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Syntheses, structures and chemistry of the high-nuclearity ruthenium hydrido cluster anions $[Ru_{10}H_2(CO)_{25}]^{2-}$ and $[Ru_{11}H(CO)_{27}]^{3-}$

Philip J. Bailey,[a] **Michael A. Beswick,**[b] **Brian F. G. Johnson,**[b] **Jack Lewis,***[,b] **Mary McPartlin,**[c] **Paul R. Raithby**[b] **and M. Carmen Ramirez de Arellano**[b]

[a] *Department of Chemistry, The University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK*
[b] *University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, UK*
[c] *School of Chemistry, University of North London, Holloway Road, London N7 8DB, UK*

Thermolysis of $[Ru_3(CO)_{12}]$ in ethanol yielded the decanuclear hydridoruthenium cluster dianion $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1**. When a mixture of methanol and water is employed as thermolysis solvent the undecaruthenium hydridoruthenium trianion $[Ru_{11}H(CO)_{27}]^{3-}$ **2** is also formed. Crystal structure analysis of **1** as its $[N(PPh_3)_2]^+$ salt and **2** as its $[NEt_3(CH_2Ph)]^+$ salt showed their metal core structures to be related, **2** being a square-faced capped congener of **1**. Cluster **2** was alternatively formed in near-quantitative yields when $[Ru_3(CO)_{12}]$ was thermolysed in acetonitrile containing traces of water for several days. It was not possible to locate the hydride ligands in the structures by potential-energy-minimisation calculations, but strong signals were seen in the ^1H NMR spectra at δ −14.2 (s, 2 H) for **1** and at −5.47 (s, 1 H) for **2**. On treatment of **1** and **2** with $[Au(PPh_3)Cl]$ in the presence of $TlPF_6$, **1** showed no reactivity, but **2** reacted smoothly adding one $[Au(PPh_3)]^+$ moiety and giving a product characterised as $[Ru_{11}H(CO)_{27}\{Au(PPh_3)\}]^{2-}$ **3**. The structural relationships between the known high-nuclearity ruthenium hydrido carbonyl clusters are discussed, and their implications for a possible cluster build-up sequence considered.

The chemistry of high-nuclearity ruthenium clusters is less extensive than that of osmium for which molecular species containing up to 20 close-packed osmium atoms are now known. These developments for osmium have been the result of significant improvements in the methods of synthesis and isolation of high-nuclearity carbonyl clusters in recent years.[1] The progress of the high-nuclearity chemistry of its lighter congener has followed a different course, partly because of the different balance between M–M and M–CO bond strengths for ruthenium which results in the formation of a range of cluster nuclearities and geometries which are different from those observed for osmium.[2] It is also a feature of this chemistry that the majority of the known high-nuclearity ruthenium clusters contain carbide or nitride ligands. These interstitial atoms serve to provide additional stability for the extended metal cores and thus to some extent compensate for the lower M–M bond strength of ruthenium.

We have recently reported the synthesis of decaruthenium carbido- and nitrido-species.[3] We report here, as an extension to this study, the synthesis of high-nuclearity ruthenium hydrido clusters. A systematic build up of ruthenium hydrido clusters has been developed employing thermolysis of the $[Ru_3(CO)_{12}]$ precursor in protic solvents. It is thought that the use of such solvents prevents carbide formation in thermolysis reactions of ruthenium carbonyls by stabilising, *via* protonation, the octahedral hexaruthenium intermediate.[4] This has the effect of blocking the formation of the carbide, which is thought to originate from a co-ordinated carbonyl at this stage of the cluster build-up process in aprotic media.[5] Parts of this work have been the subject of previous communications.[6,7]

Results and Discussion

In an attempt to parallel the synthesis of $[Os_{10}H_4(CO)_{24}]^{2-}$, prepared by thermolysis of $[Os_3(CO)_{10}(OEt)_2]$ in 2-methylpropanol,[8] $[Ru_3(CO)_{12}]$ was heated to reflux in ethanol for 18 h resulting in the formation of the hydrido monoanion $[Ru_6H(CO)_{18}]^-$, metallic ruthenium and the new dihydrido dianion $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1** in 27% yield. This new dihydride represents the first non-carbido decaruthenium cluster. Analysis of the carbonyl to metal ratio of these products reveals that for $[Ru_3(CO)_{12}]$ it is 4:1, for $[Ru_6H(CO)_{18}]^-$ it is 3:1 and in cluster **1** it is 2.5:1. In an attempt to isolate higher-nuclearity species with lower CO:Ru ratios, the effects of varying the reaction conditions were investigated. Extending the reaction time had little influence on the product ratios, however increased concentrations of $[Ru_3(CO)_{12}]$ decreased the reaction rate and also led to the observation of the tetranuclear polyhydrido systems $[Ru_4H_4(CO)_{12}]$ and $[Ru_4H_3(CO)_{12}]^-$ in the mixtures. However, no new high-nuclearity species were observed.

It is known that the decaruthenium carbido cluster $[Ru_{10}C(CO)_{24})]^{2-}$ may be directly built up by treatment of $[Ru_6C(CO)_{16}]^{2-}$ with the required quantity of $[Ru_3(CO)_{12}]$ under high-temperature thermolysis.[9] We therefore tested the possibility that the decanuclear core of **1** could be built up in a similar manner. Treatment of $[Ru_6H(CO)_{18}]^-$ with $[Ru_3(CO)_{12}]$ in diglyme (2,5,8-trioxanonane) at reflux (162 °C) was indeed found to lead to a 50% yield of $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1**, thus giving further support to the idea that the formation of high-nuclearity systems proceeds *via* a build-up series consisting, in many cases, of isolable intermediates.

It has been known for some time that water can be a useful solvent in the preparation of hydrido clusters. It was reported in 1968 that when $[Ru_3(CO)_{12}]$ is heated under reflux in octane or nonane, besides the carbido complex $[Ru_6C(CO)_{17}]$, $[Ru_4H_2(CO)_{13}]$ and $[Ru_4H_4(CO)_{12}]$ are also observed, albeit in trace amounts.[10] Initially the formation of these hydrido clusters led to the assumption that the alkane solvents were responsible for the hydrides, the metal carbonyl being involved in a process of hydrogen abstraction. Subsequent work showed that when a few microlitres of water were added to the reaction mixture the yield of the hydrido species increased.[11] When D_2O

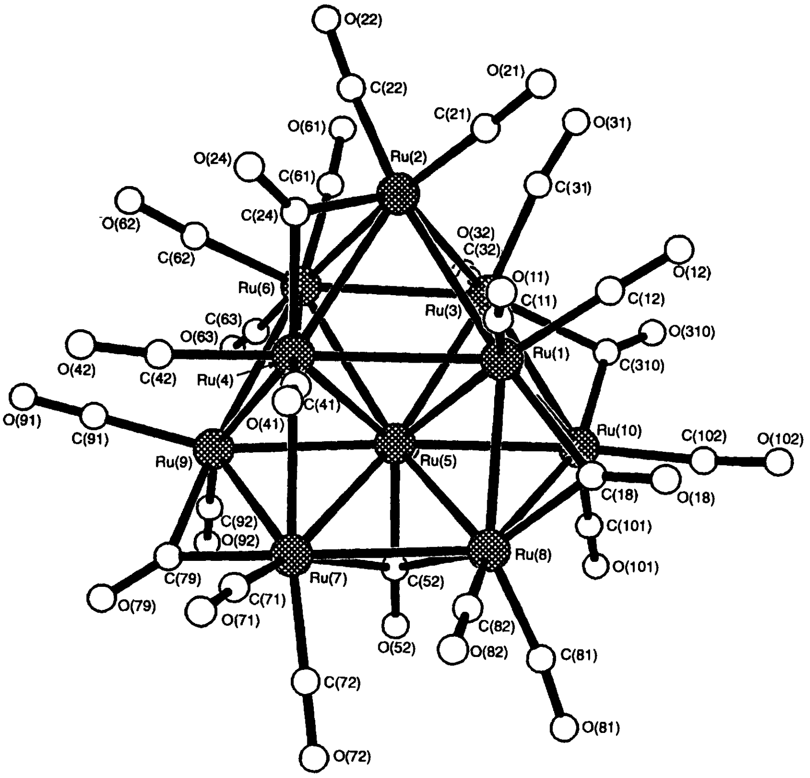

Fig. 1 Structure of $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1** as its $[N(PPh_3)_2]^+$ salt

was used total deuterium incorporation was observed. Furthermore, it was found that when $[Ru_3(CO)_{12}]$ is heated with water in a sealed Carius tube for 24 h at 135 °C, $[Ru_4H_4(CO)_{12}]$ is formed in 40% yield. It has also been shown that, in the general preparation of $[Ru_3(CO)_{12}]$ from a methanolic solution of $RuCl_3$ under carbon monoxide pressure, when a small amount of water is added the product formed is $[Ru_4H_4(CO)_{12}]$ rather than $[Ru_3(CO)_{12}]$.[12] Following these precedents, $[Ru_3(CO)_{12}]$ was dissolved in methanol–water (1:1) and thermolysed for 40 h during which time the initial orange solution turned red and then black. In addition to unreacted $[Ru_3(CO)_{12}]$, four products were isolated from the resulting solution by thin-layer chromatography on silica: $[Ru_6H(CO)_{18}]^-$, $[Ru_8H_2(CO)_{21}]^{2-}$, $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1** and the new trianion $[Ru_{11}H(CO)_{27}]^{3-}$ **2**. On increased reaction times the yield of cluster **2** increased as that of **1** decreased.

In testing the effect of changing the solvent system we have found a valuable alternative synthesis of $[Ru_{11}H(CO)_{27}]^{3-}$ **2**. The thermolysis of $[Ru_3(CO)_{12}]$ in acetonitrile in the presence of traces of water (undried acetonitrile) gives a 90% yield of **2**, with the only other product being $[Ru_6H(CO)_{18}]^-$. If reaction times are increased to days rather than hours, cluster **2** is the only product with no metal formation observed at any time. If the reaction is stopped before **2** is formed a high yield of the dianion $[Ru_6(CO)_{18}]^{2-}$ may be isolated from the solution.[13]

Single crystal X-ray analysis of compound **1** as its $[N(PPh_3)_2]^+$ salt shows that the dianion has the structure illustrated in Fig. 1. The metal core geometry may be described as the fusion of a bicapped octahedron with a bicapped square pyramid through a planar array of five metal atoms [Ru(1)–Ru(4)–Ru(5)–Ru(9)–Ru(10)]. This type of metal framework, of virtual C_s symmetry, has not previously been reported. The asymmetric distribution of the 25 carbonyl ligands reduces the overall symmetry to C_1. Of these ligands, four are symmetrical μ-bridging whilst one is semi-μ_3-bridging across the Ru(5)–Ru(7)–Ru(8) face. This carbonyl C(52)–O(52) is significantly bent [Ru(5)–C(52)–O(52) 154(2)°] with a short contact between its carbon atom and Ru(5) [1.938(10) Å] and two long ones to Ru(7) and Ru(8) [2.631(27) and 2.564(27) Å respectively, Table 1].

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Ru(1)–Ru(2)	2.903	Ru(4)–Ru(7)	2.908
Ru(1)–Ru(3)	2.895	Ru(4)–Ru(9)	2.909
Ru(1)–Ru(4)	3.001	Ru(5)–Ru(6)	2.901
Ru(1)–Ru(5)	2.815	Ru(5)–Ru(7)	2.872
Ru(1)–Ru(8)	2.791	Ru(5)–Ru(8)	2.767
Ru(1)–Ru(10)	2.802	Ru(5)–Ru(9)	2.761
Ru(2)–Ru(3)	2.956	Ru(5)–Ru(10)	2.803
Ru(2)–Ru(4)	2.853	Ru(6)–Ru(9)	2.863
Ru(2)–Ru(6)	2.871	Ru(7)–Ru(8)	2.845
Ru(3)–Ru(5)	2.793	Ru(7)–Ru(9)	2.826
Ru(3)–Ru(6)	2.886	Ru(8)–Ru(10)	2.860
Ru(3)–Ru(10)	2.796	C(52)–Ru(5)	1.938(10)
Ru(4)–Ru(5)	2.845	C(52)–Ru(7)	2.631(27)
Ru(4)–Ru(6)	2.898	C(52)–Ru(8)	2.564(27)
Ru(5)–C(52)–O(52)	154(2)		

Maximum Ru–Ru estimated standard deviations (e.s.d.s) 0.003 Å.

All attempts at crystallisation of the $[N(PPh_3)_2]^+$ salt of compound **2** yielded crystals of poor quality unsuitable for single-crystal X-ray crystallographic studies. However, good-quality crystals were finally obtained by use of benzyltriethylammonium as counter ion. The crystal structure analysis of this salt (Fig. 2, Table 2) shows that the metal core geometry (Fig. 3) may be described as the condensation of two octahedra [Ru(1), Ru(2), Ru(5), Ru(6), Ru(8), Ru(9) and Ru(1), Ru(2), Ru(3), Ru(5), Ru(7), Ru(11)], sharing the Ru(1), Ru(2), Ru(5) triangle, together with two trigonal bipyramids [Ru(1), Ru(2), Ru(3), Ru(4), Ru(9) and Ru(1), Ru(5), Ru(6), Ru(7), Ru(10)], sharing common Ru_4 butterfly units [Ru(1), Ru(2), Ru(3), Ru(9) and Ru(1), Ru(5), Ru(6), Ru(7)]. This leaves one butterfly face on the surface of the cluster [Ru(2), Ru(5), Ru(8), Ru(11)], and it is compelling to consider the addition of a further ruthenium atom over this face, to give a systematic build-up to the symmetric twelve-atom cluster. The metal core

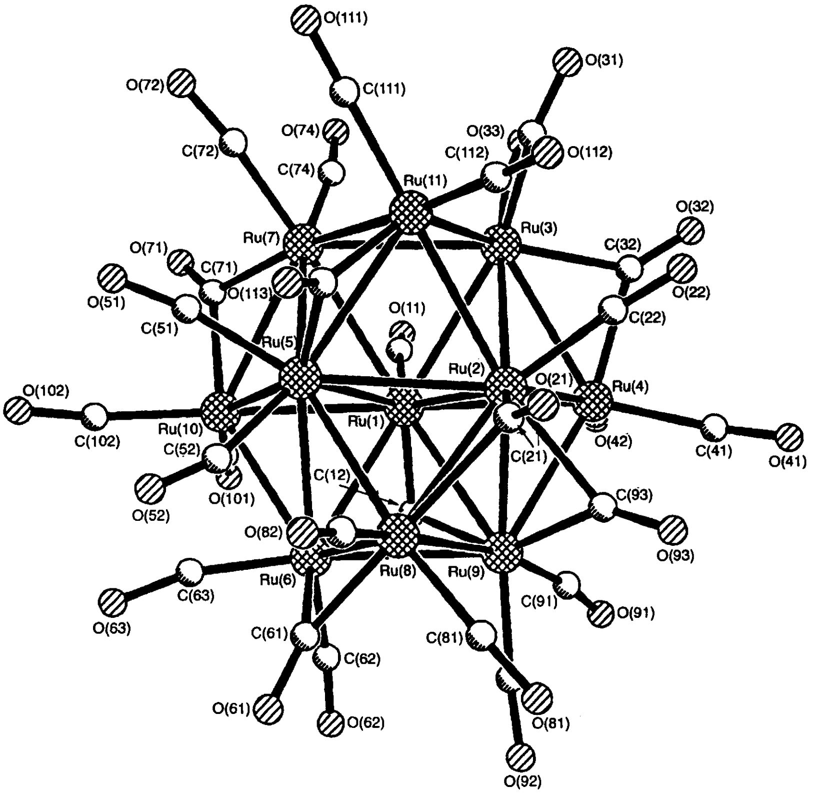

Fig. 2 Structure of $[Ru_{11}H(CO)_{27}]^{3-}$ **2** as its $[NEt_3(CH_2Ph)]^+$ salt

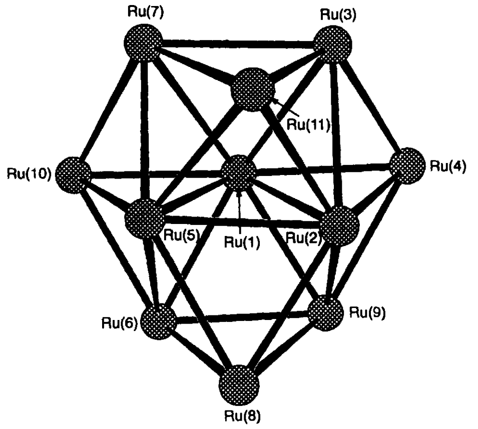

Fig. 3 Metal core structure of $[Ru_{11}H(CO)_{27}]^{3-}$ **2**

Table 2 Selected bond lengths (Å) for compound **2**

Ru(1)–Ru(2)	2.788	Ru(3)–Ru(7)	2.983
Ru(1)–Ru(3)	2.861	Ru(3)–Ru(11)	2.875
Ru(1)–Ru(4)	2.869	Ru(4)–Ru(9)	2.834
Ru(1)–Ru(5)	2.796	Ru(5)–Ru(6)	2.902
Ru(1)–Ru(6)	2.825	Ru(5)–Ru(7)	2.855
Ru(1)–Ru(7)	2.883	Ru(5)–Ru(8)	2.865
Ru(1)–Ru(9)	2.774	Ru(5)–Ru(10)	2.848
Ru(1)–Ru(10)	2.798	Ru(5)–Ru(11)	2.872
Ru(2)–Ru(4)	2.807	Ru(6)–Ru(8)	2.831
Ru(2)–Ru(5)	2.950	Ru(6)–Ru(9)	2.842
Ru(2)–Ru(8)	2.827	Ru(6)–Ru(10)	2.830
Ru(2)–Ru(9)	2.786	Ru(7)–Ru(10)	2.865
Ru(2)–Ru(11)	2.861	Ru(7)–Ru(11)	3.085
Ru(3)–Ru(4)	2.772	Ru(8)–Ru(9)	3.093

Maximum Ru–Ru e.s.d.s 0.003 Å.

in **2** may also be considered as being built up from **1** by simply adding the eleventh ruthenium atom to the square face [Ru(1), Ru(7), Ru(8), Ru(4)] of **1** (Fig. 1).

It was not possible to locate the hydride ligands in the structures of compounds **1** or **2** by potential-energy-minimisation calculations, but strong signals are observed in their ^1H NMR spectra, at δ −14.2 (s, 2 H) for **1** and at −5.47 (s, 1 H) for **2**. Attempts were made to observe infrared Ru–H vibrational modes in the solid state using both Cs^+ and $[NEt_4]^+$ salts as CsI discs at 290 and 115 K, but due to difficulties in obtaining clean samples and the presence of absorptions due to ambient water in the spectral region of interest no conclusive results could be obtained.

Variable-temperature ^{13}C NMR spectra of cluster **1** were recorded from a *ca.* 30% ^{13}CO-enriched sample in CD_2Cl_2 (290–210 K) or CD_2Cl_2–CF_2Cl_2 (190–163 K) and are shown in Fig. 4. The spectra exhibit a complex sequence of coalescence and sharpening of resonances as the temperature is reduced. At 290 K the observation of a single broad resonance implies complete carbonyl scrambling over the cluster surface. The reduced rate of carbonyl exchange at lower temperatures results in the emergence of several sharp resonances until, at 163 K, a spectrum which is partially consistent with the solid-state structure is obtained. This spectrum contains 20 resonances due to carbonyl ligands and not the 25 expected for the C_1 symmetry structure. Thus, even at this temperature, some localised carbonyl scrambling must be invoked. However, it appears that this process does not involve the four bridging carbonyls observed in the solid-state structure since four sharp signals at high frequency may be assigned to these ligands. A fifth high-frequency signal at δ 220.1 may be assigned to the semi-μ_3-bridging carbonyl identified in the structural study (see above). The remaining signals may be assigned to the 20 terminal carbonyl ligands.

On treatment of compounds **1** and **2** with $[Au(PPh_3)Cl]$ in the presence of $TlPF_6$, **1** showed no reactivity but **2** reacted smoothly adding one $[Au(PPh_3)]^+$ moiety and giving a product characterised as $[Ru_{11}H(CO)_{27}\{Au(PPh_3)\}]^{2-}$ **3**. The carbonyl stretching bands in the solution infrared spectrum of this species are shifted by 10–15 cm^{-1} to higher wavenumber as compared to those of the parent dianion as is to be expected on reduction of the negative charge carried by the cluster. Similar shifts in CO stretching bands have been observed on formation of the monogold species $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$ and $[Ru_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$ from the respective decanuclear carbido-cluster dianions.[14] Cluster **3** was also characterised by negative-ion FAB mass spectrometry, ^1H NMR spectroscopy and elemental analysis. The hydride ligand gives rise to a singlet at δ −5.09 which compares with the signal at δ −5.47 for the parent **2**.

There are now a range of high-nuclearity hydridoruthenium clusters, all of which have been observed in the present study. In all of the cluster build-up reactions described here the octahedral $[Ru_6H(CO)_{18}]^-$, or the corresponding non-hydrido dianion, is observed in the reaction mixtures as the primary build-up product from $[Ru_3(CO)_{12}]$. This species therefore appears to be the Ru_6 member of the build-up series. In aprotic solvents (diglyme) the hexanuclear dianion $[Ru_6(CO)_{18}]^{2-}$ has been shown to lead to the interstitial carbido species $[Ru_6C(CO)_{16}]^{2-}$ *via* cleavage of a co-ordinated carbonyl, and we have proposed a mechanism for this process.[5] The hexanuclear hydride, however, already contains an interstitial atom in the form of the hydride ligand, and we have shown that its diglyme thermolysis in the presence of $[Ru_3(CO)_{12}]$ leads not to carbido species, but rather to the decanuclear dihydride **1**. The interstitial hydride in $[Ru_6H(CO)_{18}]^-$ therefore appears to exert some stabilising influence upon the octahedral core, as is well known to be the case for the carbide in $[Ru_6C(CO)_{16}]^{2-}$,[15] which allows it to function as a substrate for cluster build-up rather than undergo the core transformations which are thought to lead to the carbide ligand *via* a dihapto (η^2-) carbonyl.[5]

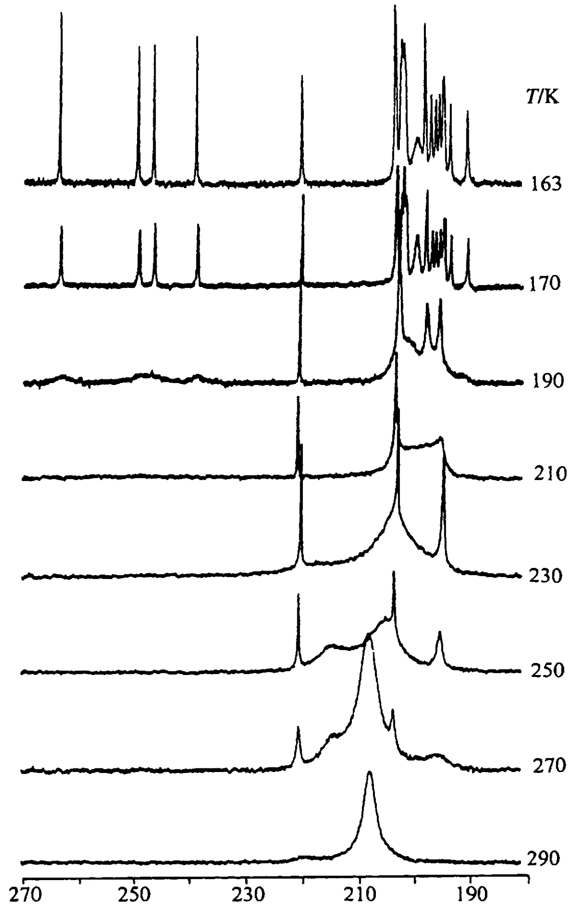

Fig. 4 Variable-temperature 100.62 MHz ^{13}C NMR spectra of $[N(PPh_3)_2]_2[Ru_{10}H_2(CO)_{25}]$ in CD_2Cl_2 (290–210 K) and CD_2Cl_2–CF_2Cl_2 (190–163 K)

Inspection of the core geometries of the known high-nuclearity ruthenium hydrido clusters provides further evidence for the existence of a cluster build-up series as is shown in Fig. 5. The octaruthenium dihydride $[Ru_8H_2(CO)_{21}]^{2-}$ has a structure derived from an octahedron by the addition of an Ru_2 unit, and may be described as an octahedron and a trigonal bipyramid sharing a common face.[16] Furthermore, one of the two hydrides in this system has been shown to occupy the interstitial octahedral site $\{$*cf.* $[Ru_6H(CO)_{18}]^-\}$. The formation of the metal core of $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1** from this species is also easy to envisage and involves a similar Ru_2 fragment addition to a second face of the octahedron generating the structure with mirror-plane symmetry. Finally, addition of a further single ruthenium to the open square face generated in the formation of the decanuclear structure generates the core geometry of the undecaruthenium system $[Ru_{11}H(CO)_{27}]^{3-}$ **2**.

Experimental

General procedures

The compounds $[N(PPh_3)_2]Cl$[17] and $[Ru_3(CO)_{12}]$[18] were prepared by published methods; $[NEt_3(CH_2Ph)]Cl$ and $TlPF_6$ were obtained from Aldrich and used as received. All reactions and manipulations were carried out in air. Infrared and NMR spectra were recorded on Perkin-Elmer FT1710 and Bruker AM400 spectrometers respectively, negative-ion fast atom bombardment mass spectra on a AEI/Kratos MS50 instrument with either glycerol or 3-nitrobenzyl alcohol as the matrix liquid. The ^{13}C NMR spectra were obtained from solutions in CD_2Cl_2 or mixtures of CD_2Cl_2–CF_2Cl_2 at 100.62 MHz and tris(acetylacetonato)chromium(III) was added as a shiftless relaxation agent. All separations were achieved chromatographically. Thin-layer chromatography was carried out using Merck glass plates (20 x 20 cm) coated with 0.25 cm layers of silica gel.

Preparations

$[N(PPh_3)_2]_2[Ru_{10}H_2(CO)_{25}]$. (*a*) The compound $[Ru_3(CO)_{12}]$ (500 mg, 0.782 mmol) was dissolved/suspended in ethanol (200 cm^3) and heated to reflux for 18 h to give a brown solution and some black solid. An excess (500 mg, 0.87 mmol) of $[N(PPh_3)_2]Cl$ was added to the hot solution and the solvent removed under vacuum. The resulting material was dissolved in the minimum volume of CH_2Cl_2 and silica gel (5 g) added, followed by hexane (100 cm^3) with rapid stirring. The silica was

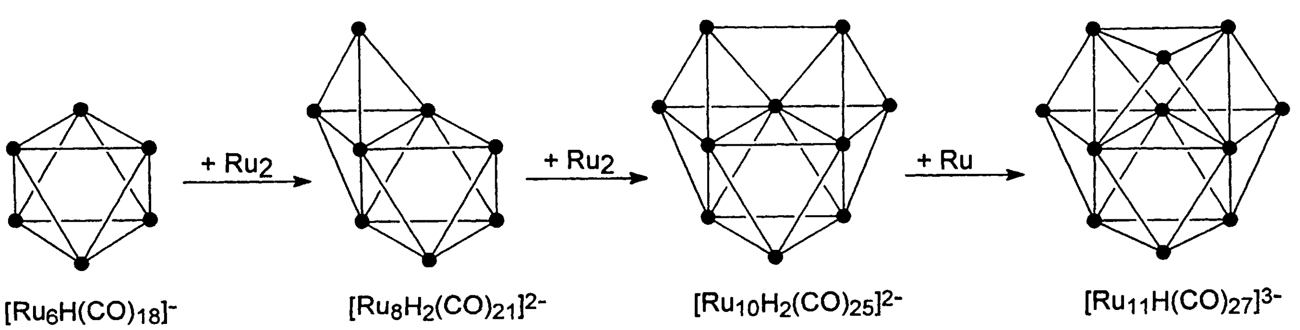

Fig. 5 Structural relationships between the known high-nuclearity ruthenium hydrido carbonyl clusters

Table 3 Crystal data for compounds **1** and **2***

	1	**2**
Empirical formula	$C_{97}H_{62}N_2O_{25}P_4Ru_{10}$	$C_{66}H_{67}N_3O_{27}Ru_{11}$
M	2790.15	2446.0
T/K	293.0(10)	290
μ(Mo-Kα)/cm^{-1}	14.74	21.36
a/Å	17.244(4)	13.714(3)
b/Å	20.487(5)	13.991(3)
c/Å	16.769(4)	21.387(4)
α/°	92.07(2)	85.55(3)
β/°	115.26(2)	81.46(3)
γ/°	67.66(2)	74.77(3)
U/Å^3	4898.92	3912.4(14)
D_c/g cm^{-3}	1.891	2.075
F(000)	2716	2368
Diffractometer	Philips PW1100	Siemens R3mV

* Details in common: λ(Mo-Kα) = 0.710 73 Å; triclinic, space group $P\bar{1}$ (no. 2); Z = 2.

filtered off, dried under vacuum and placed in an even band on top of a silica gel column. The mixture was separated (acetone–hexane, 1 : 1) to yield red $[Ru_6H(CO)_{18}]^-$ and the new dianion $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1** {isolated in *ca.* 27% yield as its $[N(PPh_3)_2]^+$ salt}. IR (CH_2Cl_2): ν(CO) 2058vw, 2015s (sh), 2008vs, 1992m (sh) and 1772m (br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.70 (m, 30 H) and −14.2 (s, 2 H). FAB mass spectrum: m/z = 1713, M^+; 2251, $[M + N(PPh_3)_2]^+$; 856, M^{2+}. Single crystals of the dianion **1** suitable for X-ray diffraction were grown at low temperature from a CH_2Cl_2–methanol mixture.

(*b*) The anion $[Ru_6H(CO)_{18}]^-$ (100 mg, 0.0606 mmol) and $[Ru_3(CO)_{12}]$ (55 mg, 0.086 mmol) were dissolved in diglyme (20 cm^3) then heated to reflux for 3 h after which an excess of $[N(PPh_3)_2]Cl$ (200 mg, 0.35 mmol) was added to the hot brown solution. Silica gel (2 g) was added to the flask followed by diethyl ether (50 cm^3) with rapid stirring. The silica was filtered off, washed with ether and dried under vacuum. It was extracted with the minimum volume of CH_2Cl_2 and the mixture separated by TLC (acetone–hexane, 1 : 1) to give the new dianion $[Ru_{10}H_2(CO)_{25}]^{2-}$ **1** {isolated in *ca.* 50% yield as its $[N(PPh_3)_2]^+$ salt} and recovered starting materials.

$[N(PPh_3)_2]_3[Ru_{11}H(CO)_{27}]$. (*a*) The compound $[Ru_3(CO)_{12}]$ (1 g, 1.56 mmol) was suspended in methanol–water (1 : 1, 200 cm^3) and heated to reflux for 40 h, during which time the initial orange solution turned red and then black. The salt $[N(PPh_3)_2]Cl$ (1 g, 1.74 mmol) was added to the hot solution and as the mixture cooled a black precipitate formed. Separation of the mixture by thin-layer chromatography on silica (eluent: acetone–hexane, 3 : 2) resulted in the isolation of four products {together with some unreacted $[Ru_3(CO)_{12}]$}: $[Ru_6H(CO)_{18}]^-$, $[Ru_8H_2(CO)_{21}]^{2-}$, $[Ru_{10}H_2(CO)_{25}]^{2-}$ and the new trianion **2** {isolated in *ca.* 15% yield as its $[N(PPh_3)_2]^+$ salt} in order of elution. When longer reaction times were employed the yield of the trianion increased at the expense of $[Ru_{10}H_2(CO)_{25}]^{2-}$. Microcrystalline **2** was obtained from the layered diffusion of EtOH into a CH_2Cl_2 solution of the cluster **2**. IR (CH_2Cl_2): ν(CO) 2051s (sh), 1993vs and 1751m (br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.70 (m, 90 H) and −5.47 (s, 1 H). FAB mass spectrum: m/z = 1866, M^+; 2409, $[M + N(PPh_3)_2]^+$.

(*b*) The compound $[Ru_3(CO)_{12}]$ (2 g, 3.13 mmol) was heated to reflux in MeCN (200 cm^3) for 20 h after which time $[N(PPh_3)_2]Cl$ (2 g, 3.48 mmol) was added and the solvent removed in vacuum. The resultant oil was dissolved in the minimum volume of CH_2Cl_2 and separated by TLC with CH_2Cl_2 as eluent to give **2** in 90% yield. A microcrystalline material was obtained by dissolving **2** in CH_2Cl_2–methanol (1 : 1) followed by slow removal of the solvent on a rotary evaporator until near dryness. Filtration followed by copious washing with ethanol to remove excess of $[N(PPh_3)_2]Cl$ yielded spectroscopically pure $[N(PPh_3)_2]_3[Ru_{11}H(CO)_{27}]$.

$[NEt_3(CH_2Ph)]_3[Ru_{11}H(CO)_{27}]$. Addition of $[NEt_3(CH_2Ph)]Cl$ in place of $[N(PPh_3)_2]Cl$ in either of the above procedures gave the required salt. Single crystals suitable for X-ray diffraction were grown from the layered diffusion of ethanol into a CH_2Cl_2 solution of the salt.

$[N(PPh_3)_2]_2[Ru_{11}H(CO)_{27}\{Au(PPh_3)\}]$. Cluster **2** (50 mg, 0.0144 mmol) was stirred with $[Au(PPh_3)Cl]$ (18 mg, 0.036 mmol) and $TlPF_6$ (13 mg, 0.036 mmol) in CH_2Cl_2 (40 cm^3) for 3 h whilst monitoring the reaction progress by IR spectroscopy until no further change occurred. The solution was reduced to near dryness in vacuum and separated using TLC (acetone–hexane, 60 : 40) yielding one band characterised as $[N(PPh_3)_2]_2[Ru_{11}H(CO)_{27}\{Au(PPh_3)\}]$ (90% yield). IR (CH_2Cl_2): ν(CO) 2049m, 2007vs, 1986s (sh), 1970m (sh) and 1776m (br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.70 (m, 90 H) and −5.09 (s, 1 H). FAB mass spectrum: m/z = 2325, M^+; 2864, $[M + N(PPh_3)_2]^+$ (Found: C, 41.0; H, 2.15. Calc.: C, 41.15; H, 2.25%).

Crystallography

Data collection and processing. A brown crystal of compound **1** of dimensions 0.32 × 0.24 × 0.18 mm was used for data collection, in the range θ 3–25° with a scan width of 0.80° using the technique described previously.[19] Lorentz-polarisation corrections were applied to the data and equivalent reflections were merged to give 7443 data with $I/\sigma(I) > 3.0$. A brown block of compound **2** of dimensions 0.2 × 0.28 × 0.36 mm was used for data collection, in the range 2θ 5–45° with a scan width of 1.60° plus the Kα separation. Lorentz-polarisation and absorption corrections (based on ψ-scan data) were applied and equivalent reflections averaged to give 6431 data with $F > 4\sigma(F)$ (see Table 3).

Structure solution and refinement. The coordinates of six of the metal atoms in compound **1** forming an octahedron were obtained from a Patterson synthesis. The remaining non-hydrogen atoms were located from Fourier and subsequent Fourier-difference syntheses.[20] The phenyl rings were given idealised geometry (C–C 1.395, C–H 1.08 Å). The hydrogen atoms were assigned fixed thermal parameters of 0.08 Å^2. An absorption correction was applied to the data using the empirical method of Walker and Stuart,[21] with all non-hydrogen atoms isotropically refined. In the final cycles of refinement all non-hydrogen atoms were given anisotropic thermal parameters and refinement, on F, converged at R = 0.0723, R' = 0.0767 for 739 parameters, with weights of $1/[\sigma^2(F) + 0.000\,024F^2]$ assigned to individual reflections. It proved impossible to locate the hydride ligands using potential-energy-minimisation techniques,[22] or examination of computed space-filling models. The arrangement of the carbonyls on the surface is rather asymmetric, and although some gaps were found between the ligands they could not unambiguously be assigned as hydrogen-atom sites. There seems a possibility that one or both of the hydrogen atoms reside in interstitial or semi-interstitial sites. In the final Fourier-difference map some residual electron-density peaks greater than 1 e Å^{-3} were observed, but they were in the proximity of ruthenium atoms; maximum and minimum residual electron densities were 2.04 and −2.12 e Å^{-3}.

The coordinates of 11 of the metal atoms in compound **2** forming a capped octahedron were obtained from a Patterson synthesis. The remaining non-hydrogen atoms were located from Fourier and subsequent Fourier-difference syntheses.[20] Hydrogen atoms were placed in idealised positions on the phenyl rings and allowed to ride on the relevant carbon atoms.

Refinement was by full-matrix least squares based on *F*. In the final cycles of refinement all non-hydrogen atoms were given anisotropic thermal parameters and refinement converged at $R = 0.0655$, $R' = 0.1074$ for 610 parameters, with weights as for **1**. Other details as for **1** except maximum and minimum residual electron densities 1.12 and -1.12 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/157.

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