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TRIOSMIUM CLUSTERS DERIVED FROM α,β-UNSATURATED ALDEHYDES

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Summary

The compounds $[Os_3H_2(CO)_{10}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ both react with the aldehydes RCH=CHCHO (R = Me or Ph) with competitive oxidative additions of the vinylic C–H groups, to give compounds of the type $[Os_3H(CO)_{10}(RC{=}CHCHO)]$, or of the aldehydic groups to give acyl clusters of the type $[Os_3H(CO)_{10}$-$(RCH{=}CHCO)]$. The alkyne PhC≡CCHO reacts with $[Os_3H_2(CO)_{10}]$ to give $[Os_3H(CO)_{10}(PhC{=}CHCHO)]$, but also two other isomers as a *cis-trans* mixture of $[Os_3H(CO)_{10}(PhCH{=}CCHO)]$, which are converted in acetone into the PhC=CHCHO compound and free cinnamaldelyde. In each of these Os_3 compounds there are Os–O bonds.

Introduction

Metal carbonyl clusters by definition involve the chemistry of oxy ligands, and in view of the importance in chemical modification of CO at clusters, we are studying oxy ligands derived from α,β-unsaturated aldhydes, ethers and ketones [1–3]. It has been shown that $[Os_3(CO)_{12}]$ and $[Os_3H_2(CO)_{10}]$ react with aldehydes and ketones to give oxidative addition products [4,5]. Acyl clusters of the type $[Os_3H(CO)_{10}(\mu$-$RCO)]$ (R = alkyl or aryl) were obtained by oxidative addition of aldehydes to $[Os_3(CO)_{12}]$ [4,5] or to $[Os_3(CO)_{10}(MeCN)_2]$ [6] but are also available by reaction of RLi with $[Os_3(CO)_{12}]$ followed by acidification [7]. There is a strong tendency to form products with the organic carbonyl groups coordinated through oxygen, a tendency also observed in reactions of α,β-unsaturated ketones [2], ethers [3], and esters [8].

In this paper we describe the synthesis of several triosmium clusters derived from the reactions of the reactive clusters $[Os_3H_2(CO)_{10}]$ and $[Os_3(CO)_{10}(MeCN)_2]$ with the α,β-unsaturated aldehydes *trans*-but-2-enal ($CH_3CH{=}CHCHO$), *trans*-3-phenyl-

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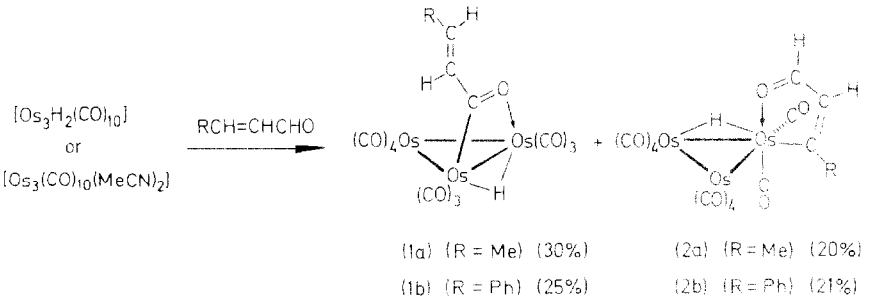


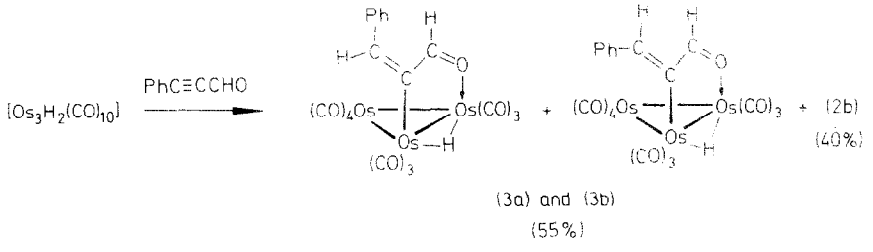
SCHEME 1

propenal (PhCH=CHCHO) and 3-phenylpropynal (PhC≡CCHO). These compounds might react at the unsaturated carbon–carbon bonds, at the CHO group, or at both. Even though both vinylic and aldehydic C–H bonds are cleaved in these reactions, the products all contain Os–O bonds.

Results and discussion

Synthesis and characterisation of reaction products

The alkyne PhC≡CCHO and the alkenes CH_3CH=CHCHO and PhCH=CHCHO react with $[Os_3H_2(CO)_{10}]$ or $[Os_3(CO)_{10}(MeCN)_2]$ to give compounds **1** to **3** (Schemes 1 and 2). The μ-acyl compounds $[Os_3H(CO)_{10}(\mu\text{-RCH=CHCO})]$, compounds **1**, have the structure shown in Scheme 1 based on ν(CO) infrared and ^{1}H NMR spectra which are quite characteristic for this known type of compound [ν(CO) 1430 cm^{-1}] [5]. The ^{1}H NMR spectra show *trans* coupling of vinylic protons (~ 16 Hz). These acyl compounds **1** do not undergo decarbonylation under our conditions. The other products from the reaction in Scheme 1, compounds **2a** and **2b** $[Os_3H(CO)_{10}(RC{=}CHCHO)]$ (R = Me or Ph), were also characterised by their infrared and ^{1}H NMR data (Table 1). There is a very close correspondence of data to those for $[Os_3H(CO)_{10}(MeC{=}CHCOMe)]$, the X-ray structure of which has been determined [2]. They are related by replacement of a formyl by an acetyl group. The coupling between the aldehydic proton and the vinylic proton in compounds **2** is consistent with the structural formulation. The fact that chelation through oxygen occurs rather than a second C–H cleavage or η^2-alkene coordination supports the idea of the strong tendency of oxygen to coordinate to metal atoms even when these are in low oxidation states. The formation of compounds **1** and **2** in similar yields



SCHEME 2

TABLE 1

INFRARED AND ^{1}H NMR DATA FOR COMPOUNDS **1** TO **3**

Compound	ν(CO) [a] (cm^{-1})	ν(CO) [b] (CHO) (cm^{-1})	^{1}H NMR [c]
$[Os_3H(CO)_{10}$-$(CH_3^xCH^y{=}CH^zCO)]$ [d] (**1a**)	2108 m, 2070 vs, 2060 s, 2026 vs, 2014 s, 2008 sh, 1974 m.	1430	1.82dd(x), 6.56dq(y), 5.62dq(z), −11.2(OsH) [J_{xy} 7.1, J_{xz} 1.8, J_{yz} 15.5]
$[Os_3H(CO)_{10}$-$(Ph^xCH^y{=}CH^zCO)]$ (**1b**)	2110 m, 2072 vs, 2061 s, 2025 vs, 2014 s, 2007 sh, 1982 m.	1430	7.38m(x), 7.24d(y), 6.22d(z), −10.3s(OsH) [J_{yz} 16.0]
$[Os_3H(CO)_{10}$-$(CH_3^xC{=}CH^yCH^zO)]$ (**2a**)	2122 w, 2068 s, 2048 vs, 2045 sh, 2018 s, 2004 m, 1990 m, 1973 m.	1455	3.32d(x), 7.08m(y), 9.30d(z), −15.2s(OsH) [J_{xz} 1.2, J_{yz} 1.6[e]]
$[Os_3H(CO)_{10}$-$(Ph^xC{=}CH^yCH^zO)]$ (**2b**)	2124 w, 2070 s, 2050 vs, 2046 sh, 2020 s, 2008 m, 1990 m, 1976 m, 1934 m.	1445	7.40m(x), 6.70d(y), 9.00d(z), −15.6s(OsH) [J_{yz} 1.2]
$[Os_3H(CO)_{10}$-$(PhCH^y{=}CCH^zO)]$ (**3a** and **3b**)	2100 m, 2064 s, 2050 s, 2022 s, 2008 m, 2002 m, 1994 br, 1968 m.	1515	~7.5m(Ph), 8.74s(y), 9.88s(z), −12.6s(OsH) [f] ~7.5m(Ph), 8.48s(y), 9.65s(z), −12.7s(OsH) [g]

[a] In cyclohexane. [b] In Fluorolube mull. [c] Recorded in $CDCl_3$ at 100 MHz at room temperature; chemical shifts in δ(ppm); J in Hz. [d] Recorded in $(CD_3)_2CO$ at 100 MHz at room temperature. [e] J_{yz} only resolved for H^z signal. [f] Minor isomer. [g] Major isomer.

shows that there is little selectivity in the oxidative addition at aldehydic vs. vinylic C–H bonds.

Good yields of two isomeric compounds **3a** and **3b** were obtained in 2/1 mol ratio from the reaction of PhC≡CCHO and $[Os_3H_2(CO)_{10}]$. By comparison of infrared and ^{1}H NMR data with those of $[Os_3H(CO)_{10}(CH_2{=}CCOMe)]$ [2] we were able to assign the structures shown. Again there is organic carbonyl coordination [ν(CO) 1515 cm^{-1}]. These isomers **3a** and **3b** cannot be separated by chromatography and have identical infrared spectra in the 2000 cm^{-1} region. Similar sets of ^{1}H NMR signals are observed for the two isomers (see Fig. 1) which we assign the *cis* and *trans* configurations shown in Scheme 2. In acetone solution the isomers **3a** and **3b** are slowly converted into the isomer $[Os_3H(CO)_{10}(PhC{=}CHCHO)]$ (**2b**), and in an attempt to accelerate this conversion by heating a solution of the isomers **3a** and **3b** in n-hexane under reflux for 2 h, we obtained compound **2b** (25%), unreacted **3a** and **3b** (34% together), and a yellowish oil identified as free cinnamaldehyde. The formation of free cinnamaldehyde in this reaction is consistent with a reductive elimination to give $[Os_3(CO)_{10}(PhCH{=}CHCHO)]$ as an undetected intermediate which either liberates free cinnamaldehyde or undergoes oxidative addition to give **2b**. None of the compound **1b** was obtained by isomerisation of **3a** and **3b**, and this suggests that the oxidative addition of PhCH=CHCHO at the aldehydic or vinylic

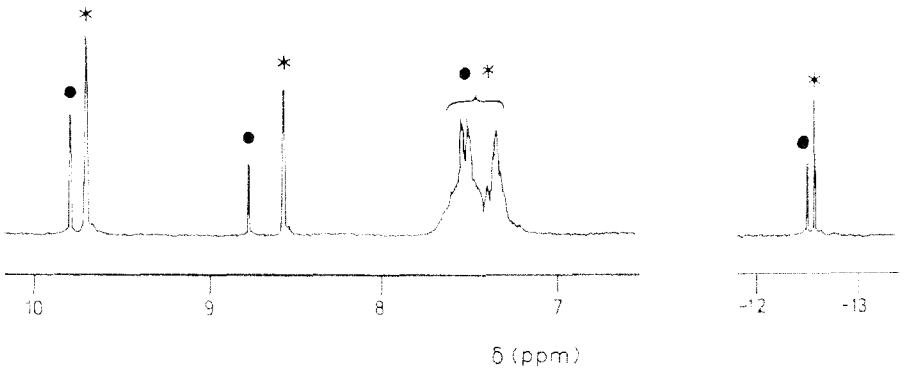


Fig. 1. ^{1}H NMR spectrum of $[Os_3H(CO)_{10}(PhCH{=}CCHO)]$ as a mixture of isomers **3a** and **3b** in $(CD_3)_2CO$ at room temperature (● = minor isomer; * = major isomer).

sites to $[Os_3(CO)_{10}(MeCN)_2]$ does not involve the same intermediate $[Os_3(CO)_{10}$-(PhCH=CHCHO)] in the two cases.

Experimental

Alcohols and acids were removed from the aldehydes before use [9]. Products were isolated by preparative TLC using Merck SiO_2 (H, type 60).

trans-But-2-enal

A solution of $[Os_3H_2(CO)_{10}]$ (0.25 g) and purified *trans*-MeCH=CHCHO (5 cm^3) in P_2O_5-dried CH_2Cl_2 (50 cm^3) was refluxed under nitrogen for 5 d. After removal of the solvent under vacuum, the orange residue was separated by TLC (eluant: pentane/diethyl ether, 10/1 by volume) to give several bands. The main yellow band gave $[Os_3H(CO)_{10}(CH_3CH{=}CHCO)]$, complex **1a**, (0.075 g, 30%) and the second yellow band gave $[Os_3H(CO)_{10}(CH_3C{=}CHCHO)]$, compound **2a** (0.050 g, 20%) both as yellow crystals. The other bands gave very small quantities of compounds which were not characterised. A similar reaction occurs in refluxing octane (1 h). The reactions with $[Os_3(CO)_{10}(MeCN)_2]$ were carried out under the same conditions and gave the same distribution of products.

3-Phenylpropenal

(i) A solution of $[Os_3H_2(CO)_{10}]$ (0.200 g) and purified PhCH=CHCHO (2 cm^3) in sodium-dried octane (50 cm^3) was heated under reflux under nitrogen for 30 min. Some $[Os_3(CO)_{12}]$ precipitated on cooling and separation as above gave several species of which two were characterised as $[Os_3H(CO)_{10}(PhCH{=}CHCO)]$, compound **1b** (0.050 g, 25%) as yellow crystals and $[Os_3H(CO)_{10}(PhC{=}CHCHO)]$, complex **2b**, (0.042 g, 21%) as yellow-orange crystals. Other products, which increased in number on extended reaction times, were not characterised. A similar reaction occurs in sodium benzophenone-dried THF at room temperature (24 h) or in P_2O_5-dried CH_2Cl_2 (10 d).

(ii) A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.3 g), purified aldehyde (2 cm^3) and P_2O_5-dried CH_2Cl_2 (20 cm^3) under vacuum in a sealed glass tube was heated at

125°C for 2.5 h and then left at room temperature overnight. Work-up gave the same distribution of products as above.

3-Phenylpropynal

(i) The purified aldehyde (0.5 cm^3) was added to a purple solution of $[Os_3H_2(CO)_{10}]$ (0.2 g) in P_2O_5-dried CH_2Cl_2 (30 cm^3) at room temperature, which became red in 30 min and was set aside at 4°C overnight. After removal of the solvent under vacuum, the orange residue was separated by chromatography (eluant: light petroleum ether (b.p. 40–60°C)] to give one orange band $[Os_3H(CO)_{10}(PhCH{=}CCHO)]$, complexes **3a** and **3b**, (0.110 g, 55%) as red-orange crystals, and one yellow band $[Os_3H(CO)_{10}(PhC{=}CHCHO)]$, compound **2b**, (0.080 g, 40%) as yellow-orange crystals.

(ii) A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.15 g) and purified aldehyde (0.5 cm^3) in P_2O_5-dried CH_2Cl_2 (50 cm^3) was stirred at room temperature under nitrogen for 5 h. Work-up gave the same main bands as above, and two other bands, in very small quantities, which were not characterised.

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