The Chemistry of Polynuclear Compounds. Part XXV.[1] Some Reactions of α-Tetrahydridododecacarbonyltetraruthenium with Cyclic Olefins

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The complexes $H_2Ru_3(CO)_9C_8H_{12}$, $HRu_3(CO)_9C_8H_{11}$, $Ru_4(CO)_{11}C_8H_{10}$, $Ru_4(CO)_{12}C_8H_{10}$, and $Ru_4(CO)_{12}C_8H_{12}$ have been identified as the products of the reaction of α-$H_4Ru_4(CO)_{12}$ with either cyclo-octa-1,5-diene or cyclo-octa-1,3-diene. The complexes are also formed by reaction of α-$H_2Ru_4(CO)_{13}$ with cyclo-octa-1,5-diene, and the complexes $H_2M_3(CO)_9C_8H_{12}$ (M = Ru or Os) are obtained by reaction of $M_3(CO)_{12}$ with cyclo-octene. Structures of the complexes are discussed, where possible, in terms of spectroscopic data and in the case of $Ru_4(CO)_{11}C_8H_{10}$ on the basis of single crystal *X*-ray analysis. ^1H N.m.r. studies of $H_2Ru_3(CO)_9C_8H_{12}$ indicate that the molecule undergoes two distinct types of fluxional behaviour involving in the first instance the C_8H_{12} ligand, and in the second the two hydrido-ligands. $\Delta G^\ddagger$ Values for these processes (and for the corresponding osmium complex) have been determined. $HRu_3(CO)_9C_8H_{11}$ reacts with hydrogen gas to give $H_2Ru_3(CO)_9C_8H_{12}$. The complexes $Ru_4(CO)_{11}C_8H_{10}$ and $Ru_4(CO)_{12}C_8H_{12}$ react with hydrogen to give $H_2Ru_3(CO)_9C_8H_{12}$ and α-$H_4Ru_4(CO)_{12}$, and $Ru_4(CO)_{12}C_8H_{10}$ forms α-$H_4Ru_4(CO)_{12}$ only. α-$H_4Ru_4(CO)_{12}$ is converted into α-$H_2Ru_4(CO)_{13}$ in *ca.* 30% yield by reaction with cycloheptene. The compounds $Ru_4(CO)_{12}C_8H_{10}$, $Ru_4(CO)_{12}C_8H_{12}$, $HRu_3(CO)_9C_8H_{11}$, and $H_2Ru_3(CO)_9C_8H_{10}$ have been obtained from the reaction of $Ru_3(CO)_{12}$ with cyclo-octa-1,3-diene.

ALTHOUGH a great deal of information is available on the synthesis and structure of the tetranuclear ruthenium-hydrido-complex α-$H_4Ru_4(CO)_{12}$ there is little information on its reactivity apart from its reactions with tertiary phosphines.[2] In earlier parts of this series[3] methods for the preparation of this compound were described but yields by these routes were low and precluded any detailed examination of its chemistry. More recently however an excellent preparative method involving the direct reaction of hydrogen with the readily available dodecacarbonyltriruthenium has been described.[4] This has permitted a closer examination of the chemistry of this hydrido-species and it appears that a diverse and reasonably systematic synthetic chemistry may be built up. This paper, our first concerned with the reactions of α-$H_4Ru_4(CO)_{12}$, reports the preparation of a series of cluster compounds based on Ru_3 and Ru_4 units which are formed from the reaction of α-$H_4Ru_4(CO)_{12}$ with cyclo-octa-1,5-diene or cyclo-octa-1,3-diene. A preliminary account of part of this work has been given.[5]

As shown in the Experimental section, the cluster compounds (1)—(5) [together with small amounts of $Ru_3(CO)_{12}$] are easily prepared by direct reaction of α-$H_4Ru_4(CO)_{12}$ with either cyclo-octa-1,5-diene or the corresponding 1,3-isomer, usually in yields in the region 5—10%. Separation of these organometallic products is difficult and is best carried out by a combination of column and thin-layer chromatography. Scheme 1 lists all the new complexes prepared and some useful data are collected in the Table. In the reaction with cyclo-octa-1,5-diene any excess of diene is either isomerised to the 1,3-isomer or reduced to cyclo-octene. With the 1,3-isomer some reduction to cyclo-octene is also observed. The complexes based on the Ru_3 unit are yellow, while those based on the Ru_4 species are black, purple, or brown. Nearly all the complexes prepared here were obtained as well defined crystals readily soluble in organic solvents. The formulations of the compounds were initially based on mass spectroscopic evidence supported by the appropriate analytical data. In addition the probable structure of the co-ordinated organo-groups have been ascertained in some cases from their ^1H n.m.r. spectra. Where appropriate, hydrido-ligands have been detected in the same way. By means of *X*-ray studies,[6] the structural features of $Ru_4(CO)_{11}C_8H_{10}$ (3) have been determined.

$$\left.\begin{array}{l}\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12} + \text{COD}(1,5\text{-or } 1,3\text{-}) \\ \alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13} + 1,5\text{-COD}\end{array}\right\}\longrightarrow \begin{array}{ll}\text{H}_2\text{Ru}_3(\text{CO})_9\text{C}_8\text{H}_{12} & (1)\\ \text{HRu}_3(\text{CO})_9\text{C}_8\text{H}_{11} & (2)\\ \text{Ru}_4(\text{CO})_{11}\text{C}_8\text{H}_{10} & (3)\\ \text{Ru}_4(\text{CO})_{12}\text{C}_8\text{H}_{10} & (4)\\ \text{Ru}_4(\text{CO})_{12}\text{C}_8\text{H}_{12} & (5)\\ \text{Ru(CO)}_3\text{C}_8\text{H}_{12} & (6)\\ \text{Ru}_3(\text{CO})_{12} & \\ \text{cyclo-octa-1,3-diene} & \\ \text{cyclo-octene} & \end{array}$$

$$\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12} + \textit{cyclo-octene} \longrightarrow \begin{array}{ll}\text{H}_2\text{Ru}_3(\text{CO})_9\text{C}_8\text{H}_{12} & (1)\\ \alpha\text{-H}_2\text{Ru}_4(\text{CO})_{13} & \\ \text{Ru}_3(\text{CO})_{12} & \end{array}$$

$$\text{M}_3(\text{CO})_{12} + \text{cyclo-octene} \longrightarrow \begin{array}{l}\text{H}_2\text{M}_3(\text{CO})_9\text{C}_8\text{H}_{12}\\ \quad [\text{M} = \text{Ru (1) or Os}]\end{array}$$

$$\text{Ru}_3(\text{CO})_{12} + 1,3\text{-COD} \longrightarrow \begin{array}{ll}\text{H}_2\text{Ru}_3(\text{CO})_9\text{C}_8\text{H}_{10} & (7)\\ \quad\text{and (2)—(6)} & \end{array}$$

SCHEME 1

Tetranuclear Derivatives.—The present study shows that organometallic compounds based on *closo*-Ru_4C_2 units may be prepared in pure, crystalline form from α-$H_4Ru_4(CO)_{12}$. Few compounds of this class appear to have been reported for ruthenium prior to this. For the particular case of $Ru_4(CO)_{11}C_8H_{10}$ (3) it has been shown that the Ru_4C_2 skeleton is essentially the same as that

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[1] Part XXIV, A. J. Deeming, R. Ettorre, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. (A)*, 1971, 1797.

[2] S. A. R. Knox and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 4594.

[3] B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 2856.

[4] H. D. Kaesz, S. A. R. Knox, J. W. Koepke, and R. B. Saillant, *Chem. Comm.*, 1971, 477.

[5] A. J. Canty, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **43**, C35.

[6] R. Mason and K. M. Thomas, *J. Organometallic Chem.*, 1972, **43**, C39.

of Co_4C_2 found in $Co_4(CO)_{10}C_2Et_2$ [7] with the C_8H_{10} ligand functioning as a chelating cyclo-octa-1-ene-5-yne [6] [see Figure 1). The compounds $Ru_4(CO)_{12}C_8H_{10}$ (4) and $Ru_4(CO)_{12}C_8H_{12}$ (5) are similar and probably based on the same Ru_4C_2 units but there is no definitive evidence regarding the precise geometry of these compounds. Thus, as for complex (3), the organo-moiety in complex (4) is probably bonded in the '-yne-' manner with a remaining unco-ordinated double-bond (although the possibility that co-ordination of this double bond does occur cannot be entirely excluded).

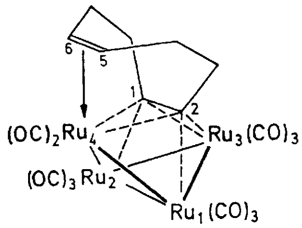

FIGURE 1 Structure of $Ru_4(CO)_{11}C_8H_{10}$ (3). Selected parameters $Ru_1–Ru_2 = 2{\cdot}823(0{\cdot}003)$ Å; other Ru–Ru bonds within the range 2·728—2·749 Å; $C_1–C_2$ and C_5C_6 within experimental error of 1·42 Å; average value of Ru–C 'σ' bonds ($Ru_1–C_2$, $Ru_2–C_1$) = 2·16 Å; average value of 'μ' bonds ($Ru_{3,4}–C_{1,2}$ = 2·21 Å; $Ru_4–C_5$ and $Ru_4–C_6$ within experimental error of 2·21 Å. From ref. 6

I.r.* and n.m.r.† spectral data and fluxional motion of ligands in complexes

			Ligand motion		Hydride exchange	
Complex	ν_{CO}/cm^{-1} (in cyclohexane)	N.m.r. resonances (τ)	T_c/°C	ΔG (T_c) kcal mol^{-1}	$T_c^{\ddagger}$/°C	$\Delta G^{\ddagger}$ (T_c) kcal mol^{-1}
$H_2Ru_3(CO)_9C_8H_{12}$ (1)	2105m, 2076s, 2054vs, 2040s, 2026m, 2013s, 2006m, 1987m	6·87m (2H),[b] 7·46m (2H),[b] 8·4 (8H), 28·06br (2H) [c,d]	46	15·6 [i]	−9	11·8 [j]
$HRu_3(CO)_9C_8H_{11}$ (2)	2093s, 2063vs, 2039vs, 2022vs, 2016s, 2003s, 1994s, 1985m, 1979m	6·34t (1H, J = 4 Hz), 7·1m(br) (2H), 7·7m (1H), 8·3m(br) (*ca.* 7 H), 30·6 (1H) [c]				
$Ru_4(CO)_{11}C_8H_{10}$ (3)	2081m, 2046vs, 2029s, 2019m, 2007w, 1999w, 1990wb, 1966wb	5·6m (2H), 6·8m(br) (4H), 7·3m (4H) [c]				
$Ru_4(CO)_{12}C_8H_{10}$ (4)	2090m, 2061vs, 2038s, 2035s, 2013wb, 2003m	5·73m (2H), 7·55br (2H), 8·04br (2H), 8·55br (4H) [c]				
$Ru_4(CO)_{12}C_8H_{12}$ (5)	2088w, 2059s, 2034s, 2010m, 1996m, 1967wb	6·7br (4H), 8·3br (8H) [c]				
$H_2Os_3(CO)_9C_8H_{12}$	2105m, 2077s, 2053vs, 2028s, 2018m, 2008s, 1997m, 1977m	6·8m (2H), 7·36m (2H),[e] 8·4br (8H), 27·65br (1H), 31·3br (1H) [c,f]	52	16·0	97	16·9 [j]
$H_2Ru_3(CO)_9C_8H_{10}$ (7)	2104m, 2076vs, 2053vs, 2044s, 2028w, 2024sh, 2012s, 2005m, 1986m	3·96d (1H), 5·03dt (1H), 7·2, 7·98, and 8·4br (*ca.* 12H), 27·9br (2·5H) [g]				
$H_2Ru_3(CO)_9C_8H_8$					4	12·3 [h]

* In range 1700—2100 cm^{-1}. † At ambient temperature.

[a] τ Values, tetramethylsilane as internal reference. [b] At >46° these absorptions are replaced by a single absorption at 7·16 (4H). [c] In $CDCl_3$. [d] The high-field signal is at 28·1 in toluene until the temperature is lowered to −9°. At lower temperatures two absorptions occur at 26·1 and 30·4. [e] Replaced above 52° by a single absorption at 7·1 (4H). [f] In toluene there is no absorption at ambient temp. in the high-field region. Above 97° there is a single absorption at 29·45. At low temp. there are two absorptions at 27·91 and 31·45. [g] In C_6D_6. See Figure 5 for high-field spectrum in CD_2Cl_2. [h] In CD_2Cl_2. [i] In $CDCl_3$. [j] In toluene.

Trinuclear Clusters.—The trinuclear clusters $HRu_3(CO)_9C_8H_{11}$ (2) and $H_2Ru_3(CO)_9C_8H_{12}$ (1) were the easiest to identify and characterise. On the basis of mass spectroscopic and ^1H n.m.r. data the presence of hydrido-ligands was clearly indicated and the infrared spectrum in the metal-carbonyl region (ν_{CO}) of complex (1) is almost identical with that of $H_2Ru_3(CO)_9C_8H_8$ [8] and that of (2) with those of $HRu_3(CO)_9C_{12}H_{15}$ [9] and $HRu_3(CO)_9C_{12}H_{17}$.[9]

From their formulae and spectroscopic properties these compounds are obviously similar to those formed directly from dodecacarbonyltriruthenium and olefins. Both Bruce *et al.*[9] and Randall *et al.*[10] have reported the preparation of derivatives containing a π-allyl-metal bond and two metal-carbon σ-bonds by reaction of $Ru_3(CO)_{12}$ with the appropriate olefin. More recently we prepared the derivative $H_2Ru_3(CO)_9C_8H_8$ [8] from the reaction of $Ru_3(CO)_{12}$ with bicyclo[3.2.1]octa-2,6-diene.

In the monohydride compound the C_8H_{11} group is obviously bound *via* a π-allyl system. The triplet at τ 6·76, which cannot be assigned to the proton of a *pseudo*-π-allyl fragment as found for the complexes $HRu_3(CO)_9C_{12}H_{15}$ and $HRu_3(CO)_9C_6H_9$, could be assigned to the central proton of an allyl fragment π-bonded to *one* metal atom of the $HRu_3(CO)_9$ unit since the shift value is similar to that of an allyl group bonded to *one* ruthenium in $Ru_4(CO)_{12}C_{12}H_{16}$ (τ 6·22).[9,11] With an allyl grouping of this type several structural possibilities may be envisaged (see Figure 2).

Reaction of $HRu_3(CO)_9C_8H_{11}$ (2) with hydrogen yields

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[7] L. F. Dahl and D. L. Smith, *J. Amer. Chem. Soc.*, 1962, **84**, 2450.

[8] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1972, **36**, C43.

[9] M. I. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and P. Woodward, *Chem. Comm.*, 1970, 735; M. I. Bruce, M. A. Carins, and M. Green, *J.C.S. Dalton*, 1972, 1293.

[10] M. Evans, M. Hursthouse, E. W. Randall, E. Rosenberg; L. Milone, and M. Valle, *J.C.S. Chem. Comm.*, 1972, 545.

[11] R. Belford, M. I. Bruce, M. A. Carins, M. Green, H. P. Taylor, and P. Woodward, *Chem. Comm.*, 1970, 1159.

$H_2Ru_3(CO)_9C_8H_{12}$ (1). Hydrogenation of the ligand presumably takes place by the prior hydrogenation of the metal cluster followed by H-transfer to the C_8H_{11} unit. Interestingly the tetranuclear species also react with hydrogen under moderate conditions to produce a series of hydrido-species based on Ru_3 and Ru_4 units (see Scheme 2).

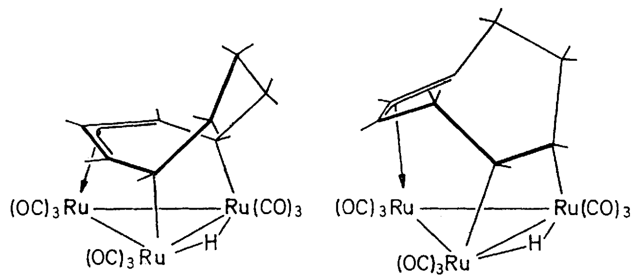

FIGURE 2 Possible structures of $HRu_3(CO)_9C_8H_{11}$ (2)

$$\mathrm{HRu_3(CO)_9C_8H_{11}}\ (2) \xrightarrow[22\ \mathrm{h}]{\mathrm{H_2\text{-}cyclohexane}} \mathrm{H_2Ru_3(CO)_9C_8H_{12}}\ (1)$$

$$\mathrm{Ru_4(CO)_{11}C_8H_{10}}\ (3) \xrightarrow[7\ \mathrm{h}]{\mathrm{H_2\text{-}toluene}} \begin{array}{l}\mathrm{H_2Ru_3(CO)_9C_8H_{12}}\ (1)\\ \alpha\text{-}\mathrm{H_4Ru_4(CO)_{12}}\end{array}$$

$$\mathrm{Ru_4(CO)_{12}C_8H_{10}}\ (4) \xrightarrow{\mathrm{H_2\text{-}cyclohexane}} \alpha\text{-}\mathrm{H_4Ru_4(CO)_{12}}$$

$$\mathrm{Ru_4(CO)_{12}C_8H_{12}}\ (5) \xrightarrow[5\ \mathrm{h}]{\mathrm{H_2\text{-}cyclohexane}} \begin{array}{l}\mathrm{H_2Ru_3(CO)_9C_8H_{12}}\ (1)\\ \alpha\text{-}\mathrm{H_4Ru_4(CO)_{12}}\end{array}$$

SCHEME 2 Reactions of complexes with hydrogen at 80—90°

The nature of the C_8H_{12} unit in complex (1) was identified by its ^1H n.m.r. spectrum. In the low-temperature ^1H n.m.r. spectrum of this complex signals appear at τ 6·87 (2H, m), 7·46 (2H, d), and 8·40 (8H, s) (Figure 3). Above *ca.* 6 °C the resonances centred at τ 6·87 and 7·46 broaden and eventually collapse to a broad absorption at τ 7·16 (46 °C). The simplest conceivable mechanism for this fluxionality is by way of conformational changes about carbon atoms C_3 and C_8 giving a $H^a_{ax} \rightleftharpoons H^b_{eq}$ interconversion. At coalescence temperature $\Delta G^‡$ is 15·6 kcal/mol. The fact that the corresponding osmium complex, prepared for this purpose from the reaction of $Os_3(CO)_{12}$ with cyclo-octene, shows the same general behaviour and a very similar $\Delta G^‡$ value (see Table) clearly indicates that the process is essentially metal-atom independent and provides good additional evidence for the proposed mechanism. A second plausible mechanism, the rotation of the ligand above the M_3 metal cluster, does not bring about the interconversion of H^a and H^b; however, the possibility that this rotation occurs *in addition to* the mechanisms oulined above cannot be eliminated.

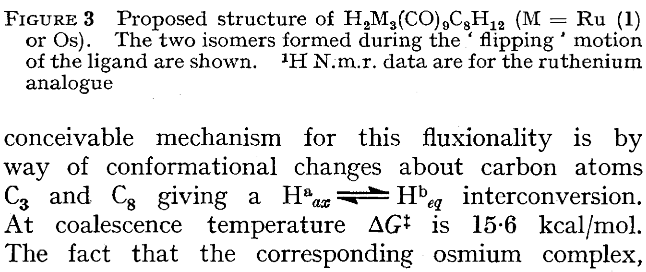

FIGURE 3 Proposed structure of $H_2M_3(CO)_9C_8H_{12}$ (M = Ru (1) or Os). The two isomers formed during the ' flipping ' motion of the ligand are shown. ^1H N.m.r. data are for the ruthenium analogue

The hydrido-ligands also undergo fluxional motion. In the high-field region the low-temperature spectrum consists of two signals of equal intensity at τ 26·10 and 30·40. As the temperature is raised these signals begin to broaden and eventually coalesce. Similar behaviour was noted previously with $H_2Ru_3(CO)_9C_8H_8$ [8] and the $\Delta G^‡$ values are similar (Table). The larger barrier to bridge flipping ($\Delta G^‡$ = 16·9 kcal/mol) in the corresponding osmium complexes discloses an increase in stability of the Os–H–Os bridge bonds.

All the features of the low-temperature ^1H n.m.r. spectrum of the complex are in line with the structure (Figure 3) containing two Ru–C σ-bonds and a π-bonded olefinic fragment. The positioning of the two H-ligands in the bridged position spanning ruthenium atoms Ru_1 and Ru_2 is based on the *effective atomic number rule* and analogy with other possibly related systems.

When these results are considered in conjunction with the observation that $Ru_3(CO)_{12}$ is also a product of the reaction of α-$H_4Ru_4(CO)_{12}$ with either cyclo-octa-1,3- or -1,5-diene it seems evident that the derivatives based on the $Ru_3(CO)_9$ unit are produced from $Ru_3(CO)_{12}$. It was with these considerations in mind that the reaction of $Ru_3(CO)_{12}$ with cyclo-octene, also a product of the reactions of α-$H_4Ru_4(CO)_{12}$ with the cyclo-octadienes, was explored. We find that this reaction yields the dihydro-derivative $H_2Ru_3(CO)_9C_8H_{12}$ (1) but no evidence for the formation of the monohydride species $HRu_3(CO)_9C_8H_{11}$ (2) was found. Some α-$H_2Ru_4(CO)_{13}$ was also obtained from this reaction. The dihydride may be formed in reactions of α-$H_4Ru_4(CO)_{12}$ with dienes, and it is significant that this hydride is known to react with cyclo-octa-1,5-diene to give products identical with those from reactions of α-$H_4Ru_4(CO)_{12}$. Dehydrogenation of α-$H_4Ru_4(CO)_{12}$ with cycloheptene gives α-$H_2Ru_4(CO)_{13}$ in *ca.* 30% yield, together with a small yield of $H_2Ru_3(CO)_9C_7H_{10}$.

From these observations it seemed to us that a detailed investigation of the reactions of the cyclo-octadienes (1,5 and 1,3) with $Ru_3(CO)_{12}$ would be instructive. These systems have been investigated by Candlin and his workers [12] who reported the compound $C_8H_{12}Ru_3(CO)_{10}$ as the product from the reaction of $Ru_3(CO)_{12}$ and 1,3-C_8H_{12}, and we have reported briefly [13] on the reaction of $Ru_3(CO)_{12}$ and 1,5-C_8H_{12}. Reaction of cyclo-octa-1,5-diene with $Ru_3(CO)_{12}$ is

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[12] J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. and Ind.*, 1966, 1960.

[13] F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4624.

both interesting and useful. In benzene as solvent it gives only one main product, namely, tricarbonyl-(cyclo-octa-1,5-diene)-ruthenium, separated in over 60% yield by column chromatography. Reaction of this complex with a range of dienes provides a convenient source of a range of previously inaccessible (diene)-$Ru(CO)_3$ complexes. Brief reports of this work have been given[14] and fuller details will provide the basis of a separate paper.

Allowing a solution of $Ru_3(CO)_{12}$ in benzene to react with cyclo-octa-1,3-diene for 14 h gives rise to a solution from which four products may be isolated by column chromatography on silica. These were identified as $H_2Ru_3(CO)_9C_8H_{10}$ (7), $HRu_3(CO)_9C_8H_{11}$ (2), $Ru(CO)_{12}C_8H_{10}$, (4), and $Ru_4(CO)_{12}C_8H_{12}$ (5). A very small amount of black material, probably $Ru_4(CO)_{11}C_8H_{10}$ (3), was also obtained. All the complexes except $H_2Ru_3(CO)_9C_8H_{10}$ (7) are identical to those obtained from α-$H_4Ru_4(CO)_{12}$. The ^1H n.m.r. spectrum at 30 °C of a sample of $H_2Ru_3(CO)_9C_8H_{10}$ (7) in deuteriobenzene is given in the Table.

The low chemical-shifts and the multiplicities of the τ 3·96 and 5·03 absorptions suggest that these can be assigned to protons of a non-co-ordinated olefin (H_3 and H_4, Figure 4) and that of the two carbon atoms adjacent to this olefin, one is a methylene carbon and the other is not bonded to any hydrogen atom. In fact, double-irradiation experiments indicate that the only other coupling exhibited by the olefinic protons, besides the vicinal coupling, is the presumably time-averaged coupling of H_4 with two methylene protons. On irradiation at τ 3·96 the τ 5·03 doublet of triplets changes to a triplet ($J_{4,5} = 5$ Hz); on irradiation at τ 5·03 the τ 3·96 doublet gives a sharp singlet and the τ 7·98 absorption loses coupling; on irradiation at the τ 7·98 multiplet, the τ 5·03 doublet of triplets changes to a sharp doublet ($J_{3,4} = 11$ Hz).

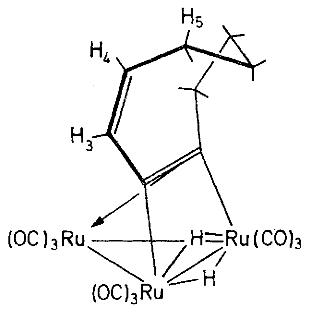

FIGURE 4 Proposed structure of $H_2Ru_3(CO)_9C_8H_{10}$ (7)

The number of protons determined by integrating the spectrum is higher (1 + 1 + 12 + 2·5) than the number predicted by mass spectrometry (12), and does not change after successive attempts to purify the sample. The high-field region of a low-temperature spectrum of a sample of (7) in deuteriodichloromethane (Figure 5) clearly indicates that the high value for the integration arises from two impurities (20 to 30%) which are also dihydride complexes, presumably complexes of $H_2Ru_3(CO)_9$. At 30 °C the still broad time-averaged absorption of (7) overlaps with those of the impurities A and B, but at higher temperatures the three absorptions become sharp and appear separate. The position of the time-averaged absorption and the separation of the two non-equivalent sites of the two hydrido ligands in A, are identical to those of the complex $H_2Ru_3(CO)_9C_8H_{12}$ (1) when in this solvent, therefore suggesting that this impurity is $H_2Ru_3(CO)_9C_8H_{12}$ (1). The nature of the impurity B is unknown.

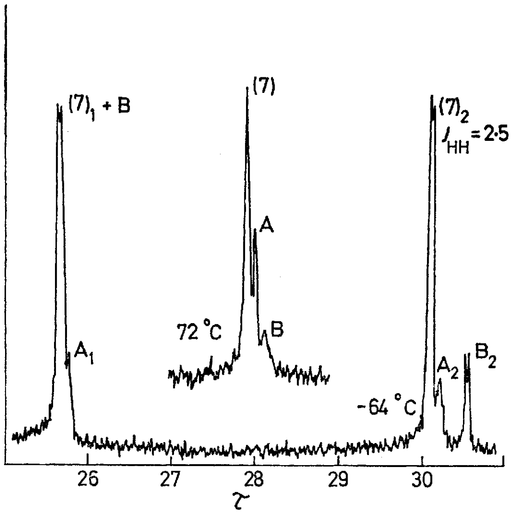

FIGURE 5 ^1H N.m.r. spectrum of $H_2Ru_3(CO)_9C_8H_{10}$ (7) at −64° and 72 °C in CD_2Cl_2. High-field region

It is apparent from reactions of $Ru_3(CO)_{12}$ and α-$H_2Ru_4(CO)_{13}$ that these compounds react with cyclo-octene and cyclo-octadienes to form some or all of the complexes formed during reactions of α-$H_4Ru_4(CO)_{12}$ with these ligands. The possibility that some or all of the complexes also arise directly from reaction of the ligands with α-$H_4Ru_4(CO)_{12}$ cannot be discounted.

Recent experimental work, notably with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, has clearly shown the ease by which organometallic trinuclear cluster compounds may be prepared. The results so far obtained can be readily understood in terms of an oxidation–addition reaction of the olefin across the Ru_3 cluster and may be correlated with the stability of the M–C and M–H bonds produced. This work on α-$H_4Ru_4(CO)_{12}$ described above serves to illustrate that the study of polynuclear clusters may provide routes to a whole new range of organometallic cluster compounds and pose new problems in organometallic reaction mechanisms.

EXPERIMENTAL

Analyses were carried out by the Microanalytical Department of the University Chemical Laboratory. Mass spectra were determined on an A.E.I. MS 12 spectrometer and were calibrated with perfluorokerosene. Nuclear

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[14] A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **49**, C33.

magnetic resonance spectra were measured with a Varian HA 100 instrument. Infrared spectra (2100—1700 cm^{-1}) of the complexes in cyclohexane were measured with a Perkin-Elmer 257 instrument with carbon monoxide as calibrant. Analysis of liquid products was carried out with a Perkin-Elmer F11 gas chromatograph using a column of tricyanoethoxypropane 10% on Chromosorb W.

All solvents and ligands were distilled over drying agents and degassed before use. Cyclo-octa-1,5-diene was purified *via* its adduct with silver nitrate.[15] α-Tetrahydridododecacarbonyltetraruthenium was prepared from dodecacarbonyltriruthenium and hydrogen gas,[4] and α-dihydridotridecacarbonyltetraruthenium was prepared from the tetrahydride and cycloheptene (see below).

The thermodynamic function, $\Delta G^{\ddagger}(T_c)$, for fluxional motion of the dihydride complexes was determined using the equation of Cramer and Mrowca.[16] The accuracy of this method has been discussed previously,[17] and we consider that although the values obtained may not be absolutely accurate they are relatively precise and permit comparison of values in the manner discussed.

Complexes were isolated by column chromatography and, when necessary, by subsequent thin-layer chromatography. Isolation of complexes from reaction of α-$H_4Ru_4(CO)_{12}$ and cyclo-octa-1,5-diene is described in detail. Separation of complexes from other reactions are only given if the method deviates from this example. Yields are based on ruthenium or osmium, and when a substantial quantity of reactant is recovered yields are based on reactant consumed. Reactions were carried out in a nitrogen atmosphere in a closed system (flask, condenser, gas bladder).

Reactions of α-Tetrahydridododecacarbonyltetraruthenium.—(a) *With cyclo-octa-*1,5-*diene* (1,5-*COD*). α-$H_4Ru(CO)_{12}$ (2·4 g) and 1,5-COD (11 ml) were heated at 80—90° in cyclohexane (250 ml) for 44 h to give a dark brown solution. The cooled reaction mixture, apart from a small portion which was distilled by trap-to-trap distillation for g.l.c. analysis, was evaporated to dryness under reduced pressure. The residue was extracted with hexane and poured onto a silica-gel column (2 × 50 cm.). The column was eluted with hexane until the colourless, yellow, orange, and brown fractions were collected. Subsequent elution with toluene–hexane (1 : 10, v/v) gave the remaining purple and black fractions.

The orange, brown, and purple fractions contained some $Ru_3(CO)_{12}$ which was separated by crystallization (0·18 g, 6·5%). Filtrates from crystallization of $Ru_3(CO)_{12}$ from the brown and purple fractions required thin layer chromatography (silica gel, hexane eluant) for purification of the brown and purple complexes. The following complexes were obtained, apart from $Ru_3(CO)_{12}$, in order of elution from the column.

(i) $C_8H_{12}Ru(CO)_3$ (6), 1-3,6-η-cyclo-octadienetricarbonylruthenium, obtained as a colourless oil from the colourless fraction. Sufficient was obtained for i.r. identification only [2066, 1995 cm^{-1}, $C_8H_{12}Ru(CO)_3$ requires: 2067, 1999 [18]].

(ii) $H_2Ru_3(CO)_9C_8H_{12}$ (1), obtained as yellow crystals on recrystallization from hexane (0·08 g, 3%) (Found: C, 30·8; H, 2·0. Calc. for $C_{17}H_{14}O_9Ru_3$: C, 30·7; H, 2·1%).

(iii) $HRu_3(CO)_9C_8H_{11}$ (2), obtained as yellow-orange crystals on recrystallization from the orange fraction after removal of $Ru_3(CO)_{12}$ (0·12 g., 4%) (Found: C, 30·6; H, 1·7. Calc. for $C_{17}H_{12}O_9Ru_3$: C, 30·8; H, 1·8%).

(iv) $Ru_4(CO)_{12}C_8H_{12}$ (5), upon separation of $Ru_3(CO)_{12}$ from the brown fraction followed by t.l.c., a brown powder was obtained on evaporation of chloroform solvent used for t.l.c. extraction (0·012 g, 0·3%).

(v) $Ru_4(CO)_{12}C_8H_{10}$ (4), similar treatment of the purple fraction gave a purple solid (0·01 g, 0·3%).

(vi) $Ru_4(CO)_{11}C_8H_{10}$ (3), recrystallization from the black fraction gave black crystals (0·22 g, 8%) (Found: C, 27·5; H, 1·2. Calc. for $C_{19}H_{10}O_{11}Ru_4$: C, 27·9; H, 1·2%).

Gas chromatography indicated that the ligand remaining was present as cyclo-octene and cyclo-octa-1,3-diene, with traces of the 1,4- and 1,5-isomers.

(b) *With cyclo-octa-*1,3-*diene*. A similar result was obtained with the products obtained in slightly different yields, and identified by i.r., n.m.r., and mass spectroscopy: $C_8H_{12}Ru(CO)_3$ (6), 4%; $H_2Ru_3(CO)_9C_8H_{12}$ (1), 3%; $HRu_3(CO)_9C_8H_{11}$ (2), 4·5%; $Ru_4(CO)_{12}C_8H_{12}$ (5), 0·02%; $Ru_4(CO)_{12}C_8H_{10}$ (4), 0·05%, $Ru_4(CO)_{11}C_8H_{10}$ (3), 3%; and $Ru_3(CO)_{12}$, 10·6%.

(c) *With cyclo-octene*. α-$H_4Ru_4(CO)_{12}$ (0·11 g) and cyclo-octene (0·5 ml) were heated at 80—90° in cyclohexane (15 ml) for 23 h to give a dark brown suspension. Chromatography gave the following complexes.

(i) $H_2Ru_3(CO)_9C_8H_{12}$ (1), evaporation of a yellow fraction gave a yellow solid (0·005 g, 4%) (i.r., mass spectroscopy identification).

(ii) A second yellow band on evaporation to dryness gave a yellow-orange solid (0·001 g) whose i.r. spectrum indicates a mixture of $Ru_3(CO)_{12}$ and α-$H_4Ru_4(CO)_{12}$.

(iii) α-$H_2Ru_4(CO)_{13}$ (toluene–hexane eluant, 1 : 20 v/v), obtained as a red solid on evaporation of the red fraction to dryness (0·017 g, 15%) [i.r., n.m.r. identification; τ 28·5 (in $CDCl_3$). lit.,[3] 28·55 (benzene)].

(d) *With cycloheptene*. α-$H_4Ru_4(CO)_{12}$ (1·37 g) and cycloheptene (7 ml) were heated at 80—90° in cyclohexane (200 ml) for 3 h. Chromatography gave the following products.

(i) $H_2Ru_3(CO)_9C_7H_{10}$, evaporation of the yellow fraction gave a yellow solid (0·012 g, 0·7%); infrared absorption: 2103m, 2074s, 2051s, 2038s, 2025m, 2012s, 2006s, and 1986m cm^{-1}. A mass spectrum has a parent ion required for $C_{16}H_{12}O_9Ru_3$.

Since the infrared spectrum is almost identical with that of the cyclo-octene complex, $H_2Ru_3(CO)_9C_8H_{12}$, and the mass spectrum is consistent with $H_2Ru_3(CO)_9$(cycloheptene), the complex is considered to have a similar structure to that of the cyclo-octene complex.

(ii) An orange fraction, when evaporated to low volume, deposited an orange solid (0·07 g) shown by i.r. spectroscopy to be a mixture of $Ru_3(CO)_{12}$ and α-$H_4Ru_4(CO)_{12}$ (2082m, 2067s, 2062vs, 2031s, 2025m, and 2011m cm^{-1}). The filtrate (0·04 g) had an i.r. spectrum consistent with the presence of these complexes and $H_2Ru_3(CO)_9C_7H_{10}$.

(iii) α-Dihydidotridecacarbonyltetraruthenium. On evaporation to dryness α-$H_2Ru_4(CO)_{13}$ was obtained from the red fraction (0·46 g, 32%) and identified by i.r. and n.m.r. spectroscopy.

Reactions of α-Dihydridotridecacarbonyltetraruthenium.—(a) *With cyclo-octa-*1,5-*diene*. α-$H_2Ru_4(CO)_{13}$ (0·32 g) and cyclo-octa-1,5-diene (1·6 ml) were heated at 80—90°

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[16] R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 1971, 528.

[17] J. Ashley-Smith, I. Douek, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 1776.

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in cyclohexane (80 ml) for 45 h. Products were separated in the same manner as in reaction of α-$H_4Ru_4(CO)_{12}$ with 1,5-COD, and upon identification by i.r. spectroscopy, were found to be identical to the products of that reaction {$C_8H_{12}Ru(CO)_3$ (6), 5%; $H_2Ru_3(CO)_9C_8H_{12}$ (1), 5%; $HRu_3(CO)_9C_8H_{11}$ (2), 7%; $Ru_4(CO)_{12}C_8H_{12}$ (5), 3%; $Ru_4(CO)_{10}C_8H_{10}$ (4) [as a mixture with α-$H_2Ru_4(CO)_{13}$, 0·006 g]; $Ru_4(CO)_{11}C_8H_{10}$ (3), 6%; and $Ru_3(CO)_{22}$ (as a mixture with a small amount of α-$H_4Ru_4(CO)_{12}$, 0·052 g}.

(b) *With cyclo-octene.* α-$H_2Ru_4(CO)_{13}$ (0·130 g) and cyclo-octene (0·7 ml) were heated at 80—90° in cyclohexane (25 ml) for 43 h. Chromatography on silica gel with hexane as eluant for the first two bands (yellow) followed by toluene–hexane (1 : 20; v : v) gave the following. (i) $H_2Ru_3(CO)_9C_8H_{12}$ (1) (0·003 g 3%) (i.r. identification). (ii) A mixture of $Ru_3(CO)_{12}$ and α-$H_4Ru_4(CO)_{12}$ (0·02 g) (i.r. identification), and from the red fraction unchanged α-$H_2Ru_4(CO)_{13}$ (0·04 g) (i.r., n.m.r. identification).

Reactions of Dodecacarbonyltriruthenium.—(a) *With cycloocta-*1,3-*diene.* Reaction in refluxing benzene for 14 h, followed by column and thin-layer chromatography gave unchanged $Ru_3(CO)_{12}$ (24%) and the following complexes: $H_2Ru_3(CO)_9C_8H_{10}$ (7) (15%), $HRu_3(CO)_9C_8H_{11}$ (2) (13%), $Ru_4(CO)_{12}C_8H_{10}$ (4) (2%), and $Ru_4(CO)_{12}C_8H_{12}$ (5) (2%). A small amount of a black compound was also obtained.

(b) *With cyclo-octene.* $Ru_3(CO)_{12}$ (0·10 g) and cyclo-octene (0·5 ml) were heated at 80—90° in cyclohexane (20 ml) for 45 h.

Evaporation to dryness under reduced pressure, extraction with hexane, and chromatography on silica gel with hexane as eluant for the first yellow fraction, followed by toluene–hexane (1 : 50; v/v) for the remaining fractions, yielded the following complexes [yields are based on $Ru_3(CO)_{12}$ consumed].

(i) $H_2Ru_3(CO)_9C_8H_{12}$ (1). Evaporation of the yellow fraction to dryness gave a yellow solid (0·01 g, 10%) identified by i.r. spectroscopy as $H_2Ru_3(CO)_9C_8H_{12}$.

(ii) $Ru_3(CO)_{12}$ crystallized as orange crystals (0·03 g) from the second yellow band (i.r. identification). The filtrate has an i.r. spectrum indicative of trace amounts of $Ru_3(CO)_{12}$ and α-$H_2Ru_4(CO)_{13}$.

(iii) A red band containing both $Ru_3(CO)_{12}$ and $Ru_6C(CO)_{17}$. Sufficient carbide was obtained for i.r. identification only.

Reaction of Dodecacarbonyltriosmium with Cyclo-octene.—$Os_3(CO)_{12}$ (0·42 g) and cyclo-octene (10 ml) were heated at 120—140° in toluene (15 ml) for 4 days. On allowing the solution to cool yellow crystals of $Os_3(CO)_{12}$ formed and were collected (0·25 g) (i.r. identification). The filtrate was passed through a silica-gel column with toluene–hexane (1 : 10; v/v) as eluant, and the orange solid recrystallized from hexane to give a cream solid (0·01 g, 4%); it was identified by i.r., mass, and n.m.r. spectroscopy as $H_2Os_3(CO)_9C_8H_{12}$.

Reactions of Organoruthenium Cluster Complexes.—(a) *Reaction of* $HRu_3(CO)_9C_8H_{11}$ (2) *with hydrogen gas.* A small amount of $HRu_3(CO)_9C_8H_{11}$ (2) (sufficient for n.m.r. spectroscopy) was dissolved in cyclohexane and heated at 80—90° under reflux for 22 h with a steady stream of hydrogen gas bubbled through the solution. During the reaction the solution darkened slightly, and i.r. absorption in the carbonyl region showed conversion to $H_2Ru_3(CO)_9C_8H_{12}$ (1) and the absence of any absorptions not due to either $HRu_3(CO)_9C_8H_{11}$ (2) or $H_2Ru_3(CO)_9C_8H_{12}$ (1). On completion of reaction n.m.r. spectroscopy in $CDCl_3$ indicated the presence of $H_2Ru_3(CO)_9C_8H_{12}$ (1) only.

(b) *Reaction of* $Ru_4(CO)_{11}C_8H_{10}$ (3) *with hydrogen gas.* Hydrogen gas was bubbled through a solution of $Ru_4(CO)_{11}C_8H_{10}$ (0·08 g) in toluene (10 ml) at 80—90° for 7 h. Solvent was removed from the yellow-black solution and hexane-soluble products were separated by t.l.c. on silica gel with hexane as eluant. The following complexes were obtained.

(i) $H_2Ru_3(CO)_9C_8H_{12}$ (1) (0·01 g, 12%) as a yellow solid identified by i.r. and mass spectroscopy.

(ii) A yellow-orange band (0·005 g) was shown by i.r. spectroscopy to be α-$H_4Ru_4(CO)_{12}$ with a small amount of $H_2Ru_3(CO)_9C_8H_{12}$ (1).

(iii) A purple band (0·002 g) was shown by i.r. spectroscopy to be α-$H_4Ru_4(CO)_{12}$. The purple complex is presumably $Ru_4(CO)_{12}C_8H_{10}$ (4) which has a very intense purple colour.

(iv) A fawn band (0·001 g). Purified again by t.l.c. to give sufficient for i.r. spectra only (2100m, 2059m, 2055s, 2052s, 2031m,br, 2001w, 1992w, and 1976w cm^{-1}).

(v) Unchanged $Ru_4(CO)_{11}C_8H_{10}$ (3) (0·002 g) identified by i.r. spectroscopy.

(c) *Reaction of* $Ru_4(CO)_{12}C_8H_{12}$ (5) *with hydrogen gas.* Hydrogen gas was bubbled through a solution of $Ru_4(CO)_{12}C_8H_{12}$ (0·01 g) in cyclohexane (10 ml) at 80—90° for 5 h. The solution was evaporated to low volume and components separated by t.l.c. on silica gel with hexane as eluant. Products were identified by i.r. spectroscopy as $H_2Ru_3(CO)_9C_8H_{12}$ (0·003g, 29%), a yellow-orange band (0·0005 g) containing α-$H_4Ru_4(CO)_{12}$ and a small amount of $H_2Ru_3(CO)_9C_8H_{12}$, and a brown band (0·002 g) containing α-$H_4Ru_4(CO)_{12}$ and unchanged $Ru_4(CO)_{12}C_8H_{12}$ (5).

(d) *Reaction of* $Ru_4(CO)_{12}C_8H_{10}$ (4) *with hydrogen gas.* Hydrogen gas was bubbled through a solution of $Ru_4(CO)_{12}C_8H_{10}$ in cyclohexane at 80—90° for 13 h. At this stage i.r. spectroscopy indicated a mixture of α-$H_4Ru_4(CO)_{12}$ and unchanged $Ru_4(CO)_{12}C_8H_{10}$ (4). The solution has a hydride resonance at τ 27·5 in $CDCl_3$ [lit.[3] values for α-$H_4Ru_4(CO)_{12}$ 27·6 in $CDCl_3$], and yellow–purple bands are obtained on a t.l.c. plate in positions appropriate for α-$H_4Ru_4(CO)_{12}$ and $Ru_4(CO)_{12}C_8H_{10}$ (4). Insufficient complex was available to attempt separation of products.

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