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Preliminary communication

Products from the reaction of $M_3(CO)_{12}$ (M = Ru or Os) with water

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SUMMARY

Reaction of the carbonyl $Ru_3(CO)_{12}$ with water leads to the formation of polynuclear hydrides α-$H_4Ru_4(CO)_{12}$, α-$H_2Ru_4(CO)_{13}$; the corresponding reaction with $Os_3(CO)_{12}$ yields the complexes $(H)(OH)Os_3(CO)_{10}$, $H_2Os_4(CO)_{13}$, $H_4Os_4(CO)_{12}$, $H_2Os_5(CO)_{16}$, $H_2Os_5(CO)_{15}$, $H_2Os_6(CO)_{18}$ and $H_2Os_7(CO)_{19}C$.

We have previously reported that dodecacarbonyltriruthenium undergoes reaction with alkanes (e.g. n-octane or n-nonane) under reflux, to produce the carbidocarbonyl $Ru_6C(CO)_{17}$ and small amounts of the tetranuclear hydrides, α-$H_2Ru_4(CO)_{13}$ and α-$H_4Ru_4(CO)_{12}$ [1]. The formation of these latter compounds was taken to indicate the *possible* activation of the alkanes by the carbonyl involving a process of H-abstraction. We now report that contrary to this suggestion, the hydrides are produced by the reaction of $Ru_3(CO)_{12}$ with minute traces of water always present under the reaction conditions employed. In a series of separate experiments we have been able to establish that (*a*) the amounts of hydrido species produced (in sealed tube reactions) are independent of the reaction times employed; (*b*) the yields of the hydrides, particularly α-$H_4Ru_4(CO)_{12}$, were increased by the addition of very small amounts of water; the addition of D_2O led to the formation of the corresponding D_4 species; (*c*) in reactions involving e.g. n-octane, neither octenes nor dimers of octane (GLC) nor organoruthenium complexes involving C_8 units were observed (TLC); (*d*) the use of totally D-solvents did not lead to either α-$D_4Ru_4(CO)_{12}$ or α-$D_2Ru_4(CO)_{13}$ but rather a mixture of α-$H_4Ru_4(CO)_{12}$ and α-$H_2Ru_4(CO)_{13}$.

These results clearly suggest that water is the source of the hydrido-ligand in these reactions and in agreement we have been able to produce moderately good yields of α-$H_4Ru_4(CO)_{12}$ directly from the reaction of $Ru_3(CO)_{12}$ with water in a sealed tube at 135°.

These observations led us to examine the corresponding reaction of water with

$Os_3(CO)_{12}$. We have previously established that direct pyrolysis of $Os_3(CO)_{12}$ yields polynuclear carbonyls based on Os_4, Os_5, Os_6, Os_7 and Os_8 units[2]. On heating $Os_3(CO)_{12}$ with small amounts of water in a sealed tube at 230° a dark brown material was obtained which after thin layer chromatography on silica was shown to consist of a mixture of polynuclear osmium species. Certain of these were found to be identical to those obtained directly from the pyrolysis of $Os_3(CO)_{12}$, whilst others viz. $(H)(OH)Os_3(CO)_{10}$, $H_2Os_4(CO)_{13}$ and $H_4Os_4(CO)_{12}$ [3] have been isolated previously either as by-products formed during the preparation of $Os_3(CO)_{12}$ or from the reaction of $Os_3(CO)_{12}$ with $NaBH_4$. However, in addition and more significantly the four hydrido carbonyl species $H_2Os_5(CO)_{16}$, $H_2Os_5(CO)_{15}$, $H_2Os_6(CO)_{18}$ and $H_2Os_7(CO)_{19}C$ have been identified (see Table 1).

TABLE 1

^{1}H NMR VALUES AND INFRARED SPECTRA OF THE PRODUCTS ISOLATED FROM THE PYROLYSIS OF $Os_3(CO)_{12}$ AND H_2O

Compound	*^{1}H NMR hydride chemical shift*[a]	*Infrared spectra*[c] *(2200–1600 cm^{-1})*
$(H)(OH)Os_3(CO)_{10}$	22.58	2114 vw, 2077 s, 2064 m, 2027 vs 2025 m(sh), 2005 m, 1992 w.
$H_2Os_4(CO)_{13}$	31.23	[d] 2085 s, 2068 s, 2059 s, 2021 m(br), 2005 2, 1860 vw(br)
$H_4Os_4(CO)_{12}$	30.35	2092 m, 2074 s, 2065 m(sh), 2026 s, 2002 w.
$H_2Os_5(CO)_{16}$	30.55	2126 w, 2088 s, 2066 s, 2053 s, 2045 m(sh), 2038 w, 2013 m.
$H_2Os_5(CO)_{15}$	31.10	2079 s, 2070 s, 2051 s, 2040 m, 2030 w, 2018 w, 2007 w, 1998 w.
$H_2Os_6(CO)_{18}$	*b*	2084 s, 2078 s, 2049 m, 2042 m.
$H_2Os_7(CO)_{19}C$	*b*	2085 s, 2071 s(br), 2042 m, 2032 w.

[a] CD_2Cl_2 as solvent. All sharp singlets. [b] Hydride signals have been observed but cannot yet be conclusively assigned. [c] Cyclohexane as solvent. Polystyrene film as calibrant. [d] n-Heptane as solvent.

The characterisation of these new polynuclear hydrides follows directly from ^{1}H NMR and mass spectroscopic studies. Thus under electron impact all show molecular ions followed by the *stepwise* loss of carbonyl groups. Their fragmentation may be represented by the schemes:

$$\text{(a)}\ [H_2Os_5(CO)_{15}]^+ \xrightarrow{-4CO} [H_2Os_5(CO)_{11}]^+ \xrightarrow{-2H,-CO} [Os_5(CO)_{10}]^+ \xrightarrow{-10\,CO} [Os_5]^+$$

$$\text{(b)}\ [H_2Os_5(CO)_{16}]^+ \xrightarrow{-5CO} [H_2Os_5(CO)_{11}]^+ \xrightarrow{-2H,-CO} [Os_5(CO)_{10}]^+ \xrightarrow{-10\,CO} [Os_5]^+$$

(d) $$[H_2Os_6(CO)_{18}]^+ \xrightarrow{-5CO} [H_2Os_6(CO)_{13}]^+ \xrightarrow{-2H,-CO} [Os_6(CO)_{12}]^+ \xrightarrow{-12\,CO} [Os_6]^+$$

(e) $$[H_2Os_7(CO)_{19}C]^+ \xrightarrow{-6CO} [H_2Os_7(CO)_{13}C]^+ \xrightarrow{-2H,-2CO} [Os_7(CO)_{11}C]^+ \xrightarrow{-11\,CO} [Os_7C]^+$$

In the ^1H NMR (XL 100 F.T.) of the pentanuclear hydrides, signals clearly associated with metal—hydrido resonances are observed at τ30.55 $[H_2Os_5(CO)_{16}]$ and τ31.10 ppm $[H_2Os_5(CO)_{15}]$ which do not alter on cooling. The infrared spectra of these four new hydrido—carbonyl species are given in Table 1. Their relative simplicity indicates that the symmetry of these molecules is high and that no bridging groups appear to be present although the possibility of the presence of triply bridging CO groups (normally weak and broad absorptions) cannot be entirely excluded. It would appear from these studies that great care must be taken in work concerned with both $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ to exclude all traces of water so that any possibility of hydride production is excluded. These and our other related studies[4] indicate that a number of distinct series of polynuclear osmium carbonyl derivatives are emerging. A full account of these studies will be published shortly.

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