

SYNTHETIC STUDIES OF THE REACTION BETWEEN ALDEHYDES AND THE TRIOSMIUM CLUSTER $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$

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Summary

The reaction of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (**1**) with aldehydes in refluxing cyclohexane affords the metal clusters $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COR})]$ (**2**, R = Me, Ph, CH_2Ph or C_6H_{13}) in ca. 50% yield. The compound **2** (R = CH_2Ph) undergoes hydrogenation under pressure to give the corresponding alcohol, while decarbonylation occurs in the presence of Me_3NO to give the Me_3N -substituted derivative $[\text{Os}_3(\text{CO})_9(\text{NMe}_3)(\mu\text{-H})(\text{COCH}_2\text{Ph})]$ in 90% yield.

Introduction

The reaction between $\text{Os}_3(\text{CO})_{12}$ and aldehydes has been reported to give triosmium clusters of the type $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COR})]$ (**2**) in low yields [1].

We now report that complex $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ (**1**) reacts smoothly with aldehydes in refluxing cyclohexane to give the compounds $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COR})]$ (**2**) (R = Me, Ph, CH_2Ph or C_6H_{13}) in ca. 50% yield. Complex **1** has also been shown [2] to react smoothly with amides in the same solvent to form the corresponding amido derivatives $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{NHCOR})]$ (**3**), R = H, Me, Ph, Et or Pr] in 50–70% yields. A preliminary report on the synthesis of cluster **1** from **2** has appeared [3].

Results and discussion

The air-stable crystalline products $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COR})]$ (**2**) (R = Me, Ph, CH_2Ph or C_6H_{13}) reported here were obtained in ca. 50% yield. Their spectroscopic properties (Table 1) are similar to those previously reported for the low yield synthesis of clusters **1** from $\text{Os}_3(\text{CO})_{12}$ and the appropriate aldehydes [1]. In order to establish fully the structure of the new clusters **2**, a single crystal X-ray

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TABLE 1
SPECTROSCOPIC PROPERTIES OF $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COR})]$ DERIVATIVES

R	IR $\nu(\text{CO})^a$	^1H NMR	(τ) ^b	m/e^c
Me	2110m, 2070s, 2058s, 2028s, 2014s, 2003w, 1998m, 1990sh, 1983m.	7.74 23.92	(CH_3 , s) (OsH, s)	900
Ph	2110m, 2070s, 2059s, 2028s, 2018s, 2012m, 1998m, 1990sh, 1983m.	2.70 24.06	(Ph, m) (OsH, s)	962
CH_2Ph	2110m, 2071s, 2060s, 2029s, 2015s, 2007m, 2000m, 1991sh, 1985m.	2.80 24.05	(Ph, m) (OsH, s)	976
C_6H_{13}	2112m, 2073s, 2961s, 2027s, 2014s, 2009w, 1998m, 1989sh, 1983m	23.79	(OsH, s)	970

^a In cyclohexane (ν in cm^{-1}). ^b In CDCl_3 (τ in ppm). ^c Based on (^{192}Os).

diffraction study was carried out on $[\text{Os}(\text{CO})_{10}(\mu\text{-H})(\text{COCH}_2\text{Ph})]$ (**2**); ($\text{R} = \text{CH}_2\text{Ph}$). The CO fragment was found to be bonded to a second metal atom in the osmium triangle via the lone pair of electrons on the oxygen (Fig. 1a). Details of this structural elucidation have been reported elsewhere [3], and the results clearly exclude the alternative structure in which coordination to the second osmium atom would be through the C–O π -electrons. A similar mode of coordination to that found here for the COR ligand in **2**, ($\text{R} = \text{CH}_2\text{Ph}$) has been observed in the complexes $[\text{Fe}(\text{CO})_3(\text{COPh})]_2$ [4] and $[(\eta\text{-C}_5\text{H}_5)\text{Ir}\text{-}\mu\text{-}(\text{COPh})\text{-}\mu\text{-}(\text{COME})\text{-}\mu\text{-}(\text{PPh}_2)\text{Mn}(\text{CO})_3]$ [5]. This mode of CO bonding is important, and may have some significance for mechanisms of the catalytic hydrogenation of CO groups attached to metal surfaces.

Minor products from these reactions were characterised as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CO}_2\text{R})]$ derivatives (Fig. 1b), on the basis of their IR, ^1H NMR and mass spectral characteristics (e.g. for $\text{R} = \text{Ph}$; Found: IR $\nu(\text{CO})$ in cyclohexane: 2113m, 2074s, 2063s, 2026s, 2016s, 2009sh, 1987m, 1982m; ^1H NMR in CD_2Cl_2 : 2.33 {m, Ph}, 20.17 {s, OsH}; m/e 978 based on ^{192}Os .) Attempts to prepare the cluster **2**, ($\text{R} = \text{H}$) from formaldehyde and $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ in refluxing cyclohexane afforded $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ in 60% yield.

The complex $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COCH}_2\text{Ph})]$ (**2**), ($\text{R} = \text{CH}_2\text{Ph}$) reacts with Me_3NO in CH_2Cl_2 at room temperature to give the Me_3N -substituted derivative $[\text{Os}_3(\text{CO})_9(\text{NMe}_3)(\mu\text{-H})(\text{COCH}_2\text{Ph})]$ (**4**), (Fig. 1c) in 90% yield. The structure (Fig. 1c) is entirely consistent with the IR, ^1H NMR and mass spectral data obtained for product **4**. Its ^1H NMR spectrum showed an intense, sharp singlet at 7.14τ (CD_2Cl_2) attributable to the $(\text{CH}_3)_3\text{N}$ protons, two doublets at 5.79 and 6.34 attributable to the (CH_2) , a multiplet centred at 2.27τ (Ph) and an Os–H singlet at 22.61τ . The mass spectrum contained a parent peak at m/e 1007 (^{192}Os); IR $\nu(\text{CO})$ (cm^{-1}) in cyclohexane: 2095m, 2052s, 2019s, 2006s, 1998s, 1980w, 1972mw, 1931m. The downfield shift of the hydride signal by 1.44 to 22.61 ppm from that for the parent cluster (Os–H 24.05 ppm) indicates coordination of the NMe_3 group to either the first or second osmium atom of the osmium triangle (Fig. 1c). By analogy

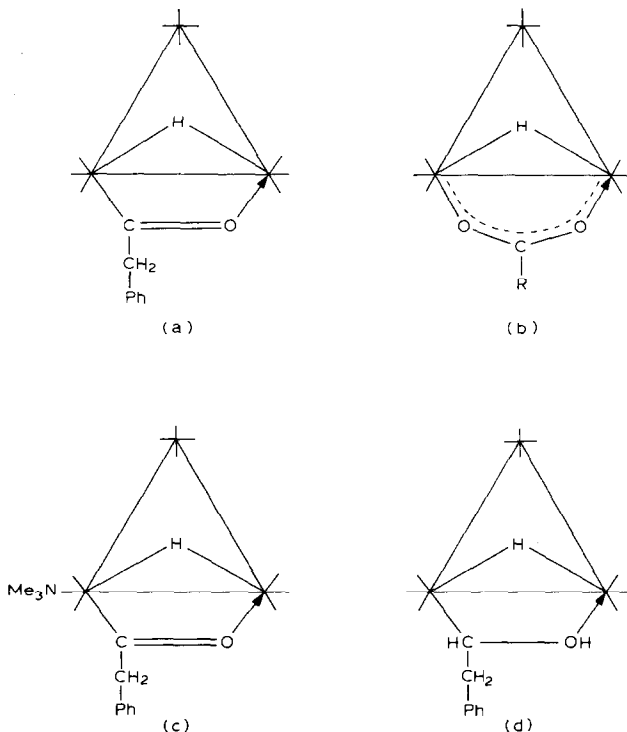


Fig. 1. Proposed structures for new triosmium derivatives. (Terminal CO ligands have been excluded for clarity.)

with the known cluster, $[\text{Os}_3(\text{CO})_9(\text{NMe}_3)(\mu\text{-NO})_2]$ [6] it is likely that the NMe_3 group in cluster **4** is bonded as shown in Fig. 1c.

Dihydrogen reacts with the cluster **1** ($\text{R} = \text{CH}_2\text{Ph}$) in hexane (20 atm, 120°C , 20 h) to give a yellow oil (50% yield). A parent peak at 978 mass units (^{192}Os) in the mass spectrum indicates that addition of molecular hydrogen to the parent cluster has taken place, and this with the IR spectrum in cyclohexane ($\nu(\text{CO})$ (cm^{-1}) 2116w, 2075vs, 2068s, 2061s, 2028sh, 2024vs, 2015m, 2009s, 1992s, 1992sh, 1989m) suggests the structure $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CHOHCH}_2\text{Ph})]$ (Fig. 1d). The ease of hydrogenation of the carbonyl group of an organic substrate attached to a cluster provides the first direct evidence for a change in the reactivity of such coordinated substrates.

Experimental

*Synthesis of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COR})]$ (**2**) derivatives*

(i) $\text{R} = \text{CH}_3$. A solution of complex **1** (0.1 g) and freshly distilled acetaldehyde (0.5 cm^3) in cyclohexane (20 cm^3) was gently refluxed for 6 h under dinitrogen. Removal of the solvent under reduced pressure afforded an oil, which was dried on the vacuum line (3 h) and taken up in a minimum volume of CH_2Cl_2 . TLC using 20% CH_2Cl_2 /hexane as eluent gave $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COMe})]$, which separated from pentane as yellow crystals in 50% yield. A minor yellow product (10% yield)

was also isolated and identified as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CO}_2\text{Me})]$ on the basis of its IR and mass spectra.

(ii) ($R = Ph$). The procedure described in (i) above, but using 0.1 g of complex **2** and 0.5 cm³ of freshly distilled, dried, and deoxygenated benzaldehyde in refluxing cyclohexane (3 h), gave $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COPh})]$ (50%) after repeated elution with pure hexane. Deep-yellow crystals of the product separated from pentane (Found: C, 21.8; H, 0.96. $\text{C}_{17}\text{H}_6\text{O}_{11}\text{Os}_3$ calcd.: C, 21.2; H, 0.63%). A pale-yellow product (lower R_f value) was also isolated in 10% yield and identified as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CO}_2\text{Ph})]$ from its IR ¹H NMR, and mass spectra (m/e 978) data.

(iii) $R = \text{CH}_2\text{Ph}$. The procedure described in (i), but using 0.1 g of complex **1** 0.5 cm³ of freshly distilled, dried, and deoxygenated phenylacetaldehyde in refluxing cyclohexane (20 cm³, 3 h) gave $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COCH}_2\text{Ph})]$ (55% yield), which separated from pentane as yellow multifaceted blocks (Found: C, 22.3; H, 0.92. $\text{C}_{18}\text{H}_8\text{O}_{11}\text{Os}_3$ calcd.: C, 22.2; H, 0.83%). Two minor products were also isolated and identified as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{CO}_2\text{CH}_2\text{Ph})]$ (10% yield) and $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (5% yield) from their IR and mass spectra. When complex **2**, ($R = \text{CH}_2\text{Ph}$) (0.026 g) was treated with an equimolar amount of Me_3NO in CH_2Cl_2 at room temperature, monitoring by IR spectroscopy showed that reaction was complete within minutes. The usual work-up, including chromatography (TLC) with 20% CH_2Cl_2 /hexane as eluant gave an orange-yellow product, which was identified as $[\text{Os}_3(\text{CO})_9(\text{NMe}_3)(\mu\text{-H})(\text{COCH}_2\text{Ph})]$ (**4**) (see Discussion) from its IR, mass, and ¹H NMR spectra.

(iv) $R = \text{C}_6\text{H}_{13}$. The procedure described in (i), but using 0.1 g of complex **1** and 0.5 cm³ of freshly distilled and deoxygenated n-heptanal in cyclohexane (20 cm³, 3 h), gave $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\text{COC}_6\text{H}_{13})]$ as a yellow solid (45%) after work-up.

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