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Preliminary communication

TETRANUCLEAR OSMIUM CLUSTERS FROM THE REACTIONS OF $H_4Os_4(CO)_{12}$ WITH ALKENES*

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Summary

Organotetraosmium cluster compounds of the general formulae $H_3Os_4(CO)_{11}HC_2HR$ and $H_2Os_4(CO)_{11}HC_2R$ (where R = H, Ph or t-Bu) have been prepared from reactions of $H_4Os_4(CO)_{12}$ with the appropriate alkene.

There is a growing interest in the use of cluster compounds as catalysts in organic systems and it is, therefore, of some importance to examine the types of reaction that unsaturated molecules undergo with the polyhedral edges and faces of such clusters. Most work reported to date has been concerned with the reactions of triangulo clusters $M_3(CO)_{10}X_2$ (M = Fe, Ru or Os, X = CO; M = Os, X = H) with alkenes and alkynes, although there is limited information available on similar reactions of $H_4Ru_4(CO)_{12}$ and $Rh_6(CO)_{16}$ [1]. In this paper we wish to report preliminary studies of the reactions of $H_4Os_4(CO)_{12}$ (I) with the alkenes $RCH{=}CH_2$ (R = H, Ph or t-Bu).

The complex $H_4Os_4(CO)_{12}$ is conveniently prepared [2] by the direct hydrogenation of $Os_3(CO)_{12}$ and potentially offers a source of unsaturated species such as "$H_2Os_4(CO)_{12}$" or "$Os_4(CO)_{12}$" in the manner suggested for $H_2Os_3(CO)_{10}$ by Shapley [3]. Work on $H_4Ru_4(CO)_{12}$ has previously shown that such species are a convenient source of *closo*-Ru_4C_2 clusters [4]. Irradiation of $H_4Os_4(CO)_{12}$ and $RCH{=}CH_2$ (R = H, Ph or t-Bu) in benzene over fairly prolonged periods (ca. 8 h, 20°C) gives a clear yellow solution which, after TLC, yields the complex $H_3Os_4(CO)_{11}HC_2HR$ (II) as an orange, air-stable crystalline solid. In contrast, treatment of $H_4Os_4(CO)_{12}$ with the same alkenes in boiling octane over extensive periods (ca. 5 days) gives only very small yields (< 5%) of $H_2Os_4(CO)_{11}HC_2R$ (III). Complexes II and III

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are obviously closely related and we find that on heating II (boiling octane, ~ 3 h), dehydrogenation occurs and complex III is obtained. The reaction is not reversible and on passing hydrogen through a solution of III at elevated temperatures only $H_4Os_4(CO)_{12}$ and osmium metal are obtained.

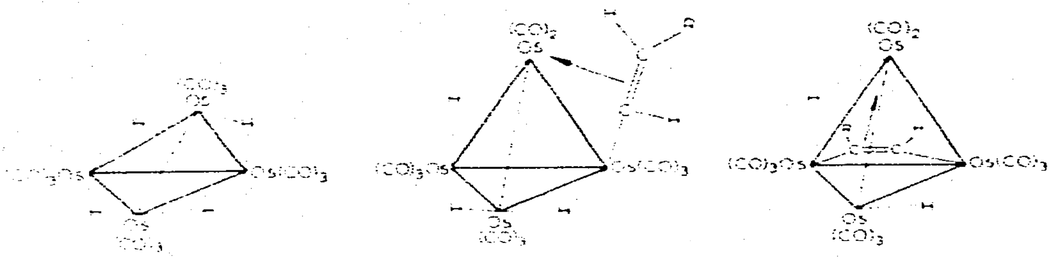
The molecular formulae of the new osmium derivatives were established directly by the mass spectroscopic method. The infrared spectra (Table 1) are complex, suggesting that the clusters have low symmetry and are different to derivatives of ruthenium which possess similar molecular formulae [4,5]. In the ^1H NMR spectrum of complex II, three separate high field resonances were observed (Table 1) in the ratio of 1:1:1 confirming its characterisation as a trihydrido species. The ^1H NMR spectrum of III contains two such high field resonances. In addition, for $H_3Os_4(CO)_{11}HC_2H_2$ resonances are observed at τ5.04 (J(H—H) 8.7 Hz) and 6.65 ppm (J(H—H) 12.3 Hz). These may be assigned to the geminal olefinic protons $HC_2\underline{HH}$ and the observed coupling constants lead to the conclusion that these protons are arranged *trans* and *cis* to the Os—C δ-bond respectively. On this basis, we believe that the probable structure of complex II is that shown in Fig. 1. This is similar to that of certain triosmium derivatives [6] and is related to them in that the capping of the triosmium system with an $Os(CO)_3$ unit produces the Os_4 cluster arrangement. Also, the agreement between the chemical shift values of the triosmium and tetraosmium derivatives is good.

TABLE 1

INFRA-RED [a], ^1H NUCLEAR MAGNETIC RESONANCE AND MASS SPECTROSCOPY MEASUREMENTS

Complex	R	ν(CO) cm^{-1} (in cyclohexane)	^1H NMR (τ, ppm) in $CDCl_3$ [b]	M^+
$H_3Os_4(CO)_{11}HC_2HR$ *(II)*				
	H	2102s, 2069vs, 2053vs, 2042vs, 2026m, 2016m, 2006s, 1996m, 1987m, 1975(sh)	1.17(dd) 1H, 5.04(d) 1H, 6.65(d) 1H, 24.15(s) 1H 29.30(s) 1H, 31.00(s) 1H; J_{AB} 8.7, J_{AC} 12.3	1106
	Ph	2100s, 2069vs, 2051vs, 2040vs, 2025m, 2015m, 2005s, 1994m, 1986m, 1979w, 1975w	0.94(d) 1H, 2.75(m) 5H, 5.18(d) 1H, 24.65(s) 1H 28.87(s) 1H, 30.8(s) 1H; J 12.1	1182
	t-Bu	2099s, 2068vs, 2052vs, 2038vs, 2025m, 2013m, 2005s, 1994m, 1982m, 1978w	1.32(d) 1H, 5.83(d) 1H, 8.90(s) 9H, 24.77(s) 1H, 29.52(s) 1H, 31.08(s) 1H; J 12.3	1162
$H_2Os_4(CO)_{11}HC_2R$ *(III)*				
	H	2101w, 2067vs, 2062 s, 2026vs, 2019(sh), 2006w, 1996w, 1981w, 1960m	0.20(s) 2H, 19.23(s) 1H, 31.60(s) 1H	1104
	Ph	2000m, 2068vs, 2060s, 2025vs, 2020s, 2005w, 1996w, 1981w, 1960m	0.07(s) 1H, 2.75(m) 5H 20.18(s) 1H, 31.22(s) 1H	1180
	t-Bu	2101m, 2067vs, 2059s, 2024vs, 2021s, 2014m, 2007m, 1994m, 1956m	0.10(s) 1H, 8.59(s) 9H, 20.21(s) 1H, 31.69(s) 1H	1160

[a] In range 1700—2200 cm^{-1}. [b] At ambient probe temperature (35°C): s, singlet; d, doublet; m, multiplet. Coupling constants (J) in Hz.



(I) $H_4Os_4(CO)_{12}$ (II) $H_3Os_4(CO)_{11}HC_2HR$ (III) $H_2Os_4(CO)_{11}HC_2R$

Fig. 1.

The proposed structure for III is based on that of II by the dehydrogenation observed above in its formation from II. The low field signal in the ^{1}H NMR of III indicates a 1,2-alkene linkage. The comparison with the known triosmium derivatives supports this postulate [7].

The work in progress includes the reactions of $H_4Os_4(CO)_{12}$ with a wide range of ligands; the results of which will be published later.

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