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Reactions of $[(\eta^5\text{-}C_5Me_5)Ru(OMe)]_2$

XIV *. Hydrolysis products: synthesis and molecular structure of $[(\eta^5\text{-}C_5Me_4Et)RuOH]_4$

A. Hörnig, U. Englert and U. Koelle

Institute for Inorganic Chemistry, RWTH-Technical University, Prof.-Pirlet-Str. 1, W-5100 Aachen (Germany)

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Abstract

Hydrolysis of the title complexes $[Cp^*RuOMe]_2$ (**2a**) and $[Cp^{\wedge}RuOMe]_2$ (**2b**) ($Cp^* = \eta^5\text{-}C_5Me_5$, $Cp^{\wedge} = \eta^5\text{-}C_5Me_4Et$) in a two phase pentane/water system yields the tetrameric hydroxides $[Cp^*RuOH]_4$ (**3a**) and $[Cp^{\wedge}RuOH]_4$ (**3b**), as rather inert, robust molecules; the tetrameric structure was established in the case of **3b** by X-ray crystallography. Hydrolysis of the precursor complexes $[Cp^*RuCl_2]_2$ (**1a**) and $[Cp^{\wedge}RuCl_2]_2$ (**1b**) with H_2O/K_2CO_3 gave a trimeric Ru–Ru–Ru complex, the hydroxo analogue of the known $Ru_3Cp^*_2(C_5Me_3\mu\text{-}CH_2)_2(\mu_3\text{-}O)(\mu_2\text{-}H)SO_4$. Reactions and electrochemical oxidation of the compounds are discussed.

1. Introduction

Our interest in the reactions of alkoxo complexes $[Cp^*M(OMe)]_2$, M = Ru (**2**) or Rh [1], and in organometallic aqua ions [2] led us in the past to study the hydrolysis reaction of these compounds. We were, however, only able to characterize fully the hydrolysis product of a DPPM stabilized adduct of $[Cp^*Ru(OMe)]_2$ (**2a**) *i.e.* $[\{Cp^{*/\wedge}Ru(\mu\text{-}OH)\}_2DPPM]$ (**4a**) [1]. Hydrolysis experiments with **2a** revealed rapid displacement of the bridging OMe groups with appearance of the signals of free methanol in the NMR spectra. The product of preparative hydrolysis, however, was of limited solubility in all solvents except CH_2Cl_2 and spectroscopy did not reveal the degree of oligomerization. Suitable variation in the Cp^* ligand has now yielded a more tractable derivative, and in the following, we report on the tetrameric hydroxo clusters $[Cp^{*/\wedge}RuOH]_4$ (**3a,b**) and on the products of hydrolysis of $[Cp^{*/\wedge}RuCl_2]_2$ (**1a, 1b**) in alkaline solution.

2. Results and discussion

2.1. Hydrolysis of $[Cp^{*/\wedge}RuOMe]_2$ (*2a, 2b*)

The hydrolysis of **2** can be conveniently monitored by ^1H NMR spectroscopy: addition of a slight stoichiometric excess of water to a solution of, *e.g.*, **2b** ($Cp^{\wedge} = \eta^5\text{-}C_5Me_4Et$) in benzene-$d_6$, causes the OMe signal to shift from δ 4.8 in **2** to the position for free methanol, and a shift of the $Cp^{\wedge}$ methyl singlets from δ 1.61/1.63 to 1.66/1.70.

Preparative hydrolysis was performed by vigorously stirring a pentane solution of **2** (either **2a** or **2b**) in the presence of a small amount of water for 1 h. In the case of **2b**, the brown reaction product isolated after evaporation of the pentane solution and drying in vacuo was insoluble in water, moderately soluble in pentane, benzene and methylene chloride and was characterized by the above mentioned methyl signals. The Cp^* derivative **2a** yields a product soluble only in methylene chloride, but with otherwise similar properties, characterized by a single Cp^* signal (1.61, CD_2Cl_2). Both compounds show a singlet hydroxo signal at δ −0.14 in **2a** and δ −0.04 in **2b**.

The hydroxo complexes **3** are insensitive to atmospheric oxygen as solids and only slightly sensitive in

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Correspondence to: Dr. U. Koelle.

* For Part XIII, see ref. 1 and references therein.

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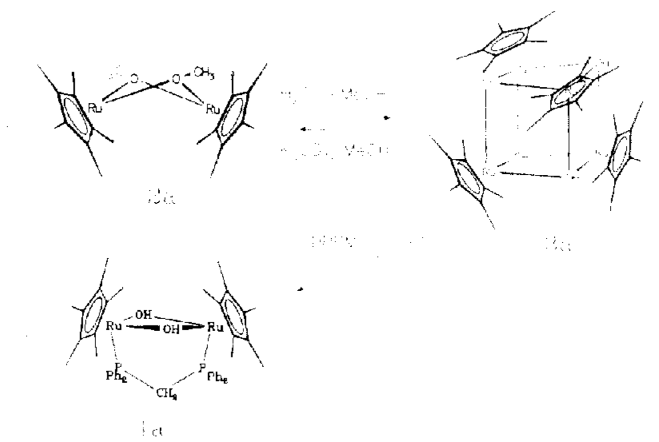


Scheme 1.

solution. Along with the characteristic yellowish-brown colour, reminiscent of the tetrameric chlorides $[\mathrm{Cp}^{\star/\wedge}\mathrm{RuCl}]_4$ (**5a, 5b**) [3], this behaviour points to coordinative saturation of Ru in a tetrameric structure (see below).

The tetramers **3a, 3b** were found to be inert towards most of the attempted cleavage and substitution reactions. The OH protons show no acidity whatsoever. Reactions with aqueous base failed, as well as attempted silylation with Me_3SiCl. The latter reaction gave, after workup, a mixture of the chloro-complexes $[\mathrm{Cp}^{\star}\mathrm{RuCl}_2]_2$ (1), $[\mathrm{Cp}^{\star}\mathrm{RuCl}]_4$ (**5**) and $[(\mathrm{Cp}^{\star}\mathrm{Ru})_2(\mu\text{-Cl})_3]$ [4], *i.e.* products of nucleophilic substitution of OH^- by Cl^- rather than electrophilic substitution of protons.

Treatment with organometallic bases (^{n}BuLi) or hydrides such as $LiBHEt_3$ resulted in reaction at the methyl group of a $\mathrm{Cp}^{\star}$ (*vide infra*) rather than deprotonation of OH. No reaction was observed on prolonged stirring with PPh_3, but DPPM slowly cleaved the tetramers to give the DPPM bridged dimers **4**. Finally, stirring **3** in MeOH in the presence of solid K_2CO_3, slowly reconverted the tetramer into the starting dimeric methoxo complex (Scheme 1).

*2.2. Molecular structure of **3b***

For the $\mathrm{Cp}^{\wedge}$ derivative **3b**, crystals suitable to allow elucidation of the essential structural features were obtained from pentane solution. The compound crystallizes in the space group $C2/c$ (No. 15), with a = 18.152(6), b = 15.97(4), c = 15.99(1), β = 92.6296°, Z = 8/2. Solution of the structure with a twofold crystallographic axis in the molecule and refinement of 1256 reflections with $I > 3\sigma(I)$ to R = 7.9% (R_w = 8.1%) showed the presence of the expected tetrameric unit $[\mathrm{Cp}^{\wedge}\mathrm{RuOH}]_4$, as shown in Fig. 1. Bond distances and angles are listed in Table 1.

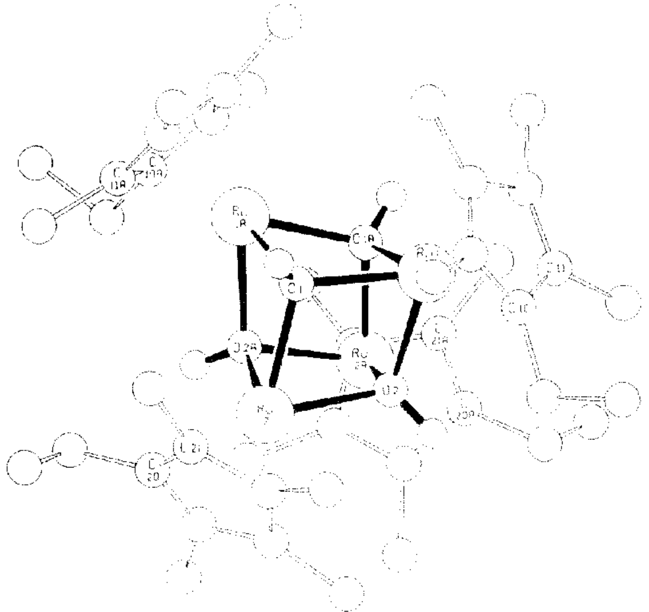


Fig. 1. SCHAKAL representation of $[\mathrm{Cp}^{\wedge}\mathrm{Ru(OH)}]_4$ (**3b**). Labelling scheme applied; extension "A" denotes the symmetry operation according to the twofold axis. In the $\mathrm{Cp}^{\wedge}$ ligand, inner ring carbon atoms are labelled C10–C14 and C20–C24, methyl and methylene carbon atoms are C15–C19 and C20–C24, peripheric carbons of the ethyl group are C01 and C02.

Apart from dimerization through two additional Ru–O bonds, a major change in the geometry of **3** as compared to **2** is a flattening of the Ru–O–Ru–O rhombus, with concomitant lengthening of the Ru–O (2.055 Å in **2a**, 2.12–2.22 Å in **3b**) and the Ru–Ru distance (2.95 Å in **2a**, 3.434(3) Å in **3b**), the latter excluding direct Ru–Ru contact. As indicated by the dihedral angle between O–Ru–O planes, which is 126° in **2a** but 161° in **3b**, the Ru–O–Ru–O rhombus is somewhat flattened but not yet planar as in the DPPM

TABLE 1. Atomic distances (Å) and bond angles (°) in **3b** [a]

Ru1–Ru1A	3.434(3) [a]	Ru2–O2	2.22(1)
Ru1–Ru2	3.469(3)	Ru2–O2A	2.18(1)
Ru1–Ru2A	3.459(3)	Ru2–O1	2.20(1)
Ru1–O1	2.12(1)	Ru1–$\mathrm{Cp}^{\wedge}$-plane	1.72
Ru1–O1A	2.16(1)	Ru2–$\mathrm{Cp}^{\wedge}$-plane	1.69
Ru1–O2	2.17(2)		
O1–Ru1–O1A	71.0(5)	Ru1–O1–Ru1A	106.4(5)
O1–Ru1–O2	73.8(4)	Ru1–O1–Ru2	106.4(5)
O1–Ru1–O2A	73.2(4)	Ru1A–O1–Ru2	104.6(4)
O1–Ru2–O2	71.2(4)	Ru1–O2–Ru2	104.2(5)
O1–Ru2–O2A	72.2(3)	Ru1–O2–Ru2A	105.2(4)
O2–Ru2–O2A	74.8(4)	Ru2–O2–Ru2A	102.5(4)

[a] Figures in parentheses are estimated standard deviations in the last digit.

adduct **4** [1]. Distortion of the Ru_4O_4 cube is such as to produce acute angles at Ru (71–75°) and obtuse angles at O (104–106°) in the same direction as found for the tetrameric chloride **5** (Cl–Ru–Cl 81–83° and Ru–Cl–Ru 96–98.7° in **5b** [3,5]).

Comparison of the extent of flattening of the Ru–O–Ru–O (or Ru–X–Ru–X) rhombus in various tetramers and addition products, *i.e.* along with those in **3**, **4** and **5**, those in the complexes $[Cp^*Ru(\mu\text{-}OEt)(CO)]_2$ (**6**) [6], a π-coordinated butenol derivative $[Cp^*Ru(\mu_2\text{-}\eta^3\text{-}O(CH_2)_2CH{=}CH_2)]_2$ (**7**) (internally coordinated through the olefinic double bond) [7] and those in the Cl-bridged ethylene complex $[Cp^*Ru(\mu\text{-}Cl)(C_2H_4)]_2$ (**8**) [8], reveals that this flattening parallels the ability of the complexing or bridging ligand to act as a soft donor towards Ru. Thus, whereas **4**, **7** and **8** show an almost planar Ru–X–Ru–X arrangement, the angle between Ru–X–Ru planes deviates from 180° in **6** (dihedral angle 162.5°) and also in **3** and **5**.

Of all the complexes $[Cp^*RuOR]_n$ (R = H, Me, Et, Pr, ^{n}Bu, σ-allyl, CF_3CH_2) and similarly $[Cp^*RuSR]_n$ the hydroxo complex is the only one that is tetrameric. Since the ligands R span a wide range of acidities, we conclude that the factors that determine the nuclearity of the complexes, whether dimeric or tetrameric, are solely steric in nature. To confirm this assumption, a tetrameric model molecule with the same geometry as **3** but with OMe instead of OH groups was generated (C–O 1.4 Å, C–H 0.98 Å) and the non-bonding interaction with adjacent Cp* ligands investigated by a molecular modelling program. Severe steric congestion due to short non-bonding contacts between OMe and Cp*–Me hydrogen atoms in any rotational conformation was immediately obvious.

The molecule had some freedom to relax by further flattening of the Ru–O–Ru–O rhombus or lengthening of the Ru–O bonds, but the latter are determined by the donor-acceptor properties of the bridging atom lone pairs (in the dimer), as discussed above, and optimization of the molecular geometry to minimize steric interactions would lead to less favorable electronic situations. Therefore the dimeric structure for all OR with R > H appears to be the best energetic compromise.

Tetrameric $[CpRuX]_4$ clusters are known for X = S with the metal in different oxidation states [9], but analogous oxygen-bridged oligomers are common only for early transition elements [10]. A tetrameric hydroxo complex of Ru, $[Ru(benzene)OH]_4(SO_4)_2$ (**9**) was crystallized in medium yield from sulphate saturated aqueous solutions containing the ion $[Ru(benzene)(H_2O)_3]^{2+}$ [11]. In the $Ru(arene)aq^{n+}$ system, the monomeric aqua ion is the species in acidic solution [12] and the μ-hydroxo cation $[(arene)Ru(\mu\text{-}(OH))_3\text{-}Ru(arene)]^+$ [13] is formed in alkaline solution. Facile cleavage of **9** into monomers and dimers under a variety of conditions [11] suggests that $[Ru(benzene)(H_2O)_2(OH)]^+$, the precursor to the tetramer **9**, is probably formed during crystallization, and may be present in solution in low concentration at intermediate values of pH. In contrast, the tetramers **3** are stable over the whole pH range, and are the only species formed under the conditions described.

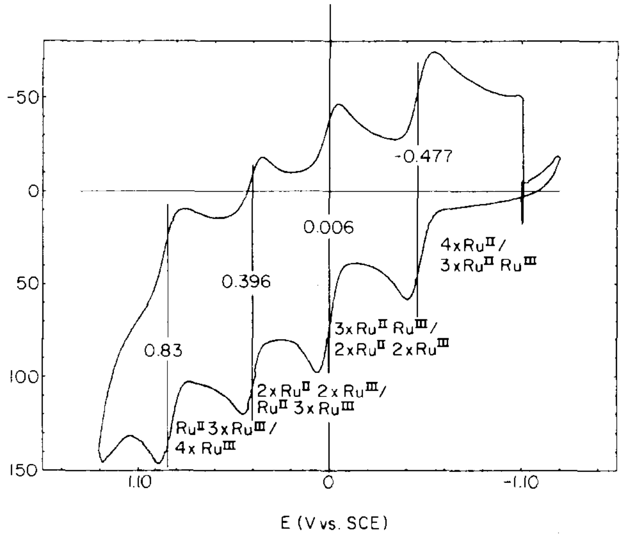


Fig. 2. Cyclic voltammogram of $[Cp^{\wedge}Ru(OH)]_4$ (**3b**) in CH_2Cl_2. Conduction electrolyte Bu_4NPF_6, $v = 100$ mV s^{-1}.

2.3. Cyclic voltammetry

The cyclic voltammogram of **3b** in methylene chloride shows four reversible oxidation waves with mean potentials and peak potential separations as indicated in Fig. 2. The waves of about equal height and nearly equally spaced on the potential scale are attributed to the stepwise oxidation of Ru^{II} to Ru^{III}, leading finally to the tetracation $[Cp^*Ru(OH)]_4^{4+}$:

$$[Cp^{\wedge}Ru(OH)]_4 \xrightleftharpoons{-e} [Cp^{\wedge}Ru(OH)]_4^{+} \xrightleftharpoons{-e}$$

$$[Cp^{\wedge}Ru(OH)]_4^{2+} \xrightleftharpoons{-e} [Cp^*Ru(OH)]_4^{3+} \xrightleftharpoons{-e}$$

$$[Cp^{\wedge}Ru(OH)]_4^{4+}$$

As can be seen from Fig. 2, there is further destructive, oxidation at a potential slightly positive with respect to the Ru_4^{III} complex, indicating that this latter may not be stable on a preparative timescale. Accordingly, attempts to carry out chemical oxidation with various oxidants (H_2O_2, Ag^+, $S_2O_8^{2-}$) led either to recovery of the starting material or to complicated mixtures of products.

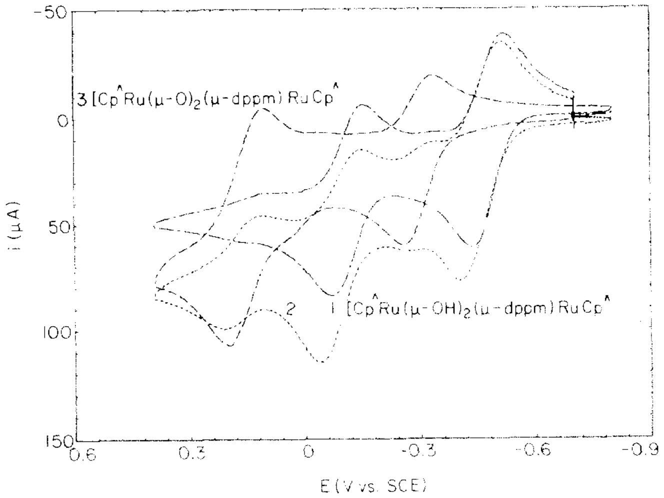


Fig. 3. Cyclic voltammogram of $[Cp^{\wedge}Ru(\mu\text{-}OH)]_2$DPPM (**4b**). 1 (·–·–·) before, 2 (······) after partial, 3 (------) after exhaustive electrolysis at 0.5 V. CH_2Cl_2, conduction electrolyte Bu_4NPF_6, $v = 100$ mV s^{-1}.

It was to be expected that deprotonation would accompany oxidation of the tetramer. Thus, the wave seen above 1.0 V in Fig. 2 can be assigned to the oxidation of partially deprotonated species. However, addition of pyridine to the methylene chloride solution of **3**, as well as leading to an enhancement of this oxidation wave also caused the four step cyclic voltammogram to collapse into two new peaks at −0.2 and 0.3 V in the oxidative scan and a number of less distinct peaks in the reductive scan, possibly due to reduction of partially deprotonated species.

Oxidation/deprotonation can be more distinctly devised in the DPPM-bridged dimer **4b** [1]. As previously found for the analogous chloro-bridged complex $Cp^{*}Ru(\mu\text{-}Cl)_2(\mu\text{-dppm})RuCp^{*}$ [14], the cyclic voltammogram consists of two reversible waves attributed to the stepwise oxidation/reduction to the mixed valence Ru^{II}/Ru^{III} and the Ru^{III}/Ru^{III} complex. Figure 3 shows the cyclic voltammogram of **4b** before electrolysis and after partial and exhaustive electrolysis at 0.5 V, *i.e.* anodic of the second oxidation wave. After electrolysis, the double step cyclic voltammogram has shifted as a whole towards more positive potential by 270 mV. The observation is consistent with the formation of a deprotonated Ru^{III}/Ru^{III} complex $[\{Cp^{\wedge}\text{-}Ru(\mu\text{-}O)\}_2\text{dppm}]$ (**10**). In **10**, the μ-O bridge is a weaker donor than μ-OH, leading to a stabilization of Ru^{II} *vs.* Ru^{III} and a positive shift of the Ru^{II}/Ru^{III} potentials. Attempts to isolate **10** in preparative oxidations, however, were unsuccessful.

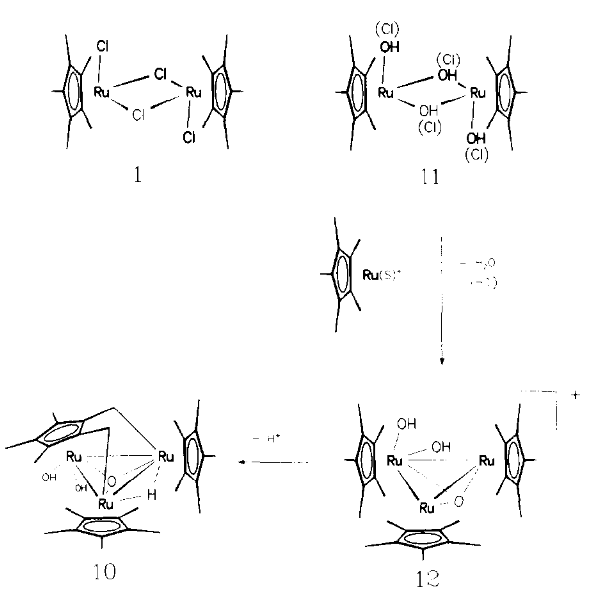
$$Cp^{\wedge}Ru(\mu\text{-}OH)_2(\mu\text{-dppm})RuCp^{\wedge} \xrightleftharpoons{-2e,2H^+} Cp^{\wedge}Ru(\mu\text{-}O)_2(\mu\text{-dppm})RuCp^{\wedge}$$

2.4. *Hydrolysis of* $[Cp^{*}/^{\wedge}RuCl_2]_2$ (**1**) in alkaline medium

In the light of the results for the hydrolysis of **2** and its electrochemical oxidation, the study of the hydrolysis of a related $Cp^{*}Ru^{III}$ complex to yield $Cp^{*}Ru^{III}$ as aqua-, hydroxo- or oxo-species appeared as a logical extension. The chloro complex **1** was considered the most reasonable starting point for this study. For solubility reasons, the experiment was conducted in a 10 : 1 methanol/water mixture, in which **1** was stirred over solid K_2CO_3. The reaction yielded a complex mixture of products with a trinuclear Ru cluster molecule **11** as the only characterizable product isolated after chromatography in about 30% yield. The identity of **11a** was established by ^1H and ^{13}C spectroscopy by comparison with the product obtained (fortuitously as in the present case) previously by Chaudret *et al.* from **2a** and $KHSO_5$ [15]; **11a** gives NMR data in close agreement with those given by the latter workers. In addition to methyl resonances in the ratio 10 : 2 : 1 there is a hydride signal at −24 ppm and an AB-quartet for the bridging methylene protons, with the low field hydrogen showing an additional long range coupling of 0.7 Hz to the bridging hydride (see Experimental section).

When the reaction was performed with the $Cp^{\wedge}$ derivative **1b** as the starting halide, the expected two isomers were found by NMR spectroscopy, and were assigned to the two possible positions of the ethyl group with respect to the bridging methylene groups. In the Chaudret cluster, one Ru is coordinated to a bidentate anion, but since the IR spectrum of **11** did not show the presence of a coordinated CO_3^{2-} ligand, two hydroxo groups are most probably bound to Ru(1), in good agreement with the analytical composition of **11a**.

The detection of cluster **11** under these conditions makes it clear that this trimer does not contain an oxygen donor but instead contains $Cp^{*}Ru$ moieties in both oxidation states. In the present case, this is the result of partial reduction of the starting Ru^{III} complex; in the reaction of Chaudret *et al.* partial oxidation of Ru^{II} to Ru^{III} by persulfate obviously leads to the same result. The outline of a possible mechanism for the formation of the compound is presented in Scheme 2. The key features are the formation of a trinuclear unit from a dimer and a monomer, which may be preceded by partial or complete hydrolysis of Cl^- ligands. A precedent for such a "one plus two addition" is provided by the formation of the cluster cation $[(Cp^{*}Ru)_3(\mu_3\text{-}OMe)_2]^+$ in high yield by the action of weak acid on **2** [16], in which a $Cp^{*}Ru^+$ unit reacts with $[Cp^{*}Ru(OMe)]_2$. The second step is deprotonation of one Cp^{*} methyl group and internal oxidative addition to a vicinal unsaturated Ru centre of a second one. Formation of fulvenic ligands from Cp^{*} is



Scheme 2.

quite common, and has been observed in many different systems under a wide variety of conditions [17,18]. (In Chaudrets reaction, a superoxide O_2^-, formed from $KHSO_5$, could abstract a methyl hydrogen, paralleling the well studied hydrogen abstraction from methyl groups of electron rich CpFe(hexamethylbenzene) or $Fe(hexamethylbenzene)_2$ by molecular oxygen [19]).

3. Experimental details

All preparations were conducted under pure nitrogen by conventional Schlenk techniques, NMR spectra are from Bruker SY 80 and Varian Unity 300 instruments. Elemental analyses are from Analytische Laboratorien, 5203 Engelskirchen, Germany.

3.1. *Tetrakis[(pentamethylcyclopentadienyl)(μ_3-hydroxo)ruthenium] (3a)*

A solution of 170 mg (0.318 mmol) of $[Cp^*Ru(\mu\text{-}OMe)]_2$ (**2a**) in 25 ml of pentane was stirred with 3 ml of air-free water for 30 min, during which the cherry red solution turned yellowish brown. The pentane layer was separated, filtered, and cooled to −78°C. Brown crystals separated after a few days, and were isolated and dried *in vacuo*. Yield was 105 mg (65%). ^1H NMR (CD_2Cl_2): δ 1.61 (s, 15H, Cp^*); −0.14 (s, 1H, OH). Anal. Found: C, 47.37; H, 6.36. $C_{10}H_{16}RuO$ calcd. (M_r 253.3): C, 47.42; H, 6.37%.

3.2. *Tetrakis[(tetramethylethylcyclopentadienyl)(μ_3-hydroxo)ruthenium] (3b)*

This compound was prepared in an analogous manner to **3a**. After separation of the pentane solution, the water layer was extracted twice with 20-ml portions of pentane. The residue that remained after evaporation of the combined pentane solutions was dried *in vacuo* and found to be spectroscopically pure. Yield 79%. Crystals for X-ray analysis were grown from pentane at −78°C. ^1H NMR (C_6D_6): δ 1.68, 1.71 (2s, 12H, $Cp^{\wedge}$); 1.10 (3H, t, $^3J = 7.4$ Hz, $Cp^{\wedge}$), 2.25 (2H, q, $Cp^{\wedge}$); −0.04 (1H, s, OH).

3.3. *Reaction of **3b** with MeOH / K_2CO_3*

A solution of 160 mg (0.15 mmol) of **3b** in 20 ml of MeOH was stirred with 2 g of dried (200°C) K_2CO_3 for 4 h during which the mixture took on the cherry red colour of **2b**. After evaporation of methanol, the residue was dried *in vacuo* and extracted with several portions of pentane. Evaporation of the pentane left 120 mg (71%) of **2b**, identified from its ^1H NMR spectrum.

3.4. *Reaction of **3b** with DPPM*

A solution of 120 mg (0.112 mmol) of **3b** in 10 ml of THF was stirred with 86 mg (0.225 mmol) of DPPM for 1 week at ambient temperature. (The reaction was taken to completion as indicated by NMR monitoring). THF was evaporated off and the residue extracted with pentane. Evaporation of the pentane left $[Cp^{\wedge}\text{-}Ru(OH)]_2DPPM$ (**5b**) (identified by spectroscopy) in quantitative yield.

3.5. *$[\{Cp^*Ru\}_2(\mu_2\text{-}H)(\mu_3\text{-}O)\{(\eta^5\text{-}C_5Me_3\eta^1:\eta^1\text{-}(CH_2)_2)Ru\}(OH)_2]$ (11a)*

A sample of $[Cp^*RuCl_2]_2$ (350 mg, 0.572 mmol) was stirred with a 10:1 mixture of methanol/water in the presence of 2 g of K_2CO_3 overnight. The solvent was evaporated from the ensuing red-brown air-sensitive solution and the residue extracted with THF. The extract was chromatographed on 30 cm Al_2O_3 (5% H_2O); THF eluted 60 mg of an unidentified species, then THF/MeOH (10:1) eluted **10a** as an orange species. After evaporation of the solvent *in vacuo*, the residue was redissolved in the minimum amount of THF by addition of a few drops of MeOH and crystallized by diffusion of pentane into this mixture. The yield was 120 mg (30%) of dark-brown, cube-shaped crystals. ^1H NMR (C_6D_6): δ 1.47 (30H, s, Cp^*); 0.70 (s, 6H); 2.18 (s, 3H); $C_5Me_3(CH_2)_2$, AB-q: δ_A 1.94, δ_B 0.34, $^2J_{AB} = 5.6$ Hz, $^3J_{A\text{-hydr.}} = 0.7$ Hz; $C_5Me_3(CH_2)_2$, −24.08 (s, 1H, μ_2-H). Anal. Found: C, 47.37; H, 5.96. $C_{30}H_{46}O_3Ru_3$ calcd. (M_r 757.9): C, 47.54; H, 6.12%.

The analogous reaction starting from 220 mg (0.344 mmol) $[Cp^{\wedge}RuCl_2]_2$ gave after nearly identical work-up (but with pentane/ether/THF for crystallization) 50 mg (27%) of red crystals of $[\{Cp^{\wedge}Ru\}_2(\mu_2\text{-}H)(\mu_3\text{-}O)\{(\eta^5\text{-}C_5Me_2Et\text{-}\eta^1:\eta^1\text{-}(CH_2)_2)Ru\}(OH)_2]$ as a mixture of isomers which could not be separated. Selected

TABLE 2. Positional parameters and their estimated standard deviations

Atom	x	y	z	B [a] (Å^2)
Ru1	0.5226(1)	0.2008(1)	0.1469(1)	4.17(5)
Ru2	0.4078(1)	0.3555(1)	0.2201(1)	4.32(5)
O1	0.4336(8)	0.2206(8)	0.2264(9)	3.7(4)
O2	0.5187(8)	0.3347(8)	0.1700(8)	3.4(4)
C01	0.515(3)	0.240(3)	−0.134(3)	23(2) *
C02	0.227(4)	0.418(5)	0.346(5)	45(6) *
C10	0.521(2)	0.194(2)	0.020(2)	6.9(8) *
C11	0.593(2)	0.177(2)	0.051(2)	8.5(9) *
C12	0.595(2)	0.109(2)	0.104(2)	7.8(9) *
C13	0.513(1)	0.083(2)	0.096(2)	5.1(7) *
C14	0.476(1)	0.136(2)	0.048(2)	5.3(7) *
C15	0.509(2)	0.269(2)	0.039(2)	15(2) *
C16	0.665(2)	0.222(3)	0.027(3)	18(2) *
C17	0.640(2)	0.053(3)	0.157(3)	15(2) *
C18	0.482(2)	0.002(2)	0.133(2)	12(1) *
C19	0.399(2)	0.134(2)	0.016(2)	13(1) *
C20	0.316(2)	0.412(2)	0.267(2)	6.4(8) *
C21	0.293(2)	0.359(2)	0.198(2)	8.7(9) *
C22	0.329(2)	0.389(2)	0.125(2)	5.8(7) *
C23	0.367(2)	0.460(2)	0.151(2)	5.8(7) *
C24	0.360(2)	0.472(2)	0.241(2)	6.6(8) *
C25	0.302(2)	0.421(3)	0.363(3)	15(2) *
C26	0.240(2)	0.288(2)	0.209(2)	15(2) *
C27	0.317(2)	0.356(2)	0.039(2)	10(1) *
C28	0.415(2)	0.508(2)	0.092(2)	11(1) *
C29	0.392(2)	0.550(2)	0.282(2)	13(1) *

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ac(\cos\beta)B_{1,3}]$.

^{1}H NMR absorptions (C_6D_6): δ $\mathrm{Cp}^{\wedge}$ 1.56, 1.57 (two s, 24H); 0.77 (s, 6H); 20.82 (s, 3H); 2.23 (s, 3H); $C_5Me_2Et(CH_2)_2$, μ_3-H −23.98, −24.15 (two s, 1H).

3.6. X-Ray structure determination of $[\mathrm{Cp}^{\wedge}\ \mathrm{RuOH}]_4$

Single crystals were grown from pentane. Geometrical and intensity data were collected on an Enraf-Nonius CAD4 diffractometer using Mo $K\alpha$ radiation (graphite monochromator) at room temperature. The compound crystallizes in the monoclinic space group $C2/c$ (No. 15) with $a = 18.152(6)$, $b = 15.969(4)$, $c = 15.992(1)$ Å, $\beta = 92.63(1)°$, $Z = 8/2$, $D_{calc} = 1.534$ g cm^{-3}, μ(Mo Kα) = 12.9 cm^{-1}. A total of 7186 reflections were collected in the $+h+k\pm l$ quadrant of the Ewald sphere; only 1240 independent intensities had $I > 2.5\sigma(I)$. To maintain a reasonable ratio between observations and variables, only the metal and oxygen atoms were refined anisotropically. The structure was solved and refined with the SDP package [20]. An empirical absorption correction was applied. With hydrogen atoms in calculated positions, refinement converged at $R = 0.079$, $R_w = 0.081$ ($w^{-1} = \sigma^2(F_o)$) with 1240 observations for 126 parameters. A final difference Fourier synthesis showed a local maximum of 0.82 e Å^{-3} close to a ring carbon atom. Coordinates for non-hydrogen atoms are listed in Table 2.

The terminal atoms C01 and C02 in the ring-ethyl groups show very high thermal parameters. This is not surprising in view of the fact that these atoms are the most peripheral ones and will suffer most from libration movements. There was, however, no indication for alternative or disordered positions for these atoms, and so no attempt was made to develop a more sophisticated model.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 56818, the names of the authors, and the journal citation.

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