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Complexation and aromatization of α,β-unsaturated cyclic ketones by $Ru(H_2O)_6^{2+}$ and $(Bz)Ru(H_2O)_3^{2+}$: molecular structure of (η^6-Tosylate)(η^5-hydroxycyclopentadienyl)Ru and of (η^6-Tosylate)(η^6-1,4-dihydroxy-2,3,5,6-tetramethylbenzene)Ru

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Abstract

$Ruaq^{2+}(OTs)_2$ complexes in aqueous solution to unsaturated cyclic ketones. These aromatized on heating to π-arene Ru complexes. Thus, with cyclohexenone the main product was $Ru(\eta^6\text{-phenol})_2^{2+}$, 4, along with some $Ru(\eta^6\text{-phenol})(\eta^6\text{-OTs})^+$, 6. Similarly gave cyclopentenone in the presence of various arenes $Ru(\eta^5\text{-hydroxycyclopentadienyl})(\eta^6\text{-arene})^+$. Duroquinone complexed to $Ruaq^{2+}$ as a monoprotonated hydroquinolate in $Ru(\eta^6\text{-2,3,5,6-tetramethyl-1,4-hydroquinone})(\eta^6\text{-OTs})$, 14. $Ru(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-OTs})$, 8, and 14 were characterized by single crystal x-ray structure analyses, data see Table 1. Whereas both ligands in 8 are planar, the 1,4-hydroquinone ligand in 14 shows distinct bending of the COH groups.

Keywords: Ruthenium; Unsaturated cyclic ketones

1. Introduction

During the last few years the amazing ability of the $Ru(H_2O)_6^{2+}$ ion (**1**$^{2+}$) to form complexes with carbon-based acceptor ligands, notably olefins, in water or alcohol has been recognized and is currently being explored by several groups. Thus, by pressurizing an aqueous solution of **1**$(OTs)_2$ with CO or N_2 the formation of $[Ru(H_2O)_5(CO)]^{2+}$, $[Ru(H_2O)_5(N_2)]^{2+}$ and even $[Ru(H_2O)_5(\mu\text{-}N_2)Ru(H_2O)_5]^{4+}$ was shown by ^{17}O and ^{15}N NMR [1]. Similarly the coordination of ethylene to **1**$^{2+}$ in water under pressure has been demonstrated followed by catalytic coupling of two molecules of ethylene to yield a mixture of butenes [2]. A variety of activated olefins such as allyl and allenyl ethers and alcohols, 3,4-unsaturated carboxylic acids as well as strained olefinic double bonds in norbornene and norbornene derivatives readily form complexes with **1**, replacing up to four water ligands [3,4]. Complex formation incorporating pending diolefins such as 1,5-hexadiene has been proven spectroscopically in solution [4]. In contrast, diolefins such as 1,5-cyclooctadiene (COD) or norbornadiene (NBD) reacted with **1**$^{2+}$ in ethanol with formation of rather stable complexes $[(COD,NBD)Ru(H_2O)_4]^{2+}$ which could be crystallized and structurally characterized [5]. Different from the monoolefin complexes where the olefinic double bond is easily displaced even by weak donor molecules, some or all of the water ligands in $[(COD,NBD)Ru(H_2O)_4]^{2+}$ could be substituted by for example, acac or bipy without removing the diolefinic ligand [5].

A somewhat different reaction is encountered if **1**$^{2+}$ is treated with cyclic or acyclic dienes in the presence of an arene; complexes of the type $Ru(arene)(dienyl)^+$ or even $Ru(dienyl)_2$ are formed in ethanol at ambient temperature [6]. In cases where **1**$(OTs)_2$ is the Ru salt and no extra arene is present a complex featuring an η^6-tosylate ligand will result. It seems, however, that the exact course of the reaction depends on subtle differences in the reaction conditions. Thus, whereas

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1$(OTs)_2$ with either 1,5- or 1,3-COD in ethanol gave $(\eta^6\text{-tosylate})Ru(C_8H_{11})^+$ in one laboratory [6], essentially the same reagents have given a quantitative yield of $[(COD)Ru(H_2O)_4]^{2+}$ in our laboratory [5]. Repeated experiments with different samples of **1**$(OTs)_2$ indicate that the water content in the reaction mixture as a critical factor.

A further point of importance is the fact that arenes do complex to $\mathbf{1}^{2+}$ only in the presence of some diene or polyene. Thus the direct formation of the well-known well-characterized stable aqua ion $[(C_6H_6)Ru(H_2O)_3]^{2+}$ ($\mathbf{2}^{2+}$) [7,8] directly from $\mathbf{1}^{2+}$ and benzene or any similar arene has never been effected. The same is true for the formation of the widely used arene complexes $[(arene)RuCl_2]_2$ (**3**) which are synthesized invariably from $RuCl_3$ and a cyclodiene but never from the arene directly [9–11]. On the contrary, arene exchange in **3**, commonly for a higher alkylated derivative is most readily achieved and has become commonly used in (arene)Ru half-sandwich chemistry.

Our experiments with $\mathbf{1}^{2+}$ have led us to the observation that olefinic double bonds of the type –CH=CH–C=O form loose complexes in aqueous solution and these can be transformed into stable bonding modes under more forcing conditions. In this way, novel η^6-arene- and η^5-cyclopentadienyl complexes featuring hydroxy and oxy functionalities are formed which may be of synthetic value and which are not easily obtained by other routes.

2. Experimental details

2.1. *Bis-(η^6-phenol)ruthenium-tosylate (4)*

A solution of 300 mg (0.54 mmol) **1**$(OTs)_2$ in 5 ml of H_2O was stirred with 0.55 ml (5.5 mmol) of 2-cyclohexenone at 70°C for 24 h. The pale-yellow solution was concentrated in vacuo and extracted several times with ether to remove excess cyclohexenone. The yellow powder remaining after the water had been evaporated was washed three times with 5 ml of acetone and dried. It is spectroscopically pure. The yield was 250 mg (74%). Crystallization from MeOH–ether gave 200 mg (60%) of analytically pure compound. The tosylate salt is air stable and soluble in polar solvents (H_2O, MeOH, dimethylsulphoxide (DMSO) and $MeNO_2$). It does not precipitate as a PF_6^- salt from water. ^1H NMR (CD_3OD): δ 6.41 (d/d, 4H, H_m), 6.16 (t, 2H, H_p), 6.06 (d, 4H, H_o), OTs: 2.35 (Me), 7.68, 7.26 (AB-quartet). ^{13}C NMR (CD_3OD): δ 142.1 (C–OH), 80.8 (*o*-C), 93.4 (*m*-C), 85.5 (*p*-C), OTs: 21.4 (Me), 142.8 (*C*-Me), 130.0, 126.8 (C_{arene}), 150.5 (*C*-SO_3). IR (KBr, cm^{-1}): ν(C–O) 1551, 1237. Anal. Found: C, 48.09; H, 4.03. $C_{26}H_{28}O_9S_2Ru$ (M_r = 649.7) ($[(C_6H_5OH)_2Ru](OTs)_2 \cdot H_2O$) calc.: C, 48.06; H, 4.34%.

2.2. *(η^5-Hydroxycyclopentadienyl)(η^6-tosylate)ruthenium (8)*

A solution of 250 mg (0.45 mmol) of **1**$(OTs)_2$ and 380 mg (4.6 mmol) of 2-cyclopentenone in 5 ml of H_2O was refluxed for 3 days. After cooling, the solution was filtered from a small amount of solid and extracted with ether; then the aqueous phase brought to dryness. The remaining greyish solid was washed with acetone and dried. The yield was 69%. Analytically pure compound was obtained by crystallization from MeOH at −80°C. ^1H NMR (CD_3OD): δ 5.04, 5.23 (4H, AA'BB', J_{AB} = 1.8 Hz, cyclopentadienyl), ^{13}C NMR (CD_3OD): δ η^6-OTs: 136.5 (*C*–SO_3), 84.4 (C(2)), 87.9 (C(3)), 103.3 (*C*–Me), 19.4 (Me), C_5H_4OH: 70.8 (C(6)), 77.7 (C(7)), 107.7 (*C*–OH). IR (KBr, cm^{-1}): ν (C–O) 1525, 1251. Anal. Found: C, 41.53; H, 3.59. $C_{12}H_{12}O_4SRu$ (M_r = 353.3) calc.: C, 40.79; H, 3.42%.

2.3. *(η^5-Hydroxycyclopentadienyl)(η^6-benzene)ruthenium-tosylate (11)*

400 mg (0.7 mmol) of $[(C_6H_6)Ru(H_2O)_3](OTs)_2$ and 1 ml (11 mmol) of 2-cyclopentenone was refluxed in 30 ml of water for 24 h. After concentration and extraction with ether the aqueous phase was brought to dryness in vacuo to leave a brown oil which solidified on treatment with a few mililitres of acetone to give an ochre solid with 62% yield. According to NMR this material contains a slight excess tosylate. Recrystallization from MeOH at −80°C gave 0.31 mmol (45%) pale-yellow crystals. ^1H NMR (CD_3OD): δ: 5.98 (s, 6H, benzene), 5.22, 4.93 (4H, AA'BB', J = 2 Hz, cyclopentadienyl), 7.16, 7.64 (4H, AB-quartet, OTs), 2.27 (s, 3H, OTs). ^{13}C NMR (CD_3OD): δ: OTs: 143.7 (*C*–SO_3), 141.8 (*C*–Me), 126.9, 129.9 (C(3), C(4)), 21.3 (Me), C_5H_4OH: 136.1 (*C*–OH), 69.3, 75.4 (C(7), C(8)), C_6H_6: 87.0. Anal. Found: C, 49.94; H, 4.00. $C_{18}H_{18}O_4SRu$ (M_r = 431.5) calc.: C, 50.11; H, 4.20%.

2.4. *(η^5-Hydroxycyclopentadienyl)(η^6-mesitylene)ruthenium-sulphate (9)*

1 mmole of $[Ru(H_2O)_6]SO_4$ was refluxed with 20 mmol of 2-cyclopentenone and 20 mmol of mesitylene in a 1:1 mixture of water–*sec*-butanol for 10 h. The product was isolated as detailed above with about 80% yield. ^1H NMR (CD_3OD–D_2O): δ 6.02 (s, 3H, mesitylene), 2.25 (s, 9H, mesitylene), 5.08, 4.87 (4H, AA'BB', J = 1.9 Hz, cyclopentadienyl).

2.5. *(η^5-Methoxycyclopentadienyl)(η^6-mesitylene)ruthenium-sulphate (13)*

A suspension of **9** was stirred in MeOH for 15 h at ambient temperature, whence the solid dissolved. The yield was quantitative. ^1H NMR (CD_3OD): δ: 5.75 (s, 3H, mesitylene), 2.21 (s, 9H, mesitylene), 4.64, 4.40 (4H, AA'BB', $J = 1.8$ Hz, cyclopentadienyl), 3.67 (s, 3H, OMe).

2.6. (η^6-1 Hydroxy-4-oxy-2,3,5,6-tetramethylbenzene)-(η^6-tosyl)ruthenium (14)

300 mg (0.54 mmol) of **1**$(OTs)_2$ and 770 mg (4.7 mmol) of duroquinone were refluxed for 15 h in 7 ml of *sec*-butylalcohol (117°C). After cooling, the green reaction mixture was concentrated to 0.5 ml, and 20 ml of ether added to precipitate 230 mg (98%) of a greenish-white solid which was dissolved in hot water and crystallized by cooling to 5°C to yield 170 mg (72%) of yellowish crystals. ^1H NMR (CD_3OD): δ: 6.045, 6.35 (4H, AB-quartet, $J_{AB} = 6.4$ Hz, OTs), 2,22 (3H, OTs), 2.19 (12H, tetramethylbenzene): ^{13}C NMR (CD_3OD): δ: η^6-OTs: 113.0, 108.6 (C–SO_3,C–Me), 91.6, 95.0 (c arene), 17.1 (Me), η^6-$C_6Me_4(OH)_2$: 141.9 (C–OH), 98.0 (C–Me), 13.9 (Me). IR (KBr, cm^{-1}): ν (C–O) 1532; 1256. Anal. Found: C, 46.92; H, 4.82. $C_{17}H_{20}O_5SRu$ ($M_r = 437.5$) Calc.: C, 46.67; H, 4.61%.

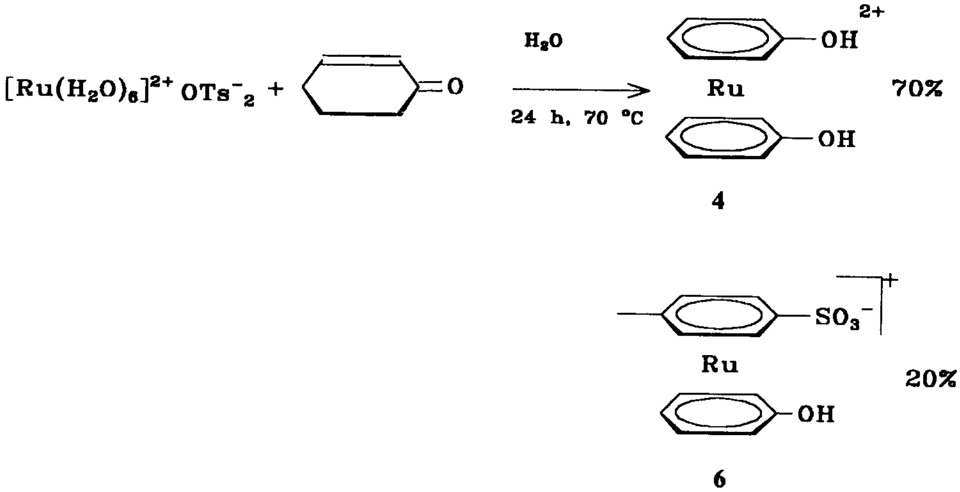
2.7. X-ray structure determinations

Both geometry and intensity data for **8** and **14** were collected on an Enraf–Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.7107 Å; graphite monochromator). The structures were solved by Patterson and difference Fourier synthesis with our local version of the SDP program system [12].

An empirical absorption correction was applied before averaging symmetry equivalent reflections [13]. Hydrogen atoms were included with refined isotropic displacement parameters in the case of **8** and calculated temperature factors ($B_{iso}(H) = 1.3 - B_{iso}(C)$) for **14**. Crystal data, data collection parameters, and convergence results are compiled in Table 1. The duroquinone moiety in **14** shows disorder; in addition to the orientation represented later in Fig. 2 (occupancy, above 0.75), the presence of a minority isomer (with an occupancy of above 0.25) was detected which corresponds to a ring rotation of 60°. The disorder extends to the oxygen atom of the water molecule, too. Only split positions for the latter were considered, because the atom positions in the duroquinone ring were not

Table 1
Crystal data, data collection parameters and refinement results

	8	**14**
Formula	$C_{12}H_{12}O_4RuS$	$C_{17}H_{22}O_6RuS$
Space group	$P2_1/n$	$Pna2_1$
a (Å)	7.003(2)	15.588(4)
b (Å)	11.918(2)	8.882(4)
c (Å)	14.023(2)	12.343(5)
β (°)	93.99(2)	90.0
V (Å^3)	1167.5(7)	1708(1)
Z	4	4
d_{calc} (g cm^{-3})	2.010	1.770
T (K)	293	258
Scan range	$0° < \theta < 35°$	$3° < \theta < 28°$
Scan type	$\omega - \theta$	ω
Number of reflections	5686	3525
Number of independent reflections	5343	3214
Number of observed independent reflections	3189	2748
Cut-off $I > n - \sigma(I)$	3	1.5
Number of parameters	175	238
R	0.039	0.035
R_w; $w^{-1} = \sigma^{2(F_0)}$	0.045	0.049



Scheme 1.

sufficiently well separated to allow for an individual refinement. The discussion of the molecular structure (see below) refers to the predominant orientation of Fig. 2.

3. Results

3.1. Syntheses

When a stoichiometric amount of 2-cyclohexene-1-one is added to an aqueous solution of **1**$(OTs)_2$ the pink solution turns red within 1 min. Displacement of the olefinic protons from 7.28(β)/6.02(α) to 6.48/5.89 ppm with concomitant decrease in the olefinic coupling is a clear indication of olefinic coordination, forming presumably a monoolefin complex **3**. However, attempted isolation of the complex resulted in decomposition. If $\mathbf{1}^{2+}$ is treated with an excess of the unsaturated ketone in water at ambient temperature, a pale-yellow material separates which shows mostly CH_2 signals altogether with minor quantities of olefinic multipletts in the ^1H NMR and bands due to C=O (1701 cm^{-1}), C=C (1667 cm^{-1}) and C–O–C (1257 cm^{-1}) in the IR, suggesting a polymer with ether linkages as well as free carbonyl groups. The NMR spectrum of the orange water solution remaining from the polymerization was rather complex and most probably contains a mixture of (olefin) Ru species.

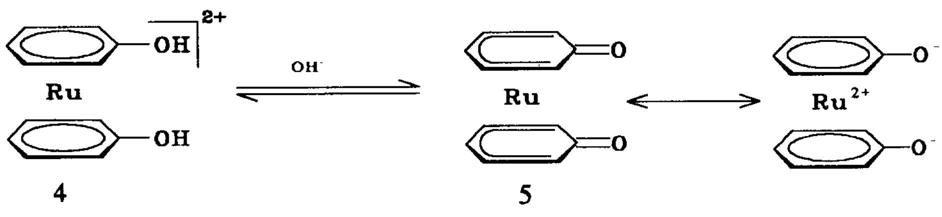
When the solution was heated for 24 h at 70°C (see Section 2), nearly all the Ru could be recovered in the form of the bis-phenol cation **4** (Scheme 1). Complete aromatization of cyclohexenone has taken place to form the phenol ligand. NMR and gas chromatography (GC) investigation of the organic material that was extracted with ether gave accordingly a higher proportion of CH_2 to CH protons than in the starting ketone, indicating the formation of some cyclohexanone by hydrogen transfer to the unsaturated ketone. Such hydrogen transfer in the course of a complexing aromatization has been observed at virtually any transition metal. [14]

Bis-(arene)Ru complexes have been intensely investigated but, since the synthesis is predominantly via arene exchange in $[(arene)RuCl_2]_2$, functionalities such as OH (or OR) groups in both arene rings are not readily accommodated. Crystallized and isolated **4** is the bis-phenol dication and dissolves as such in water. In contrast with all known bis-(arene)Ru cations it does not precipitate as for example the PF_6- salt from water, a fact that complicates isolation and purification of the compound.

Deprotonation to the neutral bis-ketone complex **5** can be effected with KOH in water and is indicated by a high field shift of the aromatic protons in the ^1H NMR spectrum (CD_2Cl_2), from 6.4 to 5.85 ppm in **4** to 5.15(d/d) and 5.6 ppm (m) in **5**. The ketonic sandwich **5**, because of its polar resonance form as indicated in Scheme 2, may be either hydrogen bonded or hydrated in water; it is therefore extracted with CH_2Cl_2 from the aqueous mixture only with difficulty and with a low yield. The same situation has been encountered previously with the corresponding Cp* complex Cp*Ru-$(C_6H_5\text{–}OH)^+$/Cp*Ru$(C_6H_5\text{=}O)$ [15]. The reaction can also be run at a lower temperature but requires a longer time (2 weeks at 20°C; 2 months at 0°C). A byproduct of the reaction was the tosylate cation **6**, which formed in increasing proportion for increasing reaction temperature.

Similarly to cyclohexenone, cyclopentenone also reacted with **1**$(OTs)_2$, first by complex formation and then under heating by aromatization to give a π-hydroxycyclopentadienyl ligand. Formation of an olefin complex on addition of the cyclopentenone to aqueous **1** was again evident from the development of an orange colour and a shift of the olefinic protons from 6.15 (α)/7.94(β) in the free ligand to 5.16/6.93 in the monoolefin complex **7**.

From **1**$(OTs)_2$ and cyclopentenone, only the tosylate hydroxycyclopentadienyl complex **8** was obtained (Scheme 3). When **1**(SO_4) was employed as the Ru salt, no complexes could be isolated, and in particular no dihydroxyruthenocene was found. In contrast, when an arene was added deliberately, as was probed with mesitylene, the corresponding (mesitylene)(hydroxycyclopentadienyl)Ru cation **9** was obtained with a good yield (Scheme 3). **1**$(OTs)_2$ and cyclopentenone in the presence of excess hexamethylbenzene (HMB) again gave mostly the tosyl complex **8** with only about 20% of (HMB)(hydroxycyclopentadienyl)Ru^+ (**10**) (Scheme 3). The reaction extended to the 2,3,4,5-tetramethylcyclopent-2-ene-1-one (a common precursor for the



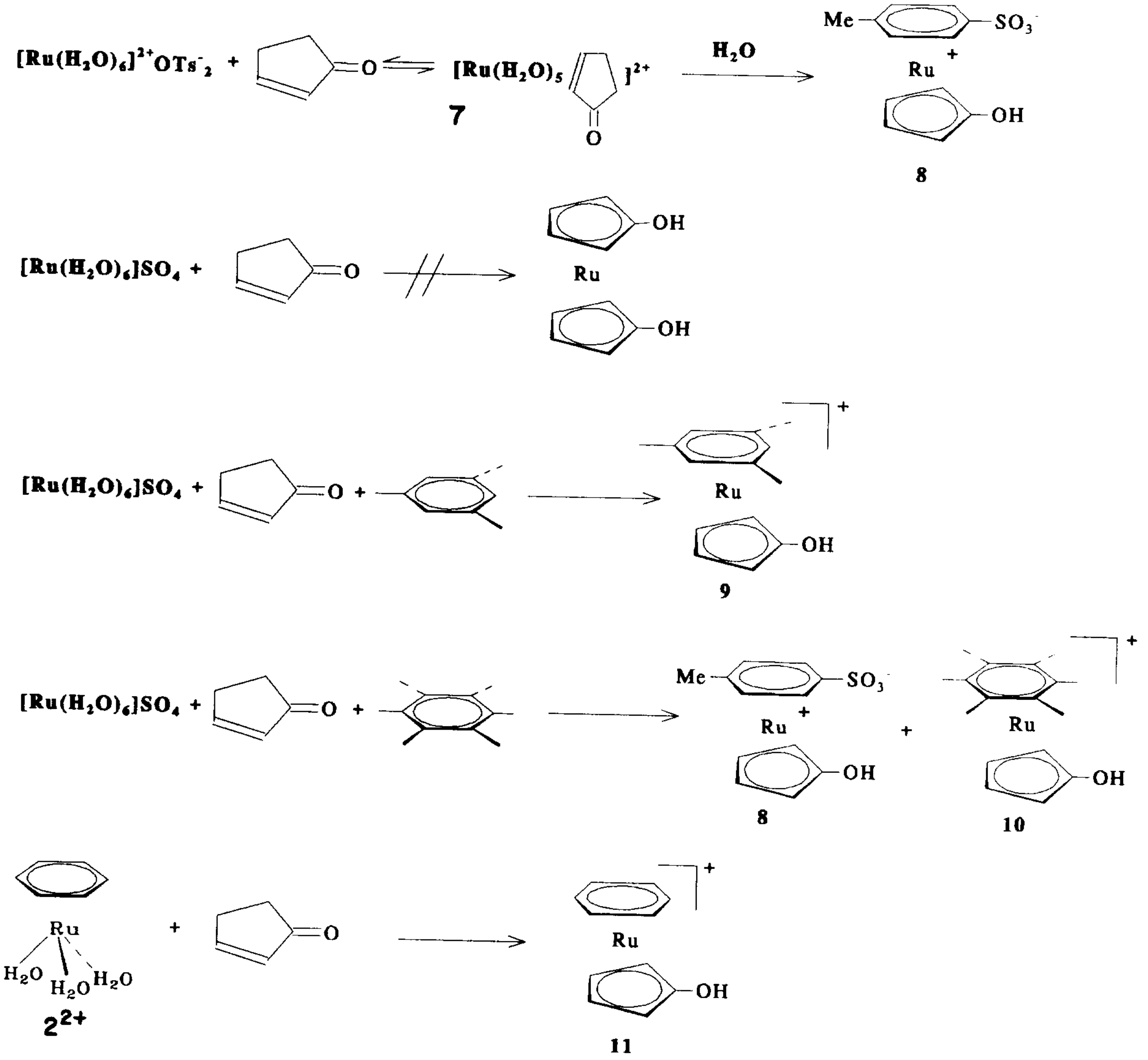
Scheme 2.

preparation of pentamethylcyclopenta-diene) failed completely. No complexation was observed.

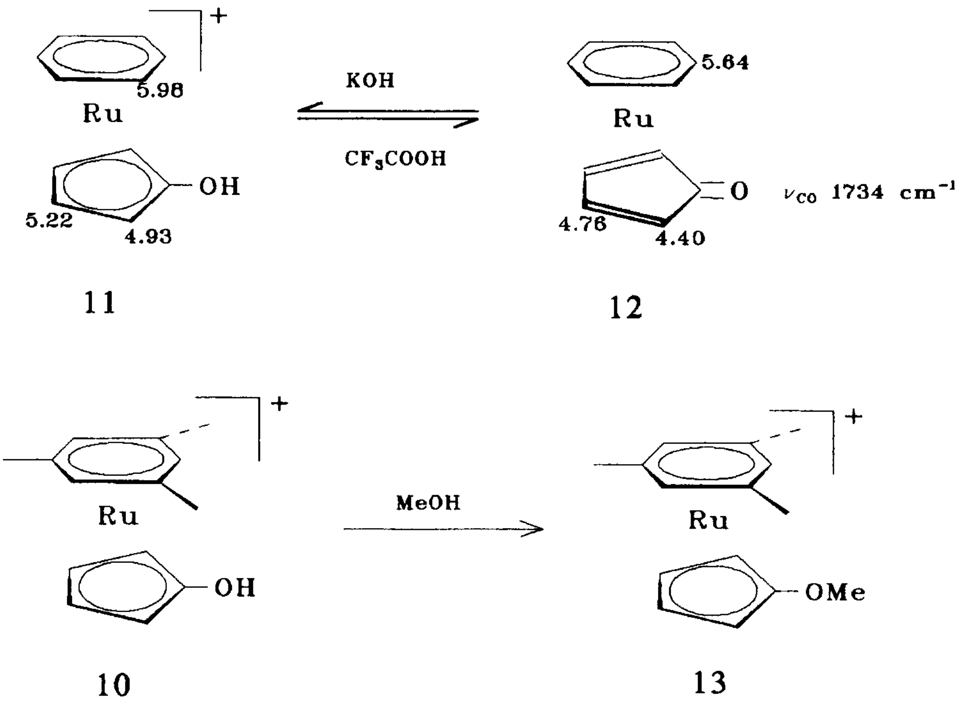
To probe whether a preformed arene-aqua ion will effect similar aromatization the benzene-aqua-ruthenium ion 2^{2+} was reacted with cyclopentenone under virtually the same conditions and gave the corresponding benzene complex **11** with a fair yield (Scheme 3). Although 2^{2+} appears to be less reactive in such complexation reactions, it can still give a purely organometallic product containing the benzene ligand, as has been demonstrated recently in the synthesis of the tetrahydride cation [(benzene)RuH]$_4$2^{+} from 2^{2+} and hydrogen under pressure [16].

(Arene)(hydroxycyclopentadienyl)Ru cations **8–11** are more easily deprotonated in water than is **4** or **5**. In particular, **11** seems to be converted completely into the keto form at pH 11 and, the neutral complex **12** is readily extracted from alkaline water solution with CH_2Cl_2. Resonances of either ring protons are shifted upfield in comparison with the hydroxo complex as indicated in Scheme 4. The high value for the C=O stretching frequency of **12**, typical for a ketonic C=O group, indicates little polarization towards the zwitterionic mersomeric form in sharp contrast with the phenol cation **5** discussed above. The main fragmentation pattern in the mass spectrum of **12** is extrusion of CO which gives (tentatively) a cyclobutadiene cation $(C_6H_6)(C_4H_4)Ru^+$. Such a reaction has recently been transferred from mass spectrometry into bulk thermolysis of $Cp^*Ru(\eta^6\text{-}C_6F_5O)$ to furnish the first pentafluorocyclopentadienyl complex, i.e. $Cp^*Ru(\eta^5\text{-}C_5F_5)$ [17].

All the more remarkable is the finding that, again in contrast with **5** which could not be alkylated or even silylated by electrophiles, **9** on standing in MeOH quantitatively converted to the methyl ether **13**. This



Scheme 3.



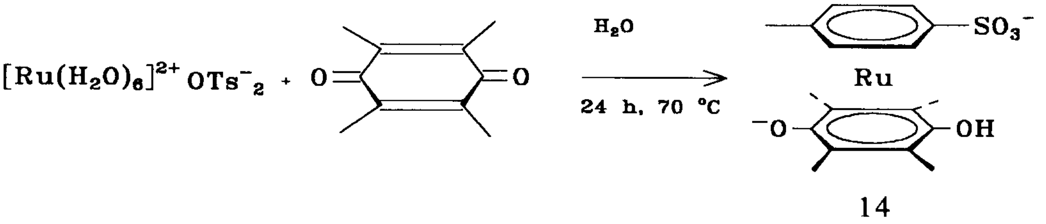
Scheme 4.

facile methylation shows that the hydroxyarene cations are susceptible to nucleophilic exchange at the ring rather than electrophilic attack at oxygen.

Finally complexation was extended to include the "preformed dihydroxyligand" duroquinone (tetramethylparaquinone). The product obtained without addition of extra arene is the η^6-tosylate complex **14** (Scheme 5). There is an ambiguity in the composition of this compound since the forms protonated to different extent, i.e. $[(\eta^6\text{-OTs})(C_6Me_4(OH)_2)Ru](OTs)$ or $[(\eta^6\text{-OTs})(C_6Me_4(OH)(O))Ru]$ cannot be distinguished in the presence of excess HOTs. The crystalline product from water did show a small amount of uncomplexed tosylate in the ^{13}C NMR spectrum. However, X-ray structure analysis of crystals grown from aqueous solution showed them to be $[(\eta^6\text{-OTs})(C_6Me_4(OH)(O))Ru] \cdot H_2O$. In a protic solvent the $p\text{-}OC_6Me_4(OH)$ ligand is of course NMR symmetric. The methyl resonances at the hydroquinone ligand are at 2.19 ppm and close to the OTs methyl group. Since methyl groups of complexed dienes tend to resonate at higher field, this is taken as an indication for an aromatic structure of the quinone ligand. The ^{13}C shift of the carbon atoms *C*–OH/O, which resonate very close to the arene carbon atoms of the OTs ligand, confirms this.

3.2. Crystal and molecular structures

Crystals of the tosyl(hydroxycyclopentadienyl) complex **8**, were obtained from MeOH without additional water. As shown in Fig. 1, the (OTs)Ru unit in **8** is bound to a planar cyclopentadienyl ligand. In the latter the inner-ring O–C distances differ by not more than 0.014 Å. The C(15)–O(4) distance amounts to 1.344(5) Å, in the range typical for phenolic C–OH bonds, but slightly shorter than C–OH in hydroxyruthenocene (1.390(7) Å) [18]. Different from the latter where all Ru–C distances are in a narrow range, the Ru atom in **8** has slipped away from the OH group, rendering the



Scheme 5.

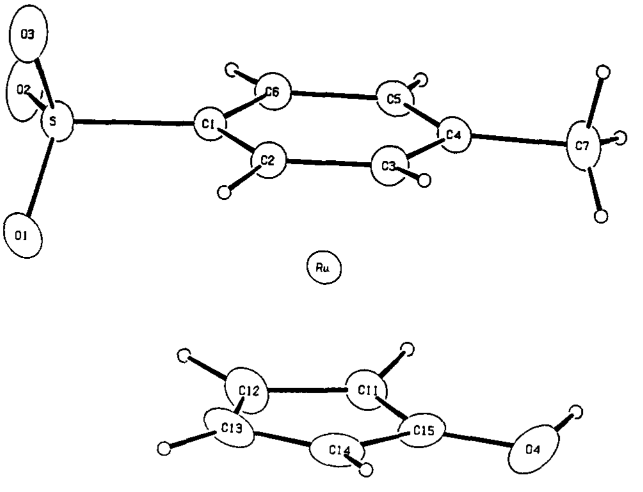


Fig. 1. Molecular structure of Ru(η^5-C_5H_4OH)(η^6-p-$MeC_6H_4SO_3$) showing 50% probability ellipsoids. The distances are as follows: Ru–C_{arene} 2.203 Å (mean); Ru–(C(11)–C(14)), 2.171 Å (mean); Ru–C(15), 2.233(3) Å; C(11)–C(12), 1.416(5) Å; C(11)–C(15) 1.410(5) Å; C(12)–C(13), 1.417(6) Å; C(13)–C(14), 1.415(6) Å; C(14)–C(15), 1.424(5) Å; C(15)–O(4), 1.344(5) Å.

Ru–C(15) sizeably longer than the other Ru–C_{Cp} distances. There is no deviation from planarity in the five-membered ring and no bending of the OH group out of the ring plane. In the crystal the OH group is hydrogen bonded to the sulphonate of an adjacent molecule, forming two sets of perpendicular strands that run through the structure.

The duroquinone complex **14** (Fig. 2) crystallizes in the orthorhombic space group $Pna2_1$ with four molecules in the unit cell. The sulphonate group is hydrogen bonded to one water molecule. The quinone is present as a hydroquinone ring featuring one C=O and one C–OH group with distinctly different C–O bond lengths of 1.276(6) and 1.312(5) Å respectively. The first is typical for C=O in a cycloenone unit [19], and the latter in the range expected for phenolic C–OH bonds [15]. Although inner-ring C–C distances in the quinone ring are rather similar and do not show any tendency for longer distances towards CO carbons atoms, the p-quinone ring nevertheless adopts a boat conformation with distinct bending away from the metal. Thus the plane defined by atoms C(2)–C(1)–C(6)–O(11) is bent outwards from the C(2)–C(3)–C(5)–C(6) plane by 10° and similarly the dihedral angle between the latter and the C(3)–C(4)–C(5)–O(14) plane is 8.7°. As a consequence, distances from Ru to the two *oxygen* bearing C atoms C(1) and C(4) are distinctly longer than to the other four.

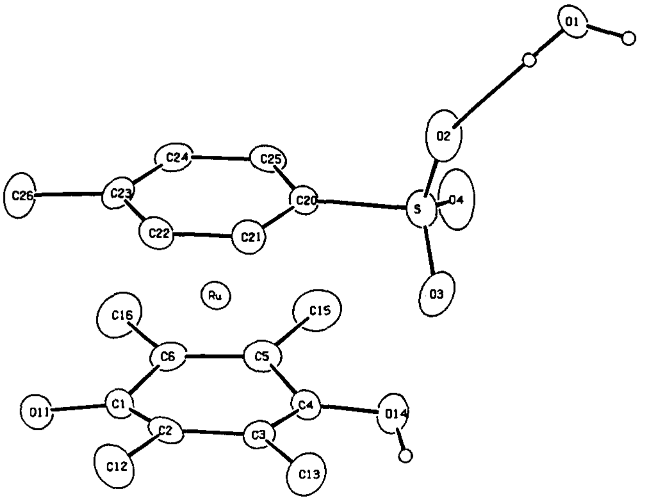


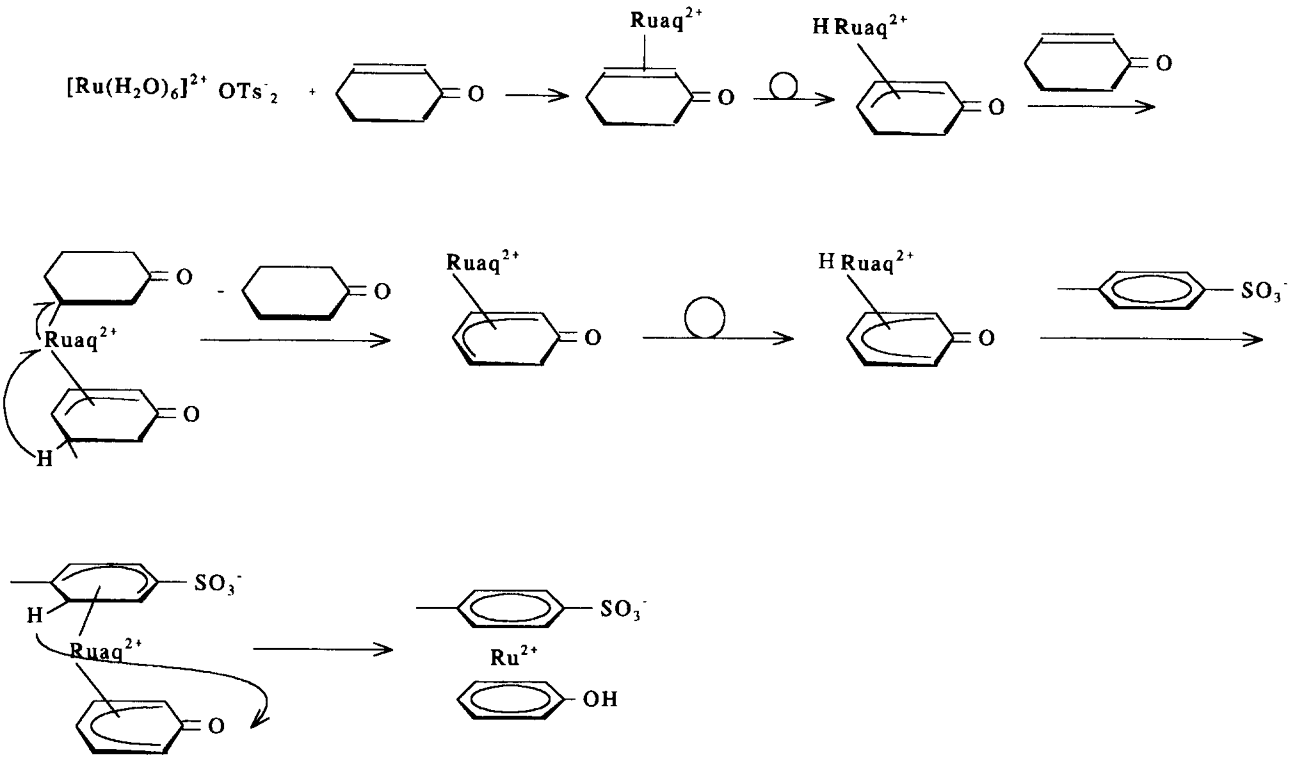
Fig. 2. Molecular structure of Ru(η^6-p-$MeC_6H_4SO_3$-H_2O)(η^6-p-OHC_6Me_4=O) showing 50% probability ellipsoids. The distances are as follows: Ru–C(1), 2.380(4) Å; Ru–C(2), 2.197(4) Å; Ru–C(3), 2.234(3) Å; Ru–C(4), 2.318(4) Å, Ru–C(5), 2.203(4) Å, Ru–C(6), 2.231(4) Å; Ru–C_{tosyl}, 2.215 Å (mean), O(11)–C(1), 1.276(5) Å; O(14)–C(4), 1.328(4) Å; C(1)–C(2), 1.405(6) Å; C(1)–C(6), 1.444(6) Å; C(2)–C(3), 1.415(6) Å; C(3)–C(4), 1.407(5) Å; C(4)–C(5), 1.433(5) Å; C(5)–C(6), 1.424(5) Å.

4. Discussion

The above experiments show that the aqua ion of Ru(II) is capable of "aromatizing" cyclic olefins when heated in water or other suitable protic solvents. This reaction is paralleled by the aromatization of cyclodienes in the preparation of complexes $[(arene)RuCl_2]_2$ by refluxing $RuCl_3$ with the precursor cyclodiene in ethanol. Similar aromatization of cyclohexenes and cyclopentenones has been observed when these cyclic olefins were treated with the $Cp^{\star}Ru^+$ cation generated in situ from $[Cp^{\star}Ru(OMe)]_2$ and acid [21]. As in the present case in this transformation one internal double bond also suffices for anchoring the Ru residue and finally induces dehydrogenative complexation.

Complex formation of $Ruaq^{2+}$ with ethylene has been devised in water at an ethylene pressure of 100 bar [2]. Complex formation with the activated olefin cyclohexenone under ambient conditions is indicated by a colour change when mixing the constituents as has been previously observed by McGrath and Grubbs [4] in the case of **1** and for example olefinic ethers. Isolation of those species is met with difficulty and has proven successful only in cases where the olefin provides more than one hapto position.

The aromatization reaction, whether of cyclohexenone or of cyclopentenone, is accompanied in most cases by concomitant complexation of an arene, notably tosylate if no other arene is present. This fact appears all the more remarkable as numerous attempts in our laboratory have shown that no arene complexation is observed if only $\mathbf{1}^{2+}$ or similar species such as $(COD)Ruaq^{2+}$ or $(benzene)Ruaq^{2+}$ is treated with excess arene under a variety of conditions. Obviously the species present in water or alcohol are not sufficiently



Scheme 6.

coordinatively unsaturated to allow simple ligand exchange complexation of an aromatic system, in contrast with arene exchange in for example [(*p*-cymene)Ru-$Cl_2]_2$ [11] or (COD)Ru(naphthalene) [20] in non-polar solvents. It thus appears that arene complexation is mechanistically tied to the dehydrogenative complexation of a cyclodiene or activated cycloalkene. A rationale for this behaviour would be the intermediacy of hydride species that are able to add an arene as suggested in Scheme 6. Key steps outlined in this scheme are successive transfer of hydrogen from the initially bound olefin to form sequentially a complexed allyl, diene and finally dienyl ligand by hydrogen transfer to the metal. From there hydrogen is transferred to either a second molecule of olefin which is hydrogenated or to the arene, giving a cyclohexadienyl which under the reaction conditions is finally reconverted to complexed arene. There are conceivable alternatives to the way outlined in Scheme 6 in that arene complexation or olefin hydrogenation could occur at different stages. The first two steps of this mechanism are in common with the dehydrogenation of cyclic olefins by "Cp*Ru$^+$" as suggested by Chaudret et al [21]. We are, however, dealing in the present case with a weakly acidic (pH 3–4) aqueous medium where formation of dihydrogen by proton–hydride reaction of a cationic Ru hydride as proposed for the analogous reaction with the Cp*Ru$^+$ unit is less likely. We therefore propose hydrogen transfer to a second molecule of olefin in accordance with the observed hydrogenation products.

Our attempts to prove the intermediacy of hydride complexes by for example effecting the complexation of arenes to $\mathbf{1}^{2+}$ in a hydrogen atmosphere have not met with success owing to the ready reduction of the aqua ion by hydrogen to metallic Ru. Nor was it possible to isolate intermediates from the above reactions. The recently obtained hydride [(benzene)RuH]$_4^{2+}$ [16] may be a good candidate for such an experiment.

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