Hydrogen Activation by Arene Ruthenium Complexes in Aqueous Solution. Part 2.[1] Build-up of Cationic Tri- and Tetra-nuclear Ruthenium Clusters with Hydrido Ligands†

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The low-pressure hydrogenation of the hydrolysis mixture of $[Ru_2(\eta^6\text{-}C_6H_6)_2Cl_4]$ in water (1.5 atm, 20 °C) led, in the presence of $NaClO_4$, to the oxo-capped trinuclear cluster cation $[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]^+$ **1** which crystallized as the perchlorate salt. The chloro-capped trinuclear cluster cation $[Ru_3(\eta^6\text{-}C_6H_2Me\text{-}1,2,4,6)_3(\mu_3\text{-}Cl)H_3]^{2+}$ **2**, crystallized as the dichloride, was accessible from the durene derivative $[Ru_2(\eta^6\text{-}C_6H_2Me\text{-}1,2,4,6)_2Cl_4]$ by high-pressure hydrogenation (60 atm, 55 °C) in water. In hot aqueous solution, the chloro-capped cluster **2** underwent hydrolysis to give the oxo-capped cluster $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]^+$ **3**. In the presence of $NaBF_4$, the low-pressure hydrogenation (1.5 atm, 20 °C) of the hydrolysis mixture of $[Ru_2(\eta^6\text{-}C_6H_6)_2Cl_4]$ led to the tetranuclear tetrahydrido cluster cation $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]^{2+}$ **4** which precipitated as the tetrafluoroborate salt. Under high-pressure conditions (60 atm, 55 °C) and in the absence of an additional salt, the hexahydrido cluster cation $[Ru_4(\eta^6\text{-}C_6H_6)_4H_6]^{2+}$ **5** was formed and obtained as the dichloride. By analogy, the *p*-cymene derivative $[Ru_2(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2Cl_4]$ gave $[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_6]^{2+}$ **6**. In contact with air, the hexahydrido clusters **5** and **6** were transformed into the corresponding tetrahydrido clusters $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]^{2+}$ **4** and $[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_4]^{2+}$ **7**. The hexahydrido cluster **5** is capable of hydrogenating fumaric acid to give succinic acid and **4**; the latter adds molecular hydrogen to regenerate the hexahydrido species **5**. The crystal and molecular structures of the cluster salts $[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]ClO_4$ (cation **1**), $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]BF_4$ (cation **3**), $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]Cl_2$ (cation **4**) and $[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_6][ClO_4]_2$ (cation **6**) have also been determined.

Arene ruthenium complexes have been the subject of intense research over the past twenty years because of their unique structures and properties and also their inherent catalytic potential.[2] Some of these complexes are reactive towards molecular hydrogen and hydrogen-transferring substrates; consequently, a considerable number of arene ruthenium complexes containing hydride ligands have been synthesized.[2,3]

A new method to synthesize arene ruthenium clusters containing bridging hydride ligands was found recently.[1] It is based on the use of the mononuclear aqua benzene ruthenium complexes $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_{3-x}Cl_x]^{(2-x)+}$ ($x = 0 - 2$), formed by hydrolysis of bis(benzene)tetrachlorodiruthenium(II).[4] These species contain both hard (water) and soft (arene) ligands at the same metal centre, thus representing a combination of classical Werner-type complexes and organometallic complexes.

In dichloromethane as solvent, bis(arene)tetrachlorodiruthenium complexes react with molecular hydrogen to give neutral binuclear complexes of the type $[Ru_2(\eta^6\text{-}C_6R_6)_2Cl_2(\mu\text{-}Cl)(\mu\text{-}H)]$. They can be converted into the cations $[Ru_2(\eta^6\text{-}C_6R_6)_2(\mu\text{-}Cl)_2(\mu\text{-}H)]^+$ by subsequent treatment with an aqueous solution of NH_4PF_6.[5] The use of water, being a far more polar solvent than dichloromethane, should favour the formation of ionic species already in the reaction with molecular hydrogen. This approach was indeed successful and resulted in the formation of cationic arene hydrido species.[1]

The tetranuclear benzene ruthenium dication thus obtained crystallized as the dichloride pentahydrate. The crystal structure analysis indicated the presence of four hydride ligands and induced us to consider it to be the $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]^{2+}$ cation,[1] in analogy to the known cations $[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_4]^{2+}$ [6] and $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$.[7,8] Recently, a reinvestigation and repeated measurements of the integrals in the ^1H NMR spectrum indicated that we had incorrectly determined the number of the hydride ligands. The correct assignment to the 60-electron *hexahydrido* species $[Ru_4(\eta^6\text{-}C_6H_6)_4H_6]^{2+}$ is now confirmed by the isolation and crystal structure analysis of the *p*-cymene derivative $[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_6][ClO_4]_2$ in which all six hydride ligands could be located. We also report the synthesis and molecular structure of the true *tetrahydrido* cluster cation $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]^{2+}$.

Results and Discussion

Synthesis and Characterisation of Trinuclear Arene Ruthenium Clusters.—The low-pressure reaction of the hydrolysis mixture of bis(benzene)tetrachlorodiruthenium(II) with hydrogen (1.5 atm) at room temperature leads to the formation of an inseparable mixture of several hydride complexes. However, the reaction can be directed with a remarkable selectivity towards the synthesis of individual hydride complexes by adding salts like NH_4PF_6, $NaBF_4$ or $NaClO_4$ to the hydrolysis mixture. The use of sodium perchlorate, for instance, results in the formation of the cluster salt $[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]ClO_4$ (cation **1**, *cf.* Scheme 1). In this reaction, molecular hydrogen is cleaved heterolytically, resulting in a large decrease of the pH of the reaction mixture.

The ^1H NMR spectrum of **1** indicates the presence of two different benzene ligands in a 2:1 ratio as well as a singlet signal in the hydride region of the spectrum (Table 1). The perchlorate salt of **1** behaves like a 1:1 electrolyte in polar organic solvents. The λ_M value of 131 Ω^{-1} cm^2 mol^{-1} found for a 10^{-3} mol dm^{-3} solution in acetonitrile and the concentration dependency of λ_M fit very well with the average values given in refs. 9 and 10.

The crystal structure analysis of the perchlorate, Fig. 1,[11]

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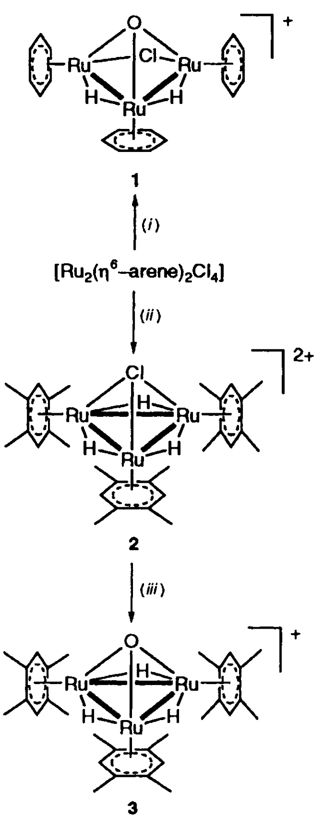
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: 1 atm = 101 325 Pa.



Scheme 1 Build-up of trinuclear arene ruthenium clusters by hydrogenation of $[Ru_2(\eta^6\text{-arene})_2Cl_4]$ in water. (*i*) 1.5 atm H_2, 20 °C, H_2O, $NaClO_4$; (*ii*) 60 atm H_2, 55 °C, H_2O, NaCl; (*iii*) $NaBF_4$, H_2O, $-2H^+$, $-Cl^-$

shows the atomic arrangement of the cation **1**. Two hydrido-bridged Ru–Ru bonds form two edges of a metal triangle. The open edge is bridged by a chloride ligand and an oxygen atom occupies a μ_3 position. The Ru–O distances are slightly longer than those in the related complex $[Ru\{\mu_3\text{-}C_5Me_3(CH_2)_2\}(\mu_3\text{-}O)(\mu\text{-}H)(\eta^5\text{-}C_5Me_5)_2(SO_4)]$[12] [2.04 *versus* 1.98 Å (mean values), *cf.* Table 2].

Another trinuclear arene ruthenium cluster which is closely related structurally to cation **1** is formed by the high-pressure hydrogenation of the hydrolysis mixture of the durene derivative $[Ru_2(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_2Cl_4]$ in water (60 atm,

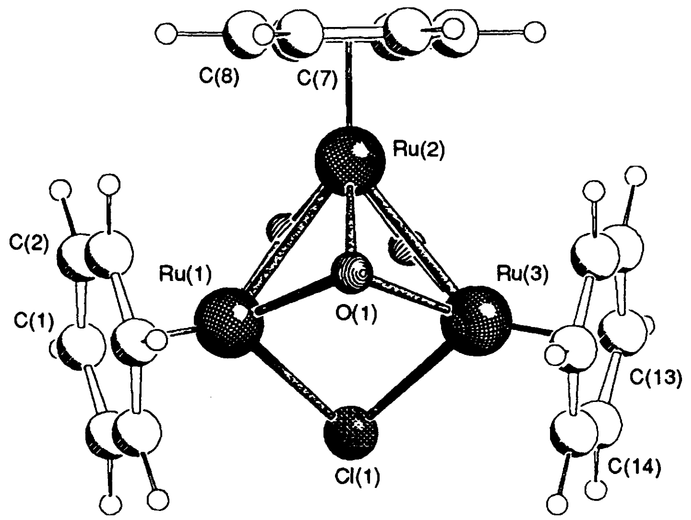


Fig. 1 SCHAKAL[11] plot of the cluster cation $[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]^+$ **1**

Table 1 Proton NMR spectra of the arene ruthenium hydrido complexes[a]

		δ[b]		
Salt	Cation	Arene	Hydride	Others
$[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]ClO_4$[c]	**1**	5.91 (s, 6 H), 5.50 (s, 12 H)	−13.35 (s)	
$[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}Cl)H_3]Cl_2$	**2**	6.39 (s)	−16.57 (s)	2.27 (s, $C_6H_2Me_4$)
$[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]BF_4$	**3**	5.63 (s)	−19.25 (s)	2.19 (s, $C_6H_2Me_4$)
$[Ru_4(\eta^6\text{-}C_6H_6)_4H_4][BF_4]_2$[c]	**4**	5.83 (s)	−17.66 (s)	
$[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]Cl_2$	**4**	6.02 (s)	−17.38 (s)	
$[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_4]Cl_2$	**7**	6.34 (d, *J* 6), 6.24 (d, *J* 6)	−18.57 (s)	2.20 (spt, C*H*Me₂), 1.88 (s, C_6H_4Me), 1.34 [d, *J* 7, C*H*(CH₃)₂]
$[Ru_4(\eta^6\text{-}C_6H_6)_4H_6]Cl_2$	**5**	6.04 (s)	−15.05 (s)	
$[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_6]Cl_2$	**6**	6.01 (d, *J* 6), 5.96 (d, *J* 6)	−15.83 (s)	2.56 (spt, C*H*Me₂), 2.23 (s, C_6H_4Me), 1.30 [d, *J* 7, C*H*(CH₃)₂]

[a] Solvent D_2O (standard sodium 3-trimethylsilylpropionate). [b] *J* values in Hz. [c] Solvent $[^2H_3]$acetonitrile.

Table 2 Selected bond lengths (Å) and angles (°) for $[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]^+$ **1**

Ru(1)–Ru(2)	2.755(1)	Ru(1)–C(av.)	2.182(3)
Ru(1)···Ru(3)	3.331(1)	Ru(2)–C(av.)	2.204(3)
Ru(2)–Ru(3)	2.744(1)	Ru(3)–C(av.)	2.184(3)
Ru(1)–O(1)	2.040(4)	Ru(1)–H(1Ru)	1.82(7)
Ru(2)–O(1)	2.021(4)	Ru(2)–H(1Ru)	1.47(7)
Ru(3)–O(1)	2.049(4)	Ru(2)–H(2Ru)	1.64(10)
Ru(1)–Cl(1)	2.433(2)	Ru(3)–H(2Ru)	1.83(11)
Ru(3)–Cl(1)	2.437(2)		
Ru(1)–Ru(2)–Ru(3)	74.57(2)	Ru(1)–Cl(1)–Ru(3)	86.31(6)
Ru(1)–O(1)–Ru(2)	85.41(16)	Ru(1)–H(1Ru)–Ru(2)	113(4)
Ru(1)–O(1)–Ru(3)	109.1(2)	Ru(2)–H(2Ru)–Ru(3)	104(5)
Ru(2)–O(1)–Ru(3)	84.79(16)		

55 °C, Scheme 1). The reaction leads to $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}Cl)H_3]^{2+}$ **2** which crystallizes as the dichloride directly from the reaction mixture. The ^1H NMR spectrum of **2** shows a hydride signal at δ −16.57 which is replaced by a signal at δ −19.25 upon treatment with tetrafluoroborate in D_2O for several hours (Scheme 1). The resulting cation **3** represents the trinuclear cluster $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]^+$, as shown by the crystal structure analysis of the tetrafluoroborate salt. The ^1H NMR spectrum of **2** displays the same signal pattern (three singlets for aromatic protons, methyl protons and hydride ligands) and the same arene to hydride ratio of 1 : 1 as for **3**. The μ_3-chloro ligand in **2** binds only weakly to the three metal atoms and undergoes slow hydrolysis in aqueous solution, in accordance with the significant decrease of the pH (Scheme 1). Until now, such an exchange was known only for μ-chloride ligands exchanging in water for μ-hydroxide ligands.[13]

The clusters **2** and **3** differ remarkably in their stability towards organic solvents. In polar solvents, such as methanol or acetonitrile, the cluster cation **2** decomposes immediately to give a mixture of unidentified hydride-containing species, whereas the cluster cation **3** is stable.

The cluster cation $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]^+$ **3** crystallizes from water as the tetrafluoroborate salt in the form of orange-red platelets. The molecular structure of **3** is shown in Fig. 2. Selected bond angles and distances are given in Table 3. The three $Ru(\eta^6\text{-}C_6H_2Me_4)$ moieties in **3** form an almost perfect equilateral triangular metal framework capped by a μ_3-oxo ligand. The μ_3-O cap is disordered, occupying two equivalent positions above and below the Ru_3 plane, with occupancy factors of 0.4 and 0.6. The three hydrido ligands could not be located in the structure. Their ^1H NMR resonance (δ −19.25) falls within the typical range of μ-hydrides and they are therefore assumed to bridge the three metal–metal bonds.

The cluster cation **3** represents the analogue of the trirhodium oxo cluster $[Rh_3(\eta^5\text{-}C_5Me_5)_3(O)H_3]^+$ described by Maitlis and co-workers.[14] A similar μ_3-capped triruthenium structure is also found in the μ_3-Cl capped analogue **2** and in the sulfur-capped clusters $[Ru_3(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_3S_2]^{2+}$ and $[Ru_3(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_3S_2]$.[15]

Synthesis and Characterisation of Tetranuclear Arene Ruthenium Clusters.—The replacement of the precipitant $NaClO_4$ by $NaBF_4$, in the low-pressure hydrogenation of the hydrolysis mixture of $[Ru_2(\eta^6\text{-}C_6H_6)_2Cl_4]$, leads to the formation of the tetranuclear cluster cation $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]^{2+}$ **4**. This is the unsubstituted parent molecule of the known[6] *p*-cymene derivative $[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_4]^{2+}$. As in the formation of the trinuclear arene ruthenium clusters, a heterolytic hydrogen cleavage takes place even in the absence of any auxiliary base (Scheme 2). Therefore, the pH of the reaction mixture decreases to values of between 1 and 2 during the hydrogenation. Proton NMR measurements confirmed the equivalence of all η^6-bound benzene ligands present in the cation as well as the equivalence of the hydride ligands for the dissociated cluster salt (Table 1).

Whereas the tetrafluoroborate salt of cation **4** did not crystallize well, single crystals of the brown-black chloride salt $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]Cl_2$, suitable for a crystal structure analysis, could be obtained from a concentrated aqueous solution. The molecular structure of **4** is shown in Fig. 3. Important bond angles and distances are given in Table 4. The cluster cation $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]^{2+}$ contains a perfectly symmetrical Ru_4 core with six, almost identical, Ru–Ru distances. The four $\eta^6\text{-}C_6H_6$ ligands are co-ordinated to the four ruthenium atoms, the metal–carbon distances varying from 2.15(3) to 2.23(2) Å [mean value 2.18(1) Å]. Only one of the four hydride ligands is bonded as a symmetrical μ_3 cap above the

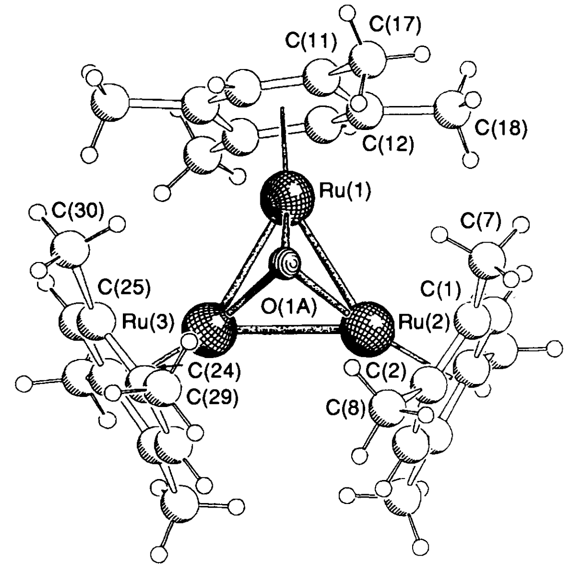


Fig. 2 SCHAKAL[11] plot of the cluster cation $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]^+$ **3**. The hydride ligands were not located

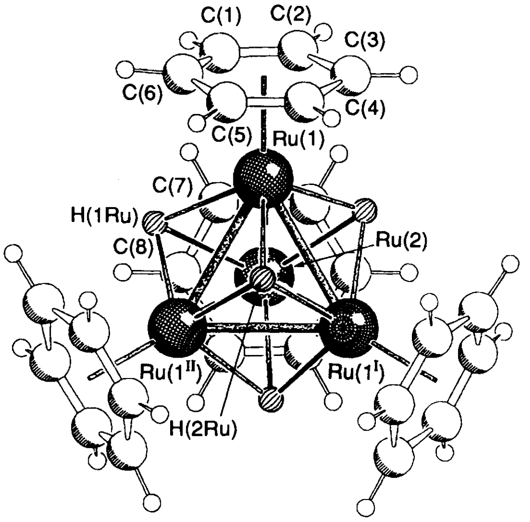
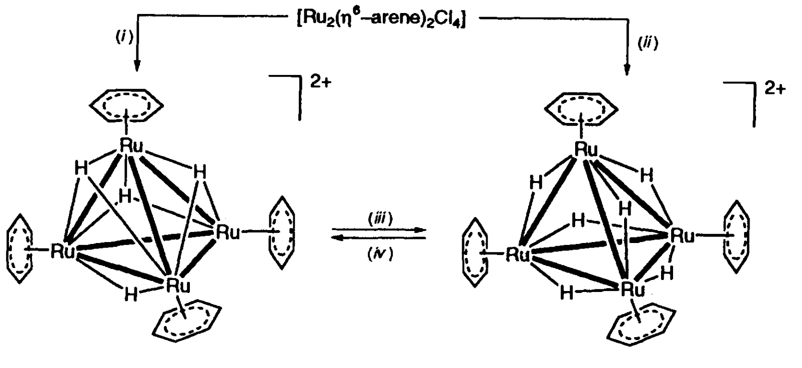


Fig. 3 SCHAKAL[11] plot of the cluster dication $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]^{2+}$ **4**

Table 3 Selected bond lengths (Å) and angles (°) for $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]^+$ **3**

Ru(1)–Ru(2)	2.788(3)	Ru(1)–O(1B)	2.03(3)
Ru(1)–Ru(3)	2.761(1)	Ru(2)–O(1A)	1.99(2)
Ru(2)–Ru(3)	2.782(3)	Ru(2)–O(1B)	2.02(4)
Ru–C(av.)	2.22(1)	Ru(3)–O(1A)	1.92(3)
Ru(1)–O(1A)	2.01(3)	Ru(3)–O(1B)	1.97(3)
Ru(1)–Ru(2)–Ru(3)	59.41(3)	Ru(2)–O(1B)–Ru(1)	87(2)
Ru(1)–Ru(3)–Ru(2)	60.40(11)	Ru(3)–O(1A)–Ru(1)	89.2(11)
Ru(2)–Ru(1)–Ru(3)	60.19(12)	Ru(3)–O(1B)–Ru(1)	87.4(11)
Ru(2)–O(1A)–Ru(1)	88.5(9)		



4 arene = C_6H_6
7 arene = $C_6H_4MePr^i$-*p*

5 arene = C_6H_6
6 arene = $C_6H_4MePr^i$-*p*

Scheme 2 Build-up of tetranuclear arene ruthenium clusters by hydrogenation of [Ru$_2$(η^6-arene)$_2$Cl$_4$] in water. (*i*) 1.5 atm H_2, 20 °C, NaBF$_4$, H_2O; (*ii*) 60 atm H_2, 55 °C, H_2O; (*iii*) 60 atm H_2, 55 °C; (*iv*) +0.5 O_2, $-H_2O$

Table 4 Selected bond lengths (Å) and angles (°) for [Ru$_4$(η^6-C$_6$H$_6$)$_4$H$_4$]$^{2+}$ **4**

Ru(1)–Ru(1$^{\rm I}$)	2.729(2)	Ru(1$^{\rm I}$)–Ru(1)–Ru(2)	60.02(2)
Ru(1)–Ru(2)	2.730(2)	Ru(1)–H(1Ru)–Ru(1$^{\rm II}$)	89(6)
Ru(1)–H(1Ru)	2.02(15)	Ru(1)–H(1Ru)–Ru(1$^{\rm I}$)	89(3)
Ru(1)–H(1Ru$^{\rm I}$)	1.83(17)	Ru(1)–H(1Ru)–Ru(2)	75(3)
Ru(1)–H(2Ru)	2.20	Ru(1)–H(2Ru)–Ru(1$^{\rm I}$)	77(3)
Ru–C(av.)	2.18(1)	Ru(1)–H(2Ru)–Ru(1$^{\rm II}$)	77(3)

Symmetry transformations used to generate equivalent atoms: I $-y + 1, x - y + 1, z$; II $-x + y, -x + 1, z$.

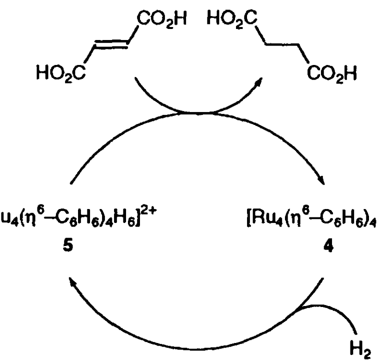
Ru(1)–Ru(1$^{\rm I}$)–Ru(1$^{\rm II}$) triangle, opposite to Ru(2) on the C_3 axis of the molecule. The other three hydrides can be considered as being in between μ- and μ$_3$-ligands.

The reaction of the hydrolysis mixture of [Ru$_2$(η^6-C$_6$H$_6$)$_2$Cl$_4$] with molecular hydrogen under forcing conditions (60 atm, 55 °C) and in the absence of any additional salt leads to the formation of the tetranuclear *hexahydrido* cluster [Ru$_4$(η^6-C$_6$H$_6$)$_4$H$_6$]$^{2+}$ **5** which crystallizes as the dichloride directly from the reaction mixture (Scheme 2). Just as for cation **4**, the ^{1}H NMR spectrum of **5** (Table 1) confirms the equivalence of all of the co-ordinated benzene rings and reveals a fluxional behaviour for the hydride ligands.

Cation **5** reacts readily with traces of oxygen to give the tetrahydrido cation [Ru$_4$(η^6-C$_6$H$_6$)$_4$H$_4$]$^{2+}$ **4**. Considering the stability of solid salts of **5** under high vacuum and of its solutions under reduced pressure, we presume that the transformation **5** $\longrightarrow$ **4** involves the formation of water instead of molecular hydrogen (Scheme 2). Nevertheless, this conversion corresponds to a reductive elimination of hydrogen. The ruthenium atoms of cation **5** undergo a change in their oxidation state from +2 to +1.5. The counterpart of the reductive elimination, the oxidative addition of hydrogen to give **4** (Scheme 2), takes place under high-pressure conditions (55 °C, 60 atm H_2).

The two labile hydrido ligands of the cluster cation **5** can be transferred not only onto oxygen, but also onto alkenes. By adding the dichloride of **5** to a D_2O solution of fumaric acid at 50 °C, the formation of succinic acid can easily be followed by ^{1}H NMR spectroscopy. This observation leads to a catalytic cycle for the hydrogenation of fumaric acid with **5** in water (Scheme 3). By choosing the reaction conditions necessary for the oxidative addition of hydrogen to **4**, the hydrogen-transferring cluster **5** can be regenerated constantly.

Whereas some examples of reversible hydrogen addition to metal clusters have been published,[16] the two cations [Ru$_4$(η^6-C$_6$H$_6$)$_4$H$_6$]$^{2+}$ **5** and [Ru$_4$(η^6-C$_6$H$_6$)$_4$H$_4$]$^{2+}$ **4** represent, to the best of our knowledge, the first fully characterised pair of hydrogen-transferring clusters. In all the catalytic cycles of olefin hydrogenation involving clusters and established mechanistically so far, only the hydrogen-donating cluster or certain other substrate–catalyst complexes have been isolated and structurally characterised.[17]



Scheme 3 Proposed cycle for the hydrogenation of fumaric acid in water catalysed by [Ru$_4$(η^6-C$_6$H$_6$)$_4$H$_6$]$^{2+}$ **5** (55 atm H_2, 50 °C, catalyst turnover rate 38 h^{-1})

Our attempt to extend the present results of the alkyl derivatives of the parent compound [Ru$_2$(η^6-C$_6$H$_6$)$_2$Cl$_4$] caused severe sterical problems. Clusters of type **4** and **5** are compact bodies, in which the aromatic protons of neighbouring rings come quite close together. Only with a 1,4-disubstituted benzene ligand is the build-up of the hexahydrido cluster [Ru$_4$(η^6-C$_6$H$_4$MePr^i-*p*)$_4$H$_6$]$^{2+}$ **6** still possible. However, the resulting structure is so dense that the arene ligands form an almost perfectly protecting shield against attacking molecules. The reaction with aerial oxygen, for instance, to form the corresponding tetrahydrido cluster [Ru$_4$(η^6-C$_6$H$_4$MePr^i-*p*)$_4$-H$_4$]$^{2+}$ **7**,[6] takes five times longer than if the unsubstituted cluster **5** is used.

In order to verify our hypothesis concerning the molecular structure of cations **5** and **6** as tetrahedral hexahydrido clusters, a crystal structure analysis of the perchlorate salt of [Ru$_4$(η^6-C$_6$H$_4$MePr^i-*p*)$_4$H$_6$]$^{2+}$ **6** was undertaken. The molecular structure of cation **6** is depicted in Fig. 4. Important bond lengths and angles are presented in Table 5. The Ru_4 framework in cation **6** shows a slightly distorted tetrahedral arrangement with Ru–Ru bond lengths varying between 2.807(2) and 2.881(2) Å. The aromatic rings of the four *p*-cymene ligands co-ordinate in the usual η^6 fashion to the respective ruthenium atoms and are planar within the experimental error. The α-carbon atoms of the alkyl substituents are displaced by 0.06 Å (CH_3) and 0.09 Å [$\mathit{C}H(CH_3)_2$], respectively, from the plane of the aromatic ring and away from the ruthenium atom. All six hydride ligands could be located and refined. Half of them occupy μ_3-capping positions above three of the four tetrahedron faces. The three metal–metal bonds of the non-capped tetrahedron face are μ-bridged by the remaining three hydride ligands. In solution, however, the hydrido ligands are equivalent, resulting in a single signal in the hydride region of the ^1H NMR spectrum. Nevertheless, NMR measurements using long delays between the individual pulses (> 5 s) confirmed the number of hydride ligands found in the crystal structure analysis of **6**.

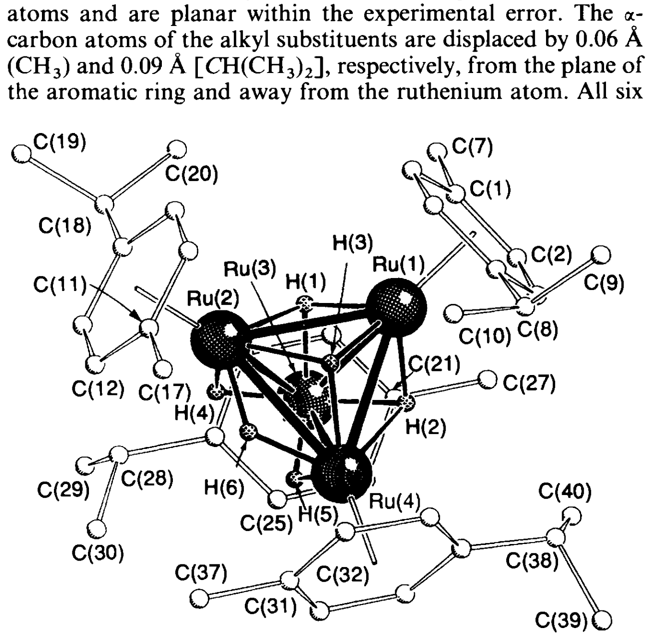


Fig. 4 SCHAKAL[11] plot of the cluster dication $[Ru_4(\eta^6-C_6H_4MePr^i-p)_4H_6]^{2+}$ **6**. The alkyl and aromatic protons have been omitted for clarity

Table 5 Selected bond lengths (Å) and angles (°) for $[Ru_4(\eta^6-C_6H_4MePr^i-p)_4H_6]^{2+}$ **6**

Ru(1)–Ru(2)	2.807(2)	H(2)–Ru(3)	1.98(5)
Ru(1)–Ru(3)	2.836(2)	H(2)–Ru(4)	1.99(5)
Ru(1)–Ru(4)	2.845(2)	H(3)–Ru(1)	1.80(6)
Ru(2)–Ru(4)	2.858(2)	H(3)–Ru(2)	1.91(6)
Ru(2)–Ru(3)	2.881(2)	H(3)–Ru(4)	1.90(6)
Ru(3)–Ru(4)	2.848(1)	H(4)–Ru(2)	1.74(6)
Ru–C(av.)	2.225(1)	H(4)–Ru(3)	1.68(6)
H(1)–Ru(1)	1.64(5)	H(5)–Ru(3)	1.73(8)
H(1)–Ru(2)	1.91(5)	H(5)–Ru(4)	1.60(8)
H(1)–Ru(3)	1.90(5)	H(6)–Ru(2)	1.64(7)
H(2)–Ru(1)	1.69(5)	H(6)–Ru(4)	1.55(7)
Ru(1)–Ru(2)–Ru(3)	59.79(4)	Ru(1)–H(2)–Ru(4)	101(2)
Ru(2)–Ru(1)–Ru(3)	61.40(5)	Ru(3)–H(2)–Ru(4)	92(2)
Ru(3)–Ru(1)–Ru(4)	60.19(3)	Ru(1)–H(3)–Ru(2)	99(2)
Ru(4)–Ru(2)–Ru(3)	59.51(3)	Ru(1)–H(3)–Ru(4)	101(2)
Ru(1)–H(1)–Ru(2)	104(2)	Ru(2)–H(3)–Ru(4)	97(2)
Ru(1)–H(1)–Ru(3)	106(2)	Ru(2)–H(4)–Ru(3)	115(2)
Ru(2)–H(1)–Ru(3)	98(2)	Ru(3)–H(5)–Ru(4)	118(3)
Ru(1)–H(2)–Ru(3)	101(2)	Ru(2)–H(6)–Ru(4)	128(3)

Experimental

All manipulations, except the hydrogenation experiments, were carried out under a dinitrogen atmosphere, using standard Schlenk techniques. The bidistilled water and all other solvents were degassed and saturated with N_2 prior to use. The NMR spectra were recorded on a Varian Gemini 200 BB instrument. Conductivity measurements were carried out using a Philips PW 9505 conductivity meter. Microanalytical data (Table 6) were obtained by the Mikroelementaranalytisches Laboratorium ETH, Zürich and by Butterworth Laboratories Ltd., Teddington (for the perchlorate salt of **1**).

The starting complexes $[Ru_2(\eta^6-C_6H_6)_2Cl_4]$,[18] $[Ru_2(\eta^6-C_6H_4MePr^i-p)_2Cl_4]$[19] and $[Ru_2(\eta^6-C_6H_2Me_4-1,2,4,6)_2Cl_4]$[19] were synthesized according to the literature procedures. All other reagents were commercially available and were used without further purification.

Syntheses.—$[Ru_3(\eta^6-C_6H_6)_3(\mu-Cl)(\mu_3-O)(\mu-H)_2]ClO_4$ (*cation* **1**). A mixture of $[Ru_2(\eta^6-C_6H_6)_2Cl_4]$ (200 mg, 0.4 mmol) and $NaClO_4$ (400 mg) in water (25 cm^3) was placed in a pressure Schlenk tube and stirred under an H_2 pressure of 1.5 atm at room temperature (r.t.). After 120 h the orange precipitate formed was filtered off and dried. It was extracted first with methanol (5 cm^3) to eliminate an unidentified yellow impurity. The subsequent extraction with acetonitrile (2 × 10 cm^3) and evaporation of the resulting orange solution yielded the pure product (90 mg, 49%).

$[Ru_3(\eta^6-C_6H_2Me_4-1,2,4,6)_3(\mu_3-Cl)H_3]Cl_2$ (*cation* **2**). A suspension of $[Ru_2(\eta^6-C_6H_2Me_4-1,2,4,6)_2Cl_4]$ (150 mg, 0.245 mmol) in H_2O (30 cm^3) containing NaCl (200 mg) was hydrogenated in a stainless-steel autoclave at 55 °C under a pressure of 60 atm. After 18 h the autoclave was cooled, the pressure released and the brown solution was filtered. Evaporation of most of the solvent under reduced pressure gave the dichloride of **2** as black-brown crystals (53 mg, 40%).

$[Ru_3(\eta^6-C_6H_2Me_4-1,2,4,6)_3(\mu_3-O)H_3]BF_4$ (*cation* **3**). To the brown solution obtained after the hydrogenation of $[Ru_2(\eta^6-C_6H_2Me_4-1,2,4,6)_2Cl_4]$ was added an excess of $NaBF_4$ (200 mg) and the resulting brown precipitate recrystallized in hot water (70 °C). The colour of the solution changed to orange-brown, and the tetrafluoroborate of **3** crystallized as thin orange-red plates (50 mg, 38%).

Table 6 Analytical data for the arene ruthenium hydrido complexes

			Analysis* (%)	
Salt	Cation	*M*	C	H
$[Ru_3(\eta^6-C_6H_6)_3(\mu-Cl)(\mu_3-O)(\mu-H)_2]ClO_4$	1	690.47	30.85 (31.30)	2.85 (2.90)
$[Ru_3(\eta^6-C_6H_2Me_4-1,2,4,6)_3(\mu_3-Cl)H_3]Cl_2$	2	815.26	43.95 (44.20)	5.45 (5.55)
$[Ru_3(\eta^6-C_6H_2Me_4-1,2,4,6)_3(\mu_3-O)H_3]BF_4$	3	811.69	44.30 (44.40)	5.60 (5.60)
$[Ru_4(\eta^6-C_6H_6)_4H_4][BF_4]_2$	4	894.37	31.95 (32.25)	3.20 (3.15)
$[Ru_4(\eta^6-C_6H_6)_4H_4]Cl_2$	4	791.67	36.60 (36.40)	3.60 (3.55)
$[Ru_4(\eta^6-C_6H_4MePr^i-p)_4H_4]Cl_2$	7	1016.10	47.35 (47.30)	6.10 (5.95)
$[Ru_4(\eta^6-C_6H_6)_4H_6]Cl_2$	5	793.69	35.95 (36.30)	3.90 (3.80)
$[Ru_4(\eta^6-C_6H_4MePr^i-p)_4H_6][PF_6]_2$	6	1237.14	38.95 (38.85)	4.80 (5.05)

* Required values are given in parentheses.

Table 7 Crystallographic and selected experimental data *

Compound	$[Ru_3(\eta^6-C_6H_6)_3(\mu-Cl)(\mu_3-O)(\mu-H)_2]-ClO_4\cdot 2H_2O$ (cation **1**)	$[Ru_3(\eta^6-C_6H_2Me_4-1,2,4,6)_3(\mu_3-O)H_3]-BF_4\cdot 2H_2O$ (cation **3**)	$[Ru_4(\eta^6-C_6H_6)_4H_4]Cl_2$ (cation **4**)	$[Ru_4(\eta^6-C_6H_4MePr^i-p)_4H_6]-[ClO_4]_2\cdot 2CH_2Cl_2$ (cation **6**)
Formula	$C_{18}H_{24}Cl_2O_7Ru_3$	$C_{30}H_{49}BF_4O_3Ru_3$	$C_{24}H_{28}Cl_2Ru_4$	$C_{42}H_{66}Cl_6O_8Ru_4$
Crystal shape	Platelets	Plate	Trigonal block	Rectangular blocks
Crystal colour	Red-orange	Orange-red	Brown-black	Dark red-violet
Crystal system	Monoclinic	Monoclinic	Trigonal	Triclinic
M	726.50	847.73	791.67	1315.98
Space group	$P2_1/c$	Pn	$P31c$	$P\bar{1}$
a/Å	10.480(1)	10.990(1)	10.375(1)	11.829(6)
b/Å	8.760(1)	9.950(3)	10.375(1)	11.967(5)
c/Å	24.736(2)	15.008(1)	17.020(2)	18.326(10)
α/°	90	90	90	82.68(5)
β/°	94.09(1)	91.53(1)	90	84.19(4)
γ/°	90	90	120	73.51(2)
U/Å^3	2265.1(4)	1640.5(5)	1586.6(3)	2461(2)
Z	4	2	2	2
D_c/g cm^{-3}	2.11	1.702	1.657	1.776
$F(000)$	1384	838	764	1320
Crystal size/mm	0.38 × 0.15 × 0.08	0.30 × 0.27 × 0.10	0.57 × 0.42 × 0.34	0.57 × 0.30 × 0.27
μ(Mo-Kα)/mm^{-1}	2.21	1.414	2.043	1.577
Scan range/°	$3 < 2\theta < 50$	$4 < 2\theta < 55$	$4 < 2\theta < 50$	$4 < 2\theta < 50$
h, k, l	±12, +10, +29	±14, +12, +19	±10, +12, +20	±14, ±14, ±21
T/K	293(2)	153(2)	293(2)	183(2)
Intensity variation (%)	< 1	< 1	< 5	< 1
Reflections observed	3990	2773	730	7367
N_r	3068	3658	942	8309
N_p	279	379	115	613
R_{int}			0.1402	0.0306
Final R indices [$I > 2\sigma(I)$]	$R = 0.040$, $R' = 0.054$	$R_1 = 0.0532$, $wR_2 = 0.1205$	$R_1 = 0.0560$, $wR_2 = 0.1528$	$R_1 = 0.0350$, $wR_2 = 0.0819$
R indices (all data)		$R_1 = 0.0826$, $wR_2 = 0.1425$	$R_1 = 0.0838$, $wR_2 = 0.1594$	$R_1 = 0.0438$, $wR_2 = 0.0886$
a (weighting coefficient)		0.0656	0.0994	0.0327
b (weighting coefficient)		4.6378	0.0000	5.9256
Goodness of fit	1.35	1.073	1.284	1.059
Maximum Δ/σ	0.001	−1.583	−0.002	−0.409
Maximum, minimum $\Delta\rho$/e Å^{-3}	0.980, −1.410	1.365, −1.251	1.026, −1.747	1.468, −1.019

* Conditions in common: Stoe-Siemens AED2 4-circle diffractometer; Mo-Kα graphite monochromated radiation, $\lambda = 0.710\,73$ Å; ω/θ scans; semi-empirical absorption correction from psi-scans made only for **6** ($T_{min} = 0.3292$, $T_{max} = 0.4253$); refinement method full-matrix least squares on F for **1**, on F^2 for **3**, **4** and **6**; structure solving program SHELXS 86;[20] structure refinement program NRCVAX[21] for **1**, SHELXL 93[22] for **3**, **4** and **6**. N_r number of reflections used, N_p number of refined parameters, $R = \Sigma(F_o - F_c)/\Sigma(F_o)$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma(wF_o^2)]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + 0.001(F_o^2)]$; goodness of fit $= [\Sigma w(F_o - F_c)^2/(N_r - N_p)]^{\frac{1}{2}}$ (for **1**); $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^4)]^{\frac{1}{2}}$, goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2]/(N_r - N_p)^{\frac{1}{2}}$ (for **3**, **4** and **6**).

Table 8 Atomic coordinates for $[Ru_3(\eta^6\text{-}C_6H_6)_3(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]ClO_4{\cdot}2H_2O$ (cation **1**)

Atom	*x*	*y*	*z*
Ru(1)	0.565 76(5)	0.075 13(6)	0.105 43(2)
Ru(2)	0.425 13(5)	0.255 97(6)	0.170 23(2)
Ru(3)	0.251 42(5)	0.062 91(6)	0.117 61(2)
O(1)	0.398 2(4)	0.192 1(5)	0.091 73(17)
Cl(1)	0.414 75(16)	−0.133 61(19)	0.112 61(7)
C(1)	0.761 0(7)	−0.003 8(13)	0.124 4(3)
C(2)	0.757 9(7)	0.152 8(13)	0.126 4(4)
C(3)	0.705 5(8)	0.238 1(11)	0.081 2(4)
C(4)	0.658 2(8)	0.160 3(12)	0.035 2(4)
C(5)	0.660 2(8)	0.002 2(13)	0.032 4(3)
C(6)	0.711 7(8)	−0.081 6(9)	0.077 6(4)
C(7)	0.481 2(11)	0.496 5(10)	0.163 3(4)
C(8)	0.565 7(9)	0.425 9(11)	0.202 1(5)
C(9)	0.520 9(11)	0.347 8(12)	0.245 1(4)
C(10)	0.393 1(11)	0.339 1(10)	0.252 2(4)
C(11)	0.303 9(9)	0.409 6(11)	0.215 7(5)
C(12)	0.345 3(11)	0.490 1(10)	0.170 7(4)
C(13)	0.078 6(8)	−0.018 1(14)	0.154 9(4)
C(14)	0.097 5(8)	−0.105 0(11)	0.108 6(4)
C(15)	0.108 4(7)	−0.032 1(13)	0.057 3(3)
C(16)	0.104 3(7)	0.125 3(13)	0.054 2(4)
C(17)	0.089 2(8)	0.213 1(12)	0.100 1(5)
C(18)	0.077 3(8)	0.141 9(13)	0.149 8(4)
H(1Ru)	0.514(6)	0.126(8)	0.172(3)
H(2Ru)	0.359(10)	0.088(11)	0.178(4)
Cl(2)	0.916 66(21)	0.569 19(22)	0.178 31(9)
O(2)	0.897 6(8)	0.431 6(8)	0.207 0(3)
O(3)	0.917 2(13)	0.696 5(10)	0.208 9(4)
O(4)	1.020 8(10)	0.558 5(10)	0.147 1(5)
O(5)	0.807 8(10)	0.587 9(13)	0.139 7(5)
O(1W)	0.382 5(8)	0.423 8(9)	0.015 1(3)
O(2W)	0.115 7(9)	0.461 4(15)	0.979 4(4)

$[Ru_4(\eta^6\text{-}C_6H_6)_4H_4][BF_4]_2$ (*cation* **4**). A mixture of $[Ru_2(\eta^6\text{-}C_6H_6)_2Cl_4]$ (150 mg, 0.3 mmol) and $NaBF_4$ (200 mg) in water (20 cm^3) was placed in a pressure Schlenk tube and stirred under an H_2 pressure of 1.5 atm at r.t. After 120 h the brown precipitate formed was filtered off and dried. The subsequent extraction with acetonitrile (2 × 10 cm^3) and evaporation of the resulting brown solution yielded the pure product (72 mg, 54%).

$[Ru_4(\eta^6\text{-}C_6H_6)_4H_6]Cl_2$ (*cation* **5**). A suspension of $[Ru_2(\eta^6\text{-}C_6H_6)_2Cl_4]$ (150 mg, 0.30 mmol) in H_2O (20 cm^3) was hydrogenated in a stainless-steel autoclave at 55 °C under a pressure of 60 atm. After 14 h the autoclave was cooled, the pressure released and the violet solution filtered. Evaporation of most of the H_2O under reduced pressure, followed by crystallisation at 2 °C, gave the dichloride of **5** as dark violet crystals (81 mg, 65%).

$[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]Cl_2$ (*cation* **4**). The filtered violet reaction mixture obtained after the hydrogenation step in the synthesis of **5** was evaporated to dryness, dissolved in methanol (10 cm^3) and stirred under air for 1 d. Evaporation of most of the solvent under reduced pressure, followed by crystallisation at 2 °C gave the dichloride of **4** as black-brown crystals (65 mg, 55%).

$[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_6][PF_6]_2$ (*cation* **6**). A suspension of $[Ru_2(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2Cl_4]$ (150 mg, 0.245 mmol) in H_2O (30 cm^3) was hydrogenated in a stainless-steel autoclave at 55 °C under a pressure of 60 atm. After 36 h the autoclave was cooled, the pressure released and the violet solution was filtered. Treatment of the solution with NH_4PF_6 (50 mg) dissolved in H_2O (2 cm^3) gave the bis(hexafluorophosphate) of **6** as a dark violet powder which was filtered off, washed with water and dried under vacuum (129 mg, 85%).

$[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_4]Cl_2$ (*cation* **7**). The filtered violet reaction mixture, obtained after the hydrogenation step in the synthesis of **6**, was stirred under air for 3 d. Evaporation of most of the solvent under reduced pressure, followed by crystallisation at 2 °C, gave the dichloride of **7** as black-brown crystals (37 mg, 30%). The yield was higher when the cation was precipitated as the bis(hexafluorophosphate) salt with NH_4PF_6 (50 mg) dissolved in H_2O (2 cm^3) (76 mg, 50%).

Table 9 Atomic coordinates (× 10^4) for $[Ru_3(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,6)_3(\mu_3\text{-}O)H_3]BF_4{\cdot}2\,H_2O$ (cation **3**)

Atom	*x*	*y*	*z*
Ru(1)	10 016(1)	8 543(3)	9 998(1)
Ru(2)	9 364(4)	6 107(1)	10 771(3)
Ru(3)	8 716(1)	8 535(3)	11 547(1)
O(1A)[a]	8 442(20)	7 741(29)	10 391(17)
O(1B)[b]	10 281(31)	7 731(28)	11 228(22)
C(1)	9 718(27)	8 922(30)	8 503(19)
C(2)	9 486(21)	10 064(29)	9 026(16)
C(3)	10 372(21)	10 614(33)	9 642(18)
C(4)	11 543(25)	10 010(23)	9 855(16)
C(5)	11 795(25)	8 770(37)	9 287(22)
C(6)	10 957(25)	8 333(24)	8 763(20)
C(7)	8 834(28)	8 237(36)	7 968(18)
C(8)	8 271(23)	10 843(27)	8 997(17)
C(9)	12 413(31)	10 658(36)	10 485(22)
C(10)	12 985(29)	8 033(40)	9 476(23)
C(11)	8 721(32)	4 402(28)	9 913(15)
C(12)	10 063(37)	4 382(33)	10 000(29)
C(13)	10 673(36)	4 426(42)	10 864(32)
C(14)	10 069(47)	4 399(36)	11 548(30)
C(15)	8 842(44)	4 398(35)	11 617(22)
C(16)	8 102(29)	4 369(42)	10 858(27)
C(17)	7 731(24)	4 458(36)	9 127(24)
C(18)	10 974(39)	4 409(23)	9 266(23)
C(19)	10 540(50)	4 503(30)	12 543(22)
C(20)	8 237(25)	4 360(36)	12 517(17)
C(21)	8 918(26)	8 902(34)	12 986(16)
C(22)	9 264(30)	10 181(27)	12 528(19)
C(23)	8 321(26)	10 662(27)	11 938(18)
C(24)	7 166(20)	10 000(27)	11 800(17)
C(25)	6 912(27)	8 790(21)	12 185(16)
C(26)	7 841(23)	8 247(28)	12 868(14)
C(27)	9 919(25)	8 359(31)	13 736(17)
C(28)	10 468(28)	10 759(34)	12 698(21)
C(29)	6 270(19)	10 618(26)	11 071(18)
C(30)	5 693(18)	8 026(26)	12 008(17)
O(1W)	11 151(19)	12 329(26)	14 623(15)
O(2W)	2 511(22)	7 677(24)	11 991(15)
B(1)	4 451(53)	4 560(28)	10 890(80)
F(1)	5 083(27)	5 383(28)	10 348(23)
F(2)	3 665(27)	5 209(38)	11 437(25)
F(3)	3 899(15)	3 444(13)	10 718(16)
F(4)	5 307(11)	4 178(16)	11 675(11)

[a] Occupancy 0.4. [b] Occupancy 0.6.

Table 10 Atomic coordinates (× 10^4) for $[Ru_4(\eta^6\text{-}C_6H_6)_4H_4]Cl_2$ (cation **4**)

Atom	*x*	*y*	*z*
Ru(1)	1 580(1)	5 788(2)	7(1)
Ru(2)	3 333	6 667	1 317(1)
C(1)	−634(32)	5 344(47)	332(21)
C(2)	−673(25)	4 135(43)	351(16)
C(3)	−246(23)	3 525(25)	−307(23)
C(4)	207(35)	4 463(45)	−1 009(18)
C(5)	213(26)	5 646(49)	−977(14)
C(6)	−279(27)	6 084(38)	−334(25)
C(7)	4 686(25)	7 958(33)	2 311(13)
C(8)	3 270(46)	7 927(30)	2 329(10)
Cl(1)	8 306(14)	11 660(15)	2 211(8)
Cl(2A)	0	10 000	−345(32)
Cl(2B)	6 667	13 333	2 164(48)
Cl(2C)	6 667	13 333	863(58)
Cl(2D)	10 000	10 000	2 398(133)
Cl(2E)	10 000	10 000	1 186(87)
H(1Ru)	2 366(117)	7 852(128)	451(61)
H(2Ru)	3 333	6 667	−894(123)

Table 11 Atomic coordinates (× 10^4) for $[Ru_4(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_4H_6][ClO_4]_2\cdot 2CH_2Cl_2$ (cation **6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	3 605(1)	7 028(1)	1 899(1)	C(32)	636(4)	5 884(5)	3 200(3)
Ru(2)	3 562(1)	7 161(1)	3 420(1)	C(33)	630(4)	6 001(4)	2 430(3)
Ru(3)	2 486(1)	9 205(1)	2 458(1)	C(34)	103(4)	7 096(4)	2 030(3)
Ru(4)	1 423(1)	7 323(1)	2 763(1)	C(35)	−392(4)	8 058(5)	2 423(3)
C(1)	5 032(4)	7 313(5)	1 029(3)	C(36)	−427(4)	7 923(5)	3 213(3)
C(2)	4 005(4)	7 378(4)	686(3)	C(37)	50(5)	6 695(7)	4 435(3)
C(3)	3 463(4)	6 453(4)	814(2)	C(38)	32(4)	7 172(4)	1 201(3)
C(4)	3 936(4)	5 430(4)	1 288(3)	C(39)	−1 187(5)	7 078(6)	1 067(3)
C(5)	4 962(4)	5 378(5)	1 647(3)	C(40)	271(5)	8 264(5)	784(3)
C(6)	5 484(4)	6 319(5)	1 525(3)	Cl(1)	−1 633(1)	4 332(1)	3 302(1)
C(7)	5 635(5)	8 271(5)	864(3)	O(1A)	−719(13)	3 386(12)	3 059(9)
C(8)	3 373(5)	4 429(4)	1 364(3)	O(2A)	−1 881(7)	5 294(7)	2 753(4)
C(9)	3 923(6)	3 624(5)	760(3)	O(3A)	−1 282(14)	4 678(13)	3 931(5)
C(10)	3 449(6)	3 729(5)	2 126(3)	O(4A)	−2 638(7)	3 938(7)	3 570(7)
C(11)	3 923(4)	5 657(4)	4 300(3)	O(1B)	−509(14)	3 857(14)	2 913(11)
C(12)	3 520(4)	6 719(4)	4 628(2)	O(2B)	−1 695(10)	5 444(11)	3 520(13)
C(13)	4 077(4)	7 622(4)	4 434(2)	O(3B)	−1 750(18)	3 609(18)	3 916(6)
C(14)	5 068(4)	7 489(4)	3 911(2)	O(4B)	−2 545(8)	4 355(11)	2 831(7)
C(15)	5 469(4)	6 429(4)	3 593(3)	Cl(2)	2 796(1)	8 823(1)	−1 331(1)
C(16)	4 904(4)	5 524(4)	3 782(3)	O(5)	1 925(6)	9 332(6)	−1 823(3)
C(17)	3 333(5)	4 690(5)	4 504(3)	O(6)	2 245(7)	8 479(7)	−680(3)
C(18)	5 677(4)	8 459(4)	3 744(3)	O(7)	3 489(7)	7 844(9)	−1 618(4)
C(19)	6 571(5)	8 283(5)	4 326(3)	O(8)	3 380(14)	9 505(12)	−1 123(7)
C(20)	6 277(5)	8 507(5)	2 972(3)	C(1S)	954(6)	6 439(6)	−1 212(3)
C(21)	2 277(5)	10 544(4)	1 445(3)	Cl(1S)	1 846(2)	5 527(2)	−545(1)
C(22)	3 303(5)	10 525(4)	1 794(3)	Cl(2S)	−520(2)	6 375(1)	−1 073(1)
C(23)	3 250(4)	10 650(4)	2 548(3)	C(2S)	−3 117(6)	1 687(6)	3 334(3)
C(24)	2 168(4)	10 851(4)	2 984(3)	Cl(3S)	−2 080(1)	945(1)	3 978(1)
C(25)	1 142(4)	10 869(4)	2 643(3)	Cl(4S)	−4 575(1)	1 803(2)	3 705(1)
C(26)	1 211(5)	10 695(4)	1 887(3)	H(1)	3 842(44)	7 899(44)	2 456(27)
C(27)	2 318(6)	10 463(5)	631(3)	H(2)	2 250(47)	7 997(46)	1 893(28)
C(28)	2 124(5)	11 050(4)	3 792(3)	H(3)	3 019(51)	6 382(51)	2 737(32)
C(29)	2 032(5)	12 345(4)	3 833(3)	H(4)	2 777(56)	8 631(56)	3 324(35)
C(30)	1 154(6)	10 679(5)	4 271(3)	H(5)	1 399(71)	8 619(71)	2 910(44)
C(31)	85(4)	6 838(5)	3 605(3)	H(6)	2 129(66)	7 404(67)	3 410(41)

Catalytic Hydrogenation of Fumaric acid.—In a stainless-steel autoclave, water (10 cm^3) and fumaric acid (250 mg) were added to $[Ru_4(\eta^6\text{-}C_6H_6)_4H_6]Cl_2$ (10 mg, 0.0126 mmol). The autoclave was then flushed with hydrogen, pressurized with 55 atm of H_2 and immersed in an oil-bath at 50 °C. After 4 h of stirring, the autoclave was cooled, the pressure released and water removed in vacuum. The residue, containing the catalyst, fumaric acid and succinic acid, was analysed quantitatively by ^1H NMR spectroscopy (19% fumaric acid, 81% succinic acid, catalyst turnover 139, catalyst turnover rate 35 h^{-1}).

Crystallography.—Table 7 summarises the crystallographic and selected experimental data for the corresponding salts of the cations **1**, **3**, **4** and **6**. Atomic coordinates are listed in Tables 8–11. Single crystals were obtained from an acetonitrile solution by slow evaporation for **1**, from concentrated aqueous solutions at 2 °C for **3** and **4**, and from a solution in dichloromethane layered with hexane for **6**. The unit-cell parameters were refined using 22 reflections (plus equivalents) in the θ range 14–19° for **1**; 22 reflections (plus equivalents) in the θ range 13–17° for **3**; 20 reflections (plus equivalents) in the θ range 14–19° for **4**; and 24 reflections (plus equivalents) in the θ range 14–20° for **6**.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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