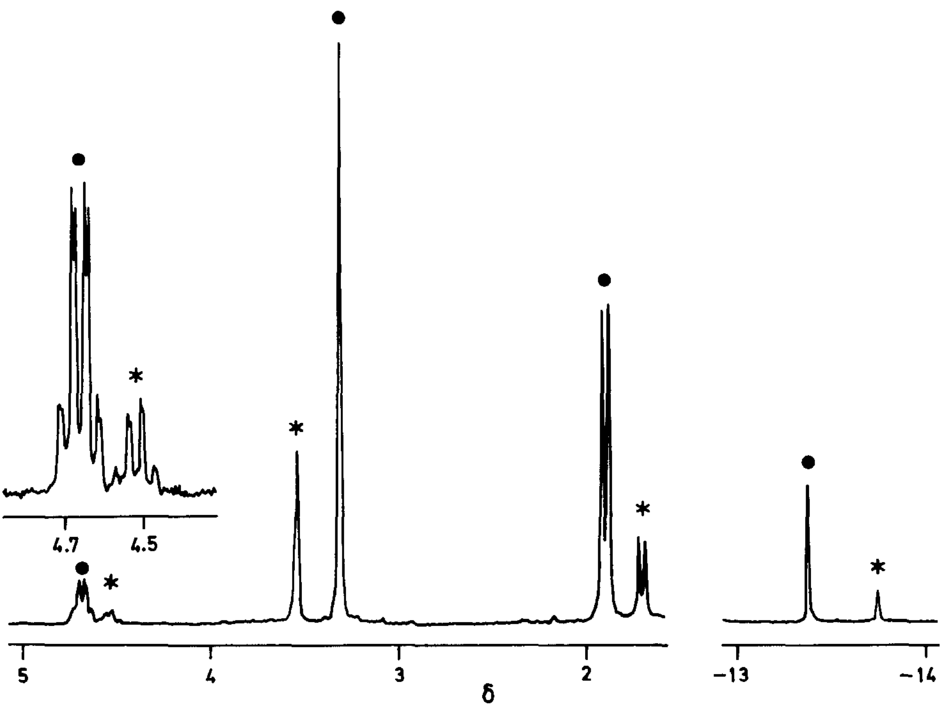


Fig. 1. ^{1}H NMR spectrum of $Os_3H(MeCHOMe)(CO)_{10}$ as a mixture of isomers 1a and 1b in $CDCl_3$ at room temperature. (● = major isomer; * = minor isomer).

signal at higher field than observed (δ 4.69 and 4.54 ppm for the two isomers) and can be ruled out. Thus we believe that ether-coordination satisfies the electronic requirements of the osmium atoms and this corresponds to ketone-coordination in other related systems [2,6].

Compound 1 is very much more inert towards β-elimination and reductive elimination than the corresponding ethyl and methyl compounds respectively. It does not react with an atmosphere of CO (it does not give MeOEt) and a dichloromethane solution of 1 in the absence of CH_2=CHOMe at room temperature takes several weeks to revert to $Os_3H_2(CO)_{10}$. The major isomer is consumed the faster so that towards the end of the reaction (after one month) the mol ratio of 1a to 1b is 1/1. Either the major isomer eliminates faster, or there is an approach to an equilibrium between them and the initial ratio represents their relative rates of formation rather than their equilibrium ratio. In an attempt to accelerate the rate of β-elimination by heating a hexane solution of 1 under reflux, we obtained $Os_3H_2(\mu_3\text{-}C{=}CH_2)(CO)_9$ (10%) and $Os_3H_2(CO)_{10}$ (25%) while six products were isolated from refluxing heptane after 1 h of which we characterised $Os_3H_2(\mu_3\text{-}C{=}CH_2)(CO)_9$ (20%), $Os_3H_3(\mu_3\text{-}CCH_3)(CO)_9$ (2%), $Os_3H_2(CO)_{10}$ (16%) and a new cluster, compound 3 (8%). Compound 3 is identified as the 1-methoxyethylidene cluster $Os_3H_2(\mu_3\text{-}MeCOMe)(CO)_9$ (infrared and ^{1}H NMR, Table 1) which is formed by decarbonylation and hydrogen atom transfer (oxidative addition). The MeCOMe ligand in 3 is a 4-electron donor and we propose the mode of bonding shown. If the oxygen

TABLE 1

INFRARED AND NMR DATA FOR COMPOUNDS 1—3

Compound	ν(CO) [a] (cm^{-1})	δ [b]	Assign.	J(Hz)		
$Os_3H^w(Me^xCH^yOMe^z)(CO)_{10}$	2103w, 2059s, 2047vs,	1.90(d)	Me^x	J_{xy}	6.8	[c]
(1)	2018vs, 2002vs, 1990m,	3.30(s)	Me^z	J_{wy}	1.6	
	1985sh, 1972m.	4.69(dq)	H^y			
		−13.38(d)	H^w			
		1.71(d)	Me^x	J_{xy}	7.1	[d]
		3.53(s)	Me^z	J_{wy}	1.4	
		4.54(dq)	H^y			
		−13.73(d)	H^w			
$Os_3H^w(CH^x{=}CH^yOMe^z)(CO)_{10}$	2102w, 2057vs, 2047s,	5.57(dd)	H^x	J_{xy}	12.0	
(2)	2018vs, 2110m, 2003s,	6.58(d)	H^y	J_{xw}	1.5	
	1992sh, 1987m, 1982sh,	3.70(s)	Me^z			
	1976sh.	−17.85(d)	H^w			
$Os_3H_2{}^{wx}(Me^yCOMe^z)(CO)_{10}$	2102w, 2077s, 2055w,	2.17(s)	Me^y	J_{wx}	1.5	
(3)	2049vs, 2026w, 2018s,	3.60(s)	Me^z			
	2006m, 1996m, 1977s,	−13.14(d)	H^w			
		−14.32(d)	H^x			

[a] In cyclohexane. [b] In $CDCl_3$, recorded at 200 MHz at room temperature. [c] Major isomer. [d] Minor isomer.

atom is pyramidal, rapid inversion or hydride migration would lead to a single set of NMR resonances without isomers being observed.

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