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Preliminary communication

Organoruthenium clusters obtained from α-$H_4Ru_4(CO)_{12}$

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SUMMARY

The reaction of α-$H_4Ru_4(CO)_{12}$ with cyclic diolefins provides organoruthenium cluster complexes based on three or four metal atoms.

Recently we reported the isolation and characterisation of $H_2Ru_3(CO)_9C_8H_8$ [1]. The formation of this complex from the reaction of dodecacarbonyltriruthenium with bicyclo[3.2.1]octa-2,6-diene in benzene may be viewed as an oxidative addition of olefinic C(2)–H and C(3)–H groupings to the triruthenium cluster, and provides direct evidence for the ability of the Ru_3 cluster to cleave C–H bonds. This observation has led us to consider the corresponding reactions of other ruthenium clusters. In this communication we report the products of the reaction of cycloocta-1,5-diene with the tetrameric cluster α-$H_4Ru_4(CO)_{12}$. To-date little is known of the chemistry of this compound or of other related compounds having bridging hydrogen atoms.

As shown in Scheme 1 the reaction of α-$H_4Ru_4(CO)_{12}$ with excess cycloocta-1,5-diene in cyclohexane under reflux yields a dark brown suspension. Six compounds were obtained after removal of solvent and separation on silica gel with hexane as eluent. One was identified as $Ru_3(CO)_{12}$, the others were found to be clusters based on three and four ruthenium atoms. These products were identified on the basis of mass spectroscopic analysis as $H_2Ru_3(CO)_9C_8H_{12}$ (I) (yellow), $HRu_3(CO)_9C_8H_{11}$ (II) (yellow), $Ru_4(CO)_{11}C_8H_{10}$ (III) (black), $Ru_4(CO)_{12}C_8H_{12}$ (IV) (brown) and $Ru_4(CO)_{12}C_8H_{10}$ (V) (purple). These proposed formulations were fully substantiated by ^1H NMR spectroscopy, some analytical data (complexes (I)–(III)) and in one case (complex (III)) by full X-ray analysis[2]. All exhibit relatively simple infrared spectra in the metal–carbonyl region and no bands assignable to bridging CO groups have been obtained.

$\alpha\text{-}H_4Ru_4(CO)_{12}$

$\alpha\text{-}H_2Ru_4(CO)_{13}$ $\xrightarrow{\text{cycloocta-1,5-diene}^{*}}$ dark brown suspension

$\downarrow$

(I) $H_2Ru_3(CO)_9C_8H_{12}$
(II) $HRu_3(CO)_9C_8H_{11}$
(III) $Ru_4(CO)_{11}C_8H_{10}$
(IV) $Ru_4(CO)_{12}C_8H_{12}$
(V) $Ru_4(CO)_{12}C_8H_{10}$
(VI) $Ru_3(CO)_{12}$
cycloocta-1,3-diene
cyclooctene

$M_3(CO)_{12} \xrightarrow{\text{cyclooctene}} H_2M_3(CO)_9C_8H_{12}$ (M = Ru (I)* or Os**)

$HRu_3(CO)_9C_8H_{11}$ (II) $\xrightarrow[\text{cyclohexane, 80–90}^\circ]{H_2\text{, 1 atm}}$ $H_2Ru_3(CO)_9C_8H_{12}$ (I)

*in cyclohexane, 80–90°, 44h, under N_2 in closed system; **in toluene, 120–140°, 100 h, in sealed tube.

Scheme 1

The ^1H NMR spectrum of complex (I) is consistent with a structure related to that previously proposed[1] for $H_2Ru_3(CO)_9C_8H_8$ (Fig. 1). At low temperatures (–55°) in toluene two hydride resonances of equal intensity are observed at τ 26.10 and τ 30.40; these broaden as the temperature is raised and eventually coalesce (46°) to a single absorption at τ 28.10. A similar observation was made for $H_2Ru_3(CO)_9C_8H_8$ and the $\Delta G^\ddagger$ values found are very similar (see Table 1). In the low field region (for solutions in $CDCl_3$) the low temperature spectrum exhibits a multiplet at τ 6.87 (2H), a doublet at τ 7.46 (2H) and a sharp singlet at τ 8.40 (8H); these we assign according to Fig. 1. Above ca. 6° the resonances centred at τ 6.87 and τ 7.46 broaden and eventually coalesce to a single broad absorption at τ 7.16 (46°) indicating some fluxional behaviour of the C_8H_{12} ring. It is

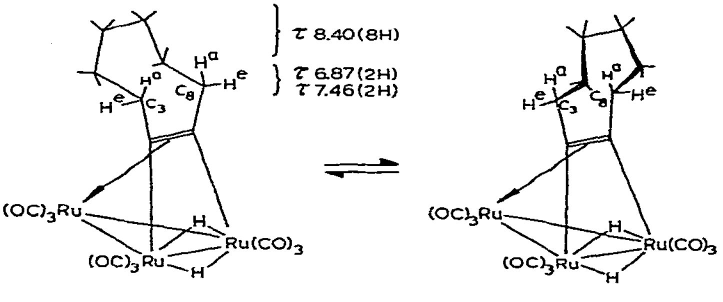

Fig. 1. Proposed structure of $H_2Ru_3(CO)_9C_8H_{12}$ and its osmium analogue. The two isomers formed during the "flipping" motion are shown.

TABLE 1

FLUXIONAL MOTION OF LIGANDS IN DIHYDRIDE COMPLEXES

Complex	*Ligand motion*		*Hydride exchange*	
	T_c(°C)	$\Delta G^{\ddagger}(T_c)$ (kcal mol^{-1})	T_c(°C)	$\Delta G^{\ddagger}(T_c)$ (kcal mol^{-1})
$H_2Ru_3(CO)_9C_8H_8$	–	–	4	12.3^a
$H_2Ru_3(CO)_9C_8H_{12}$	46	15.6^b	–9	11.8^c
$H_2Os_3(CO)_5C_8H_{12}$	52	16.0^b	97	16.9^c

^{a} In CD_2Cl_2. ^{b} In $CDCl_3$. ^{c} In toluene.

likely that this fluxionality arises from conformational changes about carbon atoms C_3 and C_8 thereby interconverting $H^a_{axial} \longleftrightarrow H^b_{equatorial}$. In order to test this idea we have prepared the corresponding osmium derivative from the reaction of $Os_3(CO)_{12}$ and cyclooctene. The variation of the ^{1}H NMR spectrum of this derivative closely follows that of the ruthenium analogue. As anticipated on the above interpretation $\Delta G^{\ddagger}$ for the interconversion of the two hydrido ligands (16.9 kcal/mole) is higher in this case whereas $\Delta G^{\ddagger}$ for the C_8H_{12} interconversions is about the same (16.0 kcal/mole). This independence of the C_8H_{12} fluxionality from the metal atom provides good evidence for the proposed mechanism. An X-ray analysis of complex (I) is in progress[3].

The precise nature of the monohydride (II) has not been determined and awaits the results of X-ray analysis. The ^{1}H NMR of this derivative is extremely complex in the region τ 0–10 and cannot be interpreted in terms of the pseudo π-allyl bonding scheme proposed for $HRu_3(CO)_9C_{12}H_{15}$ [4] and $HRu_3(CO)_9C_6H_9$ [5]. A hydride resonance is observed at τ 30.6 (1H). The complex is not fluxional. It reacts with hydrogen gas under moderate conditions (1 atm. 80–90°) to generate the dihydrido species $H_2Ru_3(CO)_9C_8H_{12}$ (I).

From X-ray studies the structural features of complex (III) have been determined[2]. Perhaps most significant is the demonstration that the Ru_4C_2 skeleton adopts a "butterfly" arrangement of Ru atoms similar to that observed for the Co_4C_2 skeleton in $Co_4(CO)_{10}C_2Et_2$ [6]. In this complex the organic ligand may be regarded as bidentate cycloocta-1-ene-5-yne.

These studies have shown that α-$H_4Ru_4(CO)_{12}$ may serve as a source of the Ru_4 cluster unit leading in this case to organometallic derivatives. The formation of the Ru_3 cluster compounds is possibly due to the formation of $Ru_3(CO)_{12}$ during the reaction. In support of this view we have prepared complex (I) and its osmium analogue directly from the parent carbonyls $M_3(CO)_{12}$ (M = Ru or Os) and cyclooctene, and have established that cyclooctene is produced from cycloocta-1,5-diene and α-$H_4Ru_4(CO)_{12}$. This dehydrogenation of α-$H_4Ru_4(CO)_{12}$ by cycloocta-1,5-diene may proceed via α-$H_2Ru_4(CO)_{13}$ since we have found that simple olefins readily dehydrogenate α-$H_4Ru_4(CO)_{12}$ to produce α-$H_2Ru_4(CO)_{13}$, and that this dihydride reacts with cycloocta-

1,5-diene to give complexes (I)–(V) and $Ru_3(CO)_{12}$. The reaction of α-$H_4Ru_4(CO)_{12}$ with cycloheptene offers a convenient synthesis of α-$H_2Ru_4(CO)_{13}$ (yields ca. 30%).

The relevance of the reactions reported here to hydrogen transfer to unsaturated species on metal surfaces is obvious.

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