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Clusters and water: build-up of multinuclear organometallic compounds in aqueous solution [☆]

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Contents

Abstract

The review covers the synthesis of organometallic cluster compounds in aqueous solution. Structural and catalytic aspects are also presented.

Keywords: Water-soluble organometallics; Cluster build-up; Aqueous solution

1. Introduction

Classical coordination chemistry is typically considered as chemistry in aqueous solution. In contrast, organometallic coordination chemistry takes place almost exclusively in organic solutions. Owing to the high sensitivity of many organometallics towards hydrolysis, the organic solvents employed in most organometallic syntheses and reactions are thoroughly dried prior to use. The rigorous exclusion of water has become a general feature of laboratory techniques in this field, to such an extent

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[☆] Dedicated to Professor Lord Jack Lewis on the occasion of his 67th birthday.

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that water is rarely considered to be a suitable reaction medium for organometallic complexes.

The obvious gap between organometallic and classical coordination chemistry is bridged by a rather small interface of complexes containing both soft organic and hard aqua ligands. The first complex of this type is presumably the dinuclear cation $[(\eta^5\text{-}C_5H_5)_2Ti_2(H_2O)_2O]^{2+}$, first synthesized and isolated as the bromide by Wilkinson and Birmingham in 1954 and erroneously addressed as $[(\eta^5\text{-}C_5H_5)_2Ti(OH)Br]\cdot H_2O$ [1]. The correct nature of this cationic species was established later by IR and nuclear magnetic resonance (NMR) measurements [2] and by a single-crystal X-ray structure analysis of the dithionate salt [3]. The existence of arene(aqua)ruthenium complexes was observed NMR-spectroscopically in 1972 by Zelonka and Baird in the reaction of $[(\eta^6\text{-}C_6H_6)_2Ru_2Cl_4]$ with D_2O [4]. The osmium complex $[(\eta^6\text{-}C_6H_6)Os(H_2O)_3]^{2+}$ was synthesized by analogy and characterized spectroscopically by Hung et al. [5]. Stebler-Röthlisberger et al. finally succeeded in isolating the cationic benzene aqua complexes $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ and $[(\eta^6\text{-}C_6H_6)Os(H_2O)_3]^{2+}$ as the tosylate salts; the structure of the triaqua(benzene)ruthenium(II) cation was confirmed by a single-crystal X-ray structure analysis of the sulphate [6].

Since these early pioneering reports, the chemistry of organometallic aqua ions of the transition metals has been steadily developed during the 1980s. Recently this topic was comprehensively reviewed by Koelle [7]. Related reviews deal with water-soluble organometallics complexed by hydrophilic ligands [8], metal-mediated organic synthesis in water [9] and catalysis by water-soluble organometallic complexes in biphasic systems [10].

In this work we report on the synthesis of organometallic clusters in aqueous solution. The use of water as the solvent favours the formation of ionic species in cluster build-up reactions and thus provides access to new organometallic cluster cations. Since the use of water is not widespread in organometallic chemistry, water-soluble organometallic clusters are rather scarce and this promising field is still very limited. This article covers the literature up to 1993 without claiming to be comprehensive; only multinuclear organometallic systems containing metal–metal bonds and at least three metal atoms have been considered as clusters.

2. Hydrogenation in aqueous solution

In 1979 Espinet et al. observed the cationic dinuclear rhodium complex $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu_2\text{-}OH)_3]^+$ to react in water with molecular hydrogen; as a product the tetranuclear cluster dication $[(\eta^5\text{-}C_5Me_5)_4Rh_4H_4]^{2+}$ (**1**) was isolated in the form of the chloride, hexafluorophosphate, tetrafluoroborate and tetrachloroplatinate salts [11]. In this reaction two bis(pentamethylcyclopentadienyl)dirhodium units are fused to give an $(\eta^5\text{-}C_5Me_5)_4Rh_4$ framework bridged by four hydrido ligands; the H_2 molecules are obviously cleaved heterolytically to give the hydrido ligands and the protons which eliminate the hydroxo ligands as water molecules (Eq. (1)).

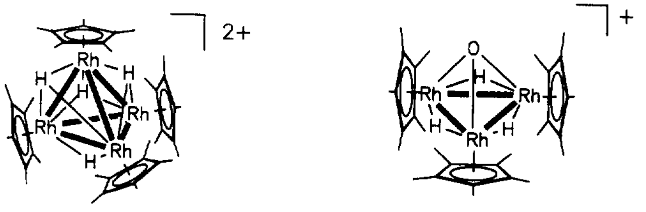
$$2[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu_2\text{-OH})_3]^{2+} + 5\text{H}_2 \xrightarrow[\text{H}_2\text{O, 90 °C}]{\text{1 atm}} [(\eta^5\text{-C}_5\text{Me}_5)_4\text{Rh}_4\text{H}_4]^{2+} + 6\text{H}_2\text{O} \qquad (1)$$

(1)

The structure of the tetranuclear cation **1** was solved by a single-crystal X-ray structure analysis of the tetrafluoroborate. The four rhodium atoms define a significantly distorted tetrahedral metal core, two Rh–Rh bonds being 2.655 Å and four Rh–Rh bonds being 2.829 Å (D_{2d} symmetry). Each rhodium atom is coordinated to a η^5-pentamethylcyclopentadienyl ligand [11]. The positions of the four hydrido ligands have been located by a low temperature neutron diffraction analysis. The H atoms stand almost symmetrically over the triangular metal faces and represent μ_3-capping ligands (Fig. 1) [12].

If molecular hydrogen is replaced by isopropanol as hydrogen donor, the reaction of the dinuclear complex $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu_2\text{-OH})_3]^+$ in aqueous solution not only leads to the tetranuclear cluster cation **1** but also to the trinuclear cluster cation $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{Rh}_3(\mu_3\text{-O})\text{H}_3]^+$ (**2**) [13,14]. The single-crystal X-ray structure analysis of the hexafluorophosphate hydrate of **2** reveals a trinuclear Rh_3 framework symmetrically capped by a μ_3-oxo ligand; each ruthenium atom is bonded to a $\eta^5\text{-C}_5\text{Me}_5$ ligand, the planes of which are almost perpendicular with respect to the Rh_3 plan [14]. The three hydrido ligands are equivalent and represent μ_2-bridges; their ^{1}H NMR resonance remains unchanged over a temperature range from −60 to 100 °C, indicating an extremely rigid and non-fluxional behaviour [13,14].

An analogy can be drawn between the isoelectronic (η^5-cyclopentadienyl)-rhodium(III) and (η^6-arene)ruthenium half-sandwich units. Consequently, the reaction of $[(\eta^6\text{-1,4-MeC}_6\text{H}_4^{i}\text{Pr})_2\text{Ru}_2(\mu_2\text{-OH})_3]^+$ with isopropanol gives the tetranuclear cluster dication $[(\eta^6\text{-1,4-MeC}_6\text{H}_4^{i}\text{Pr})_4\text{Ru}_4\text{H}_4]^+$ (**3**) [15] analogous to **1**. The substitution at the aromatic ligands is crucial for this reaction. For the rhodium systems only the pentamethylcyclopentadienyl derivatives are known; for the ruthenium systems the condensation of cationic Ru_2 to Ru_4 units is restricted



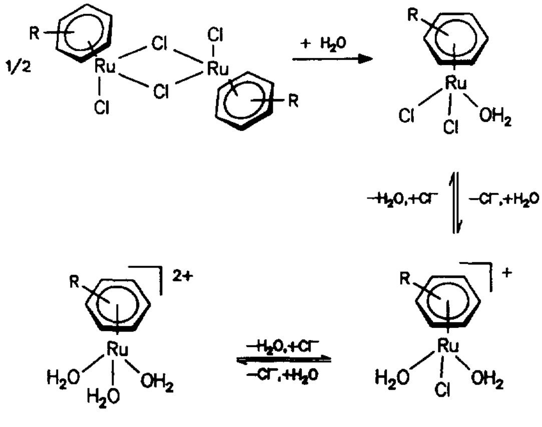
$[(\eta^5\text{–C}_5\text{Me}_5)\text{Rh}_4(\mu_3\text{–H})_4]^{2+}$

(1)

$[(\eta^5\text{–C}_5\text{Me}_5)_3\text{Rh}_3(\mu_3\text{–O})(\mu_2\text{–H})_3]^+$

(2)

Fig. 1.



Scheme 1. Hydrolysis of bis(arene)tetrachlorodiruthenium(II) according to Ref. [16].

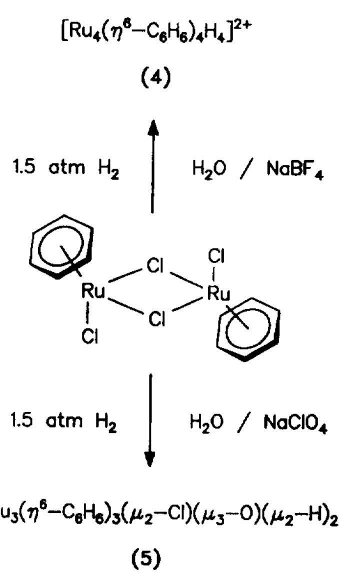
to the *p*-cymene derivatives, since the unsubstituted dinuclear cation $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu_2\text{-}OH)_3]^+$ is not known.

Recently we found a more general access to cationic (η^6-arene)ruthenium clusters in the dinuclear complexes $[(\eta^6\text{-arene})_2Ru_2Cl_4]$ which undergo hydrolysis in aqueous solution to give a mixture of mononuclear complexes $[(\eta^6\text{-arene})Ru(H_2O)_{3-n}Cl_n]^{(2-n)+}$ ($n=0$–2) (Scheme 1) [16]. The low pressure (1.5 bar) hydrogenation of the hydrolysis mixture of $[(\eta^6\text{-}C_6H_6)_2Ru_2Cl_4]$ in water leads, in the presence of sodium tetrafluoroborate, to the tetranuclear dication $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ (**4**) [17,18], which represents the parent compound of **3**. In the presence of sodium perchlorate, however, the trinuclear cation $[(\eta^6\text{-}C_6H_6)_3Ru_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)(\mu_2\text{-}H)_2]^+$ (**5**) is obtained (Scheme 2) [17].

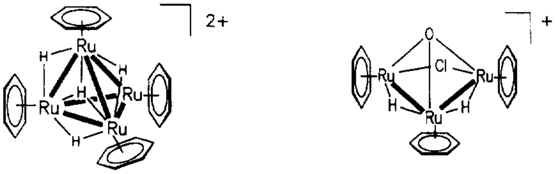
The tetranuclear cluster dication $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ (**4**), crystallized as the dichloride, contains a perfectly symmetrical Ru_4 core, the six Ru–Ru distances being almost identical. Each ruthenium atom is coordinated to an $\eta^6\text{-}C_6H_6$ ligand; only one of the four hydrido ligands is bonded as a symmetrical μ_3 bond cap, whereas the other three hydrides are better considered as μ_2 rather than as μ_3 ligands.

The trinuclear cluster cation $[(\eta^6\text{-}C_6H_6)_3Ru_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)(\mu_2\text{-}H)_2]^+$ (**5**), crystallized as the perchlorate, consists of an Ru_3 triangle with one open metal–metal edge, the three Ru atoms being capped by a μ_3-oxo ligand. The two Ru–Ru bonds carry a hydride bridge, while the open edge is bridged by a μ_2-chloro ligand [17]. The obvious analogy to the rhodium cation **2** [13,14] (Fig. 1) resides in the μ_3-oxo cap over the three metal atoms, the difference being the closed Rh_3 triangle (48*e*) as opposed to the open Ru_3 triangle (50*e*) due to the presence of a hydrido bridge instead of a chloro bridge (Fig. 2).

In contrast with the results of low pressure hydrogenation, the benzene and *p*-cymene derivatives $[(\eta^6\text{-R}{-}C_6H_4{-}R')_2Ru_2Cl_4]$ react in water with molecular hydrogen under a pressure of 60 bar at 55 °C to give the tetranuclear hexahydrido cluster dications $[(\eta^6\text{-R}{-}C_6H_4{-}R')_4Ru_4H_6]^{2+}$ (**6**: R ≡ R′ ≡ H; **7**: R ≡ Me, R′ ≡ ^{i}Pr) (Eq. (2)). The aqueous solutions of **6** and **7** are very air sensitive and give, upon exposure



Scheme 2.



$[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$
(4)

$[(\eta^6\text{-}C_6H_6)_3Ru_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)(\mu_2\text{-}H)_2]^+$
(5)

Fig. 2.

to air, the corresponding tetrahydrido dications **4** and **3**, presumably with elimination of water (Eq. (3)). The tetrahydrido benzene derivative **4**, however, can be converted back into the corresponding hexahydrido complex **6** by oxidative addition of molecular hydrogen (60 atm, 55 °C) (Eq. (4)). The tetrahydrido/hexahydrido couple **4** and **6** (as well as **3** and **7**) represents a new example of a tetrahedral metal framework with both 58 and 60 electrons.

$$2[(\eta^6\text{-}R-C_6H_4-R')_2Ru_2Cl_4]+6H_2 \xrightarrow[H_2O,\ 55\,^\circ C]{60\text{ atm}} [(\eta^6\text{-}R-C_6H_4-R')_4Ru_4H_6]^{2+}+6H^{+}+8Cl^{-} \qquad (2)$$

$(\mathbf{6}\text{: } R \equiv R' \equiv H;\ \mathbf{7}\text{: } R \equiv Me,\ R' \equiv {}^iPr)$

$$[(\eta^6\text{-R}-C_6H_4-\text{R}')_4Ru_4H_6]^{2+} + 0.5O_2 \xrightarrow[H_2O]{\text{air}}$$

$$[(\eta^6\text{-R}-C_6H_4-\text{R}')_4Ru_4H_4]^{2+} + H_2O \qquad (3)$$

$$(\mathbf{4}\text{: R} \equiv \text{R}' \equiv \text{H; } \mathbf{3}\text{: R} \equiv \text{Me, R}' \equiv {}^i\text{Pr})$$

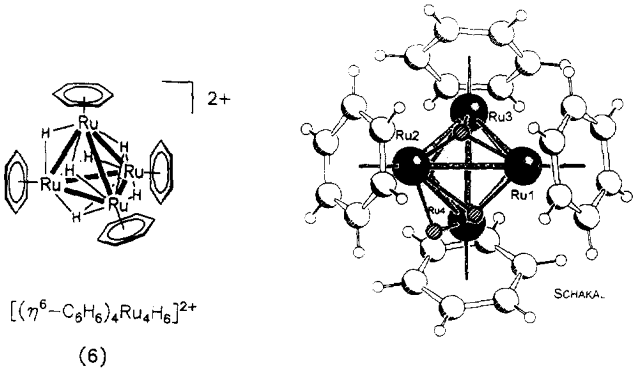
$$\underset{(\mathbf{4})}{[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}} + H_2 \xrightarrow[H_2O,\ 55\ ^\circ C]{60\ \text{atm}} \underset{(\mathbf{6})}{[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}} \qquad (4)$$

The structure of the hexahydrido cluster dications has been solved by X-ray analysis of a single crystal of $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]Cl_2\cdot 5H_2O$ (cation **6**). As opposed to the tetrahydrido cation **4**, the Ru_4 framework in **6** shows a distorted tetrahedral arrangement with two short and four long Ru–Ru distances, each ruthenium atom being bonded to an η^6-benzene ligand. Five of the six hydrido ligands could be localized in the structure; the precise position of the sixth hydride is unknown [18] (Fig. 3 [19]).

The high pressure hydrogenation of $[(\eta^6\text{-arene})_2Ru_2Cl_4]$ in water depends strongly on the nature of the arene ligand. With 1,2,4,5-tetramethylbenzene the reaction affords, instead of a tetranuclear hexahydrido dication, the trinuclear dication $[(\eta^6\text{-}C_6H_2Me_4)_3Ru_3(\mu_3\text{-Cl})H_3]^{2+}$ (**8**) (Eq. (5)). The chloro-capped dication **8** crystallizes as the dichloride from the reaction mixture. Upon addition of sodium tetrafluoroborate, the chloro-capped dication **8** is transformed into the oxo-capped cation $[(\eta^6\text{-}C_6H_2Me_4)_3Ru_3(\mu_3\text{-O})H_3]^+$ (**9**) which crystallizes as the tetrafluoroborate (Eq. (6)). The cation **9** is analogous to the pentamethylcyclopentadienyl rhodium cation **2**, described earlier by Maitlis and co-workers [13,14].

$$3[(\eta^6\text{-}C_6H_2Me_4)_2Ru_2Cl_4] + 6H_2 \xrightarrow[H_2O,\ 55\ ^\circ C]{60\ \text{atm}}$$

$$2\underset{(\mathbf{8})}{[(\eta^6\text{-}C_6H_2Me_4)_3Ru_3(\mu_3\text{-Cl})H_3]^{2+}} + 6H^+ + 10Cl^- \qquad (5)$$



$[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$

(6)

Fig. 3.

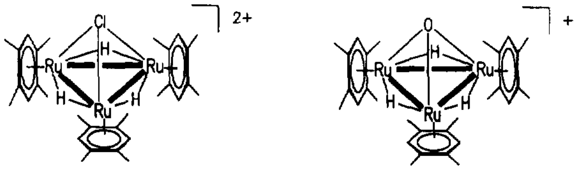
$$\begin{aligned}&[(\eta^6\text{-}C_6H_2Me_4)_3Ru_3(\mu_3\text{-}Cl)H_3](BF_4)_2 + H_2O \rightarrow\\ &\quad\text{(cation } \mathbf{8}\text{)}\\ &\quad[(\eta^6\text{-}C_6H_2Me_4)_3Ru_3(\mu_3\text{-}O)H_3](BF_4) + HCl + HBF_4\\ &\qquad\text{(cation } \mathbf{9}\text{)}\end{aligned} \tag{6}$$

The intermediacy of the chloro-capped dication **8** in the formation of the oxo-capped dication **9** may be a general feature in the hydrogenation of organometallic chloro complexes in water. In the case of the (η^5-C_5Me_5)Rh system only the μ_3-O-capped cation **2** was found. With the (η^6-C_6H_6)Ru system only the (μ_3-O,μ_2-Cl)-bridged cation **5** was obtained, whereas with the tetramethylbenzene derivative not only the μ_3-O-capped cation **9** but also the μ_3-Cl-capped intermediate **8** could be isolated. The structure of cation **9**, crystallized as the tetrafluoroborate, was confirmed by a single-crystal X-ray structure analysis [18] (Fig. 4).

3. Sulphurization in aqueous solution

The versatility of the (η^6-arene)Ru unit for cluster build-up in aqueous solution is also demonstrated by the synthesis of the first arene metal sulfido clusters. The *p*-cymene derivative $[(\eta^6\text{-Me—}C_6H_4\text{—}^i\text{Pr})_2Ru_2Cl_4]$ reacts in water with an aqueous solution of $Na_2S{\cdot}9H_2O$ to give the dication $[(\eta^6\text{-Me—}C_6H_4\text{—}^i\text{Pr})_3Ru_3(\mu_3\text{-}S)_2]^{2+}$ (**10**) which crystallizes as the hexafluorophosphate salt (Eq. (7)). The X-ray crystal structure analysis shows the cation **10** to contain an almost regular trigonal bipyramidal Ru_3S_2 core with a closed Ru_3 metal framework (Fig. 5) [20].

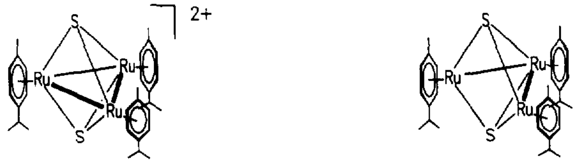
$$\begin{aligned}&3[(\eta^6\text{-Me—}C_6H_4\text{—}^i\text{Pr})_2Ru_2Cl_4] + 4S^{2-} \xrightarrow{H_2O}\\ &\quad 2[(\eta^6\text{-Me—}C_6H_4\text{—}^i\text{Pr})_3Ru_3(\mu_3\text{-}S)_2]^{2+} + 12Cl^-\\ &\qquad\qquad (\mathbf{10})\end{aligned} \tag{7}$$



$[(\eta^6\text{–}C_6H_2Me_4)_3Ru_3(\mu_3\text{–}Cl)H_3]^{2+}$
(8)

$[(\eta^6\text{–}C_6H_2Me_4)_3Ru_3(\mu_3\text{–}O)H_3]^{+}$
(9)

Fig. 4.



$[(\eta^6\text{-Me-C}_6\text{H}_4\text{-}^i\text{Pr})_3\text{Ru}_3(\mu_3\text{-S})_2]^{2+}$ (10)

$[(\eta^6\text{-Me-C}_6\text{H}_4\text{-}^i\text{Pr})_3\text{Ru}_3(\mu_3\text{-S})_2]$ (11)

Fig. 5.

$$[(\eta^6\text{-Me}-\text{C}_6\text{H}_4-{}^i\text{Pr})_3\text{Ru}_3(\mu_3\text{-S})_2]^{2+} + 2(\eta^5\text{-C}_5\text{H}_5)_2\text{Co} \xrightarrow{\text{CH}_3\text{CN}}$$

(10)

$$[(\eta^6\text{-Me}-\text{C}_6\text{H}_4-{}^i\text{Pr})_3\text{Ru}_3(\mu_3\text{-S})_2] + 2[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]^+ \qquad (8)$$

(11)

Cyclic voltammetry established that the dication **10** undergoes two very closely spaced one-electron reductions which are reversible. As suggested by the electrochemical studies, the dication **10** can be reduced by cobaltocene to give the neutral species $[(\eta^6\text{-Me}-\text{C}_6\text{H}_4-{}^i\text{Pr})_3\text{Ru}_3(\mu_3\text{-S})_2]$ (**11**) (Eq. (8)). The X-ray crystal structure analysis of **11** reveals a distorted square pyramidal Ru_3S_2 arrangement with an open Ru_3 triangle. The addition of two electrons to the 48-electron system **10** to give the 50-electron system **11** therefore results in the opening of a metal–metal bond.

The osmium analogue of **10** was obtained in anhydrous tetrahydrofuran (THF) from $[(\eta^6\text{-Me}-\text{C}_6\text{H}_4-{}^i\text{Pr})_2\text{Os}_2\text{Cl}_4]$ and bis(trimethylsilyl)sulphide; this method can also be applied to the ruthenium dication **10** [20].

4. Carbonylation in aqueous organic solution

A series of carbonylation reactions to give cationic clusters has been described by Puddephatt et al. involving aqueous methanol or acetone solutions. In the case of **14** and **16** water not only favours the formation of ionic species but also acts as oxidizing agent [21].

$$3[\text{MX}_2(\mu_2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)] + 3\text{CO} + 2\text{H}_2\text{O} \rightarrow$$

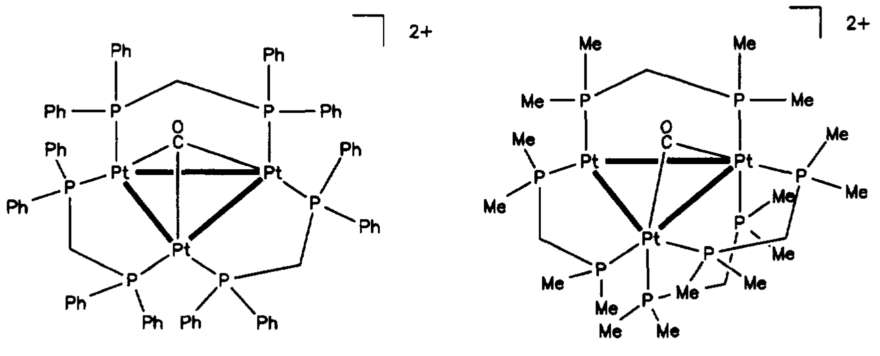
$$[\text{M}_3(\mu_3\text{-CO})(\mu_2,\eta^2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3]\text{X}_2 + 4\text{HX} + 2\text{CO}_2 \qquad (9)$$

(cation **12**: M ≡ Pd; **13**: M ≡ Pt; X ≡ CF_3CO_2)

$$\begin{aligned}&3[(\mathrm{PPh_3})\mathrm{Pt_2}(\mu_2\text{-}\mathrm{Me_2PCH_2PMe_2})_3] + 2\mathrm{CO} + 4\mathrm{H_2O} \rightarrow \\ &\quad 2[\mathrm{Pt_3}(\mu_2\text{-}\mathrm{CO})(\mu_2,\eta^2\text{-}\mathrm{Me_2PCH_2PMe_2})_4]^{2+} \\ &\qquad\qquad \textbf{(14)} \\ &\quad + 3\mathrm{PPh_3} + \mathrm{Me_2PCH_2PMe_2} + 4\mathrm{OH^-} + 2\mathrm{H_2} \qquad (10)\end{aligned}$$

Palladium acetate was found to react in the presence of bis(diphenylphosphino)methane and trifluoroacetic acid with carbon monoxide in aqueous acetone to give the dicationic 42-electron cluster $[\mathrm{Pd_3}(\mu_3\text{-CO})(\mu_2,\eta^2\text{-}\mathrm{Ph_2PCH_2PPh_2})_3]^{2+}$ (**12**) [22,23] (Eq. (9)). The analogous formation of the platinum homologue $[\mathrm{Pt_3}(\mu_3\text{-CO})(\mu_2,\eta^2\text{-}\mathrm{PPh_2CH_2PPh_2})_3]^{2+}$ (**13**) requires elevated temperatures [24]. With bis(dimethylphosphino)methane, platinum forms the 46-electron cluster dication $[\mathrm{Pt}(\mu_2\text{-CO})(\mu_2,\eta^2\text{-}\mathrm{Me_2PCH_2PMe_2})_4]^{2+}$ (**14**) (Eq. (10)), presumably owing to the lower steric bulk of the methyl-substituted diphosphine of the ligands [25] (Fig. 6).

The structure of the trinuclear 42-electron species **13** was solved by X-ray structure analysis of a single-crystal of the hexafluorophosphate salt. The three Pt atoms form a triangle which is capped by a μ_3-carbonyl ligand. The three Pt–Pt edges are bridged by three diphenylphosphine ligands, the atoms of the $\mathrm{Pt_3P_6}$ moiety being approximately coplanar [24]. The skeleton of the 46-electron dication **14**, crystallized as the tetraphenylborate salt, is based on an isosceles triangle of platinum atoms, the three edges being bridged by three latitudinal $\mathrm{Me_2PCH_2PMe_2}$ ligands. One of the Pt–Pt bonds is further supported by a longitudinally bridged $\mathrm{Me_2PCH_2PMe_2}$ ligand as well as by a μ_2-carbonyl ligand [25]. In this way the formal addition of a fourth four-electron diphos ligand to the 42-electron $\mathrm{Pt_3}$ system results in a displacement of the μ_3-CO cap into a μ_2 position.



$[\mathrm{Pt_3}(\mu_3\text{–CO})(\mu_2,\eta^2\text{–}\mathrm{Ph_2PCH_2PPh_2})_3]^{2+}$
(13)

$[\mathrm{Pt_3}(\mu_2\text{–CO})(\mu_2,\eta^2\text{–}\mathrm{Me_2PCH_2PMe_2})_4]^{2+}$
(14)

Fig. 6.

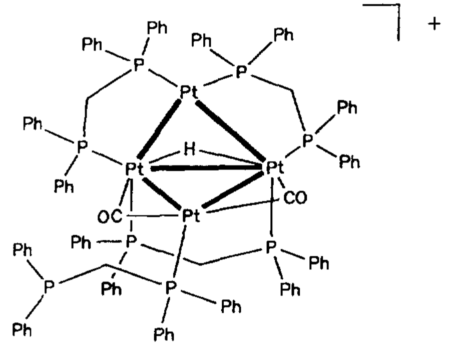
When the reaction of $[(\eta^2\text{-}Ph_2PCH_2PPh_2)Pt(O_2CCF_3)_2]$ with carbon monoxide in aqueous methanol to give the trinuclear cation **13** was slightly modified, a further reduction step was discovered affording a tetranuclear platinum cluster $[Pt_4(\mu_2\text{-}H)(\mu_2\text{-}CO)_2(\mu_2,\eta^2\text{-}Ph_2PCH_2PPh_2)_3(\eta^1\text{-}Ph_2PCH_2PPh_2)]^+$ (**15**). The cation **15** was obtained in good yield as the hexafluorophosphate by the reaction of $[(\eta^2\text{-}Ph_2PCH_2PPh_2)Pt(O_2CCF_3)_2]$ in methanol–water solution with CO (5 bar, 100 °C) for 3 days, followed by anion exchange using NH_4PF_6 [26]. The overall reaction is represented by Eq. (11) in a simplified version of the more complex redox process [27].

$$\begin{aligned}&4[PtX_2(\mu_2\text{-}Ph_2PCH_2PPh_2)] + 6CO + 4H_2O) \rightarrow\\ &\quad[Pt_4(\mu_2\text{-}H)(\mu_2\text{-}CO)_2(\mu_2,\eta^2\text{-}Ph_2PCH_2PPh_2)_3(\eta^1\text{-}Ph_2PCH_2PPh_2)]X\\ &\qquad\qquad\qquad\text{(cation } \mathbf{15}\text{)}\\ &+4CO_2 + 7HX \end{aligned} \tag{11}$$

$$\begin{aligned}&2[Pt_2(\mu_2\text{-}H)(H)_2(\mu_2\text{-}Ph_2PCH_2PPh_2)_2]^+ + 0.5O_2 + 2CO \rightarrow\\ &\quad[Pt_4(\mu_2\text{-}CO)_2(\mu_2\text{-}Ph_2PCH_2PPh_2)_3(\eta^1\text{-}Ph_2PCH_2P(:O)Ph_2)] + 2H^+ + 2H_2\\ &\qquad\qquad\qquad\qquad(\mathbf{16})\end{aligned} \tag{12}$$

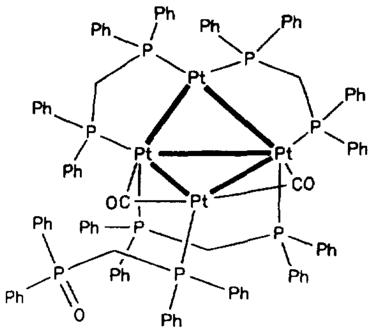
Another tetranuclear platinum cluster, the neutral complex $[Pt_4(\mu_2\text{-}CO)_2(\eta^2,\mu_2\text{-}Ph_2PCH_2PPh_2)_3(\eta^1\text{-}Ph_2PCH_2PPh_2O)]$ (**16**), was obtained from the reaction of the dinuclear cation $[Pt_2H_2(\mu_2\text{-}H)(\eta^2,\mu_2\text{-}Ph_2PCH_2PPh_2)_2]^+$ with carbon monoxide in aqueous solution under air (Eq. (12)). Obviously, in the formation of the red crystalline compound **16**, the monohapto-bonded diphos ligand has been oxidized at the non-coordinated phosphorus atom to a phosphine oxide moiety [28].

Both tetranuclear platinum clusters, the cation **15** and the neutral species **16**, represent 58-electron systems whose structure is based on a Pt_4 butterfly arrangement, as shown by single-crystal X-ray structure analyses (Fig. 7). In **15** one of the Pt_3 butterfly wings carries the three μ_2,η^2-diphos bridges, whereas the other Pt_3 butterfly wing is bridged by the two μ_2-CO and the μ_2-H ligands in such a way that the hydride bridges the backbone of the Pt_4 butterfly. The platinum atom ligated by the two carbonyl bridges also carries the monohapto-bonded diphos ligand [26]. The structure of the neutral complex **16** has essentially the same arrangement, except that the μ_2-hydrido ligand is missing and the non-coordinated phosphorus atom is bonded to an oxygen atom [28]. In solution the cluster cation **15** was shown to be highly fluxional by temperature-dependent NMR spectroscopy. The variable-temperature ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra are suggestive of an edge-to-edge migration of the μ_2-H ligand and the $Pt(\mu_2\text{-}CO)_2(\eta^1\text{-}Ph_2PCH_2PPh_2)$ moiety with respect to the $Pt_3(\mu_2,\ \eta^2\text{-}Ph_2PCH_2PPh_2)_3$ triangle [26].



$[Pt_4(\mu_2\text{-}H)(\mu_2\text{-}CO)_2(\mu_2,\eta^2\text{-}Ph_2PCH_2PPh_2)_3(\eta^1\text{-}Ph_2PCH_2PPh_2)]^+$

(15)



$[Pt_4(\mu_2\text{-}CO)_2(\mu_2,\eta^2\text{-}Ph_2PCH_2PPh_2)_3(\eta^1\text{-}Ph_2PCH_2P(:O)Ph_2]$

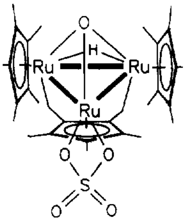
(16)

Fig. 7.

5. Oxidation in a biphasic medium

A two-phase medium such as dichloromethane–water has been used for rather fancy oxidation reactions to give trinuclear, high valent, hydrido oxo ruthenium clusters. The reaction of $[(\eta^5\text{-}C_5Me_5)_2Ru_2(OMe)_2]$ with sodium hydrogenoperoxosulphate ($KHSO_5$) in CH_2Cl_2/H_2O affords in high yield the cluster $[Ru_3\{\mu_3,\eta^7\text{-}C_5Me_3(CH_2)_2\}(\mu_3\text{-}O)(\mu_2\text{-}H)(\eta^5\text{-}C_5Me_5)_2(\eta^2\text{-}SO_4)]$ (**17**) [29] (Fig. 8).

The structure of **17** was determined by X-ray diffraction. It consists of a triangle



$[Ru_3\{\mu_3-\eta^7-C_5Me_3(CH_2)_2\}(\mu_3-O)(\mu_2-H)(\eta^5-C_5Me_5)_2(\eta^2-SO_4)]$

(17)

Fig. 8.

of ruthenium atoms containing a μ_3-oxo cap and a μ_2-hydride bridge. Each metal atom is also coordinated to an η^5-pentamethylcyclopentadienyl ring; the ruthenium atom not bridged by the hydride is chelated by an η^2-sulphate. Furthermore, two adjacent methyl groups of the pentamethylcyclopentadienyl ligand bonded to this ruthenium atom have been activated to give a unique example of a μ_3,η^7-$C_5Me_3(CH_2)_2$ ligand. An analogous cluster containing two η^1-$O_2CC_6H_4Cl$ ligands instead of the η^2-sulphato ligand was obtained from a similar reaction with *m*-chloroperoxobenzoic acid [29].

Hörnig et al. have shown that neither the formation of the oxo cap nor the deprotonation of the two methyl groups in the pentamethylcyclopentadienyl ligand requires the peroxosulphate reagent, since a compound strictly analogous to **17**, $[Ru_3\{\mu_3-\eta^7-C_5Me_3(CH_2)_2\}(\mu_3-O)(\mu_2-H)(\eta^5-C_5Me_5)_2(OH)_2]$, can be obtained simply by hydrolysing $[(\eta^5-C_5Me_5)_2Ru_2Cl_4]$ in aqueous methanol over potassium carbonate [30].

6. Catalytic aspects

Water-soluble organometallic clusters are particularly interesting with regard to catalytic applications in aqueous solution, because water as a cheap and environmentally friendly solvent is likely to receive steadily growing attention in catalysis research. Of the clusters presented in this article, two catalytic implications have been described so far.

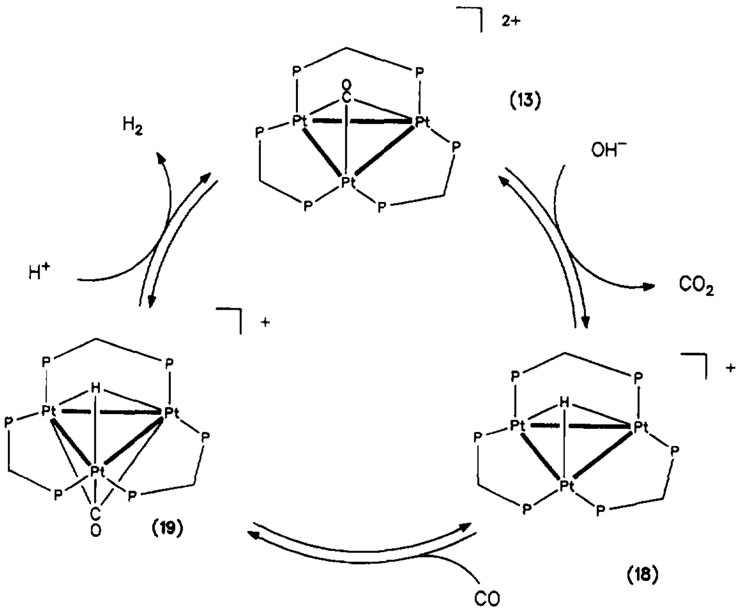
One of the most obvious catalytic processes to be performed in aqueous solution using water-soluble organometallic clusters is the water–gas shift reaction (Eq. (13)) in which water is involved not only as solvent but also as reactant. The cationic platinum cluster $[Pt_3(\mu_3-CO)(\mu_2,\eta^2-Ph_2PCH_2PPh_2)_3]^{2+}$ (**13**) has been reported to be a useful catalyst in this process [21].

$$CO+H_2O \rightleftarrows CO_2+H_2 \tag{13}$$

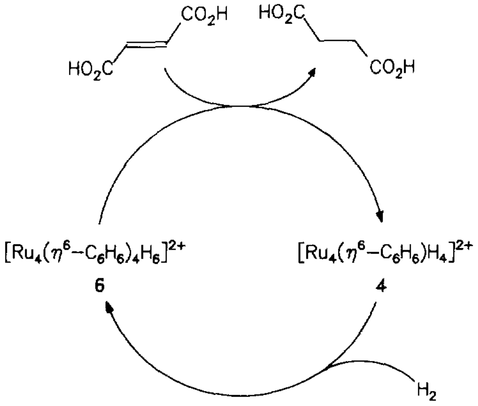
The catalytic reaction of carbon monoxide and water to give carbon dioxide and hydrogen, catalysed by **13**, is carried out in aqueous methanol at 100 °C; up to 25 catalytic turn-overs per hour were observed. From a kinetic point of view the catalysis is first order in catalyst concentration and inverse first order in pressure of carbon monoxide. The mechanism depicted in Scheme 3 has been suggested for the catalytic cycle [21]. In the first step hydroxide is assumed to attack **13** to give CO_2 and the hydrido cluster $[Pt_3(\mu_3\text{-}H)(\mu_2,\eta^2\text{-}Ph_2PCH_2PPh_2)_3]^+$ (**18**); presumably this step is rate determining. The cation **18** takes up carbon monoxide to give the cationic cluster $[Pt_3(\mu_3\text{-}H)(\mu_3\text{-}CO)(\mu_2,\eta^2\text{-}Ph_2PCH_2PPh_2)_3]^+$ (**19**), which upon protonation converts back into the dication **13** with elimination of hydrogen. The intermediary monocationic species **18** and **19** have been characterized spectroscopically and the individual steps of the proposed catalytic cycle have been shown to occur readily, with the exception of the first step involving attack of hydroxide on **13**, but **18** has been prepared from **13** by reduction with $NaBH_4$ [31].

The tetranuclear ruthenium clusters $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ (**6**) and $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ (**4**) represent an interesting redox couple which is interconvertable with hydrogen and with oxygen respectively. This potential can be used for the hydrogenation of olefinic double bonds in aqueous solution. Thus fumaric acid is hydrogenated to give succinic acid in the presence of catalytic amounts of **6** [17].

The hydrogenation of fumaric acid in water is catalysed by $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$ (**6**) at 50 °C under a pressure of 55 bar of hydrogen. The catalytic turn-over rate was found to be 48 per hour. After a catalytic run the solution contains a mixture of both the hexahydrido cluster **6** and the tetrahydrido cluster **4**. Both steps suggested in the catalytic cycle (Scheme 4) can be realized individually. The hexahydrido cluster



Scheme 3. Proposed cycle for the water–gas shift reaction catalysed by $[Pt_3(\mu_3-CO)(\mu_2,\eta^2\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$ (13) [21].



Scheme 4. Proposed cycle for the hydrogenation of fumaric acid in water catalysed by $[Ru_4(\eta^6-C_6H_6)_4H_6]^{2+}$ (**6**) [17].

6 transfers hydrogen to fumaric acid to give succinic acid and the tetrahydrido cluster **4** then takes up molecular hydrogen to give the hexahydrido cluster **6** [17].

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