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Organometallic aqua ions of the transition metals

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ABSTRACT

A state-of-the-art report on organometallic water complexes of the general composition $[L_\pi M(H_2O)_n]^{n+}$, where L_π is a carbon π ligand, arene, cyclopentadienyl (pentamethylcyclopentadienyl, Cp^*) or olefin. Systems studied to date are $[Cp_2^{(*)}Ti(H_2O)_2]^{2+}$, $[Cp^{(*)}Cr(H_2O)_3]^{2+}$, $[Cp^*Co(Rh,Ir)(H_2O)_3]^{2+}$, $[(arene)Ru(Os)(H_2O)_3]^{2+}$, $[(TMT)Ru(H_2O)_3]^{2+}$ (TMT = tetramethylthiophene), $[(COD, NBD)Ru(H_2O)_4]^{2+}$ (COD = 1,5-cyclooctadiene; NBD = norbornadiene), $[(CO)Ru(H_2O)_5]^{2+}$, $[(C_4R_4)M(H_2O)_3]^{2+}$ (M = Ni, Pd, Pt) as well as some olefin aqua complexes of Rh(I). In many of these systems, the tripodal oxygen ligand $[CpCo\{PO(OR)_2\}_3]^-$ can serve as a model for three coordinated water molecules, where tripod complexes are stabilized in comparison with analogous water complexes. Structural, electrochemical and kinetic parameters of water exchange are discussed.

1. INTRODUCTION

Complexes which combine organic carbocyclic ligands, such as π-arene and π-Cp, or even olefins with water at the same metal center are still relatively rare species. In their report on the first two examples, i.e. $(C_6H_6)Ru(H_2O)_3^{2+}$ and

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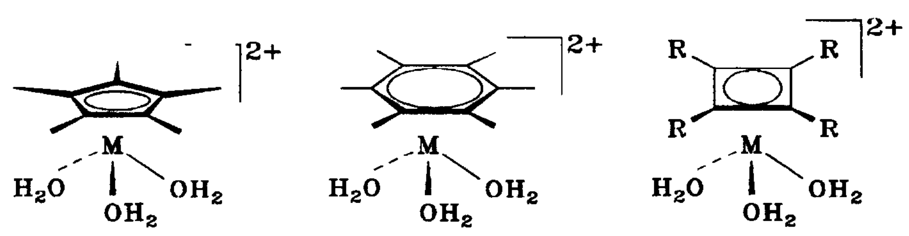
$(C_6H_6)Os(H_2O)_3^{2+}$ [1], Taube and co-workers drew attention to this obvious gap between organometallic and classical coordination chemistry of the transition metals. In fact, this gap, which can be recognized more generally in the relative paucity of complexes that feature the above types of π ligand along with hard coligands of purely σ donor character, to some extent has chemical justification but also may reflect a prejudice of organometallic chemists fighting the moisture sensitivity of many of their compounds.

Since a metal center generally wants to be either “hard” or “soft”, but not both at the same time, many examples of the disproportionation of “hard or soft” complexes (cf. for example, the valence disproportionation of $Co_2(CO)_8$ in the presence of amines or alcohols into a hard-ligand-stabilized Co^{2+} cation and a soft $Co(CO)_4^-$ anion) [2,3] testify to the justification of distinguishing a “soft organometallic” from a “hard coordination” chemistry. However, very recent discoveries of, for example, the amazing coordination capabilities of the $Os(NH_3)_5^{2+}$ moiety [4] have demonstrated how exciting the exceptions to the rule can be, provided mostly by the electronically more flexible Pt metals. Therefore, as was often the case in human history where fruitful developments were triggered by mixing of different populations, violently or peaceful, so in chemistry the combination of the extremes may highlight new possibilities in reactivity and new insights in bonding concepts. It is because of such promise that the increasing number of organometallic aqua ions deserve our interest.

A number of reports on possible organometallic aqua ions appeared independently from several laboratories between 1980 and 1982. They comprised the Cp and benzene complex types I and II depicted in Scheme 1. A logical extension of this scheme into Group 10 would be the cyclobutadiene (Cbd) complexes of the Ni triad, type III, which have been explored recently in our laboratory [5]. Hydrogen and methyl groups have been utilized as ring substituents for the Cp and benzene



M = Cr, Co, Rh, Ir

M = Ru, Os

M = Ni, Pd, Pt

I II III

Scheme 1. Types of π-arene aqua complex.

ligands, whereas Cbd complexes with mostly Me and Ph substituents are presently known.

Concomitant with the detection of new types of compound, such as olefin complexes of Ru, structural as well as kinetic characterization of the longer known members has progressed in recent years. In the following, an account is given, partly stemming from our own current research efforts, and including the older examples along with new species.

2. AQUA IONS OF THE TRANSITION METALS

Table 1 lists the known aqua ions $M(H_2O)_n^{q+}$ of the transition metals [6]. The features of principal importance for aqua ions are as follows:

(i) redox potentials of couples containing aqua ions;
(ii) the acidity of coordinated water;
(iii) water exchange kinetics.

The first property determines the thermodynamic stability towards disproportionation of a given oxidation state into the metal and higher valence ion or oxide. The acidity determines the resistance to deprotonation and condensation of the ensuing hydroxo species, and the third point gives an overall characterization of the lability (substitutional stability) in solution of the specific oxidation state. All these properties may be affected to a large extent by the presence of a π ligand.

As can be seen from Table 1, the list is complete for the 3d transition series but is rather incomplete for 4d and 5d ions. Except for Mo^{3+}, no 4d and 5d monomeric aqua ions are known for Groups 4–7. In Groups 8, Os is missing and,

TABLE 1

$M(H_2O)_n^{q+}$ aqua ions of the transition metals [6]

Metal	Hydration number n	Charge q
Ti	6	4, 3
V	6	3, 2
Cr	6	3, 2
Mn	6	3, 2
Fe	6	3, 2
Co	6	3, 2
Ni	6	2
Cu	(6)	1, 2
Mo	6	3
Ru	6	3, 2
Rh	6	3
Ir	6	3
Pd	4	2
Pt	4	2

in the Co triad, the lower valent Rh and Ir are represented only by dimeric $Rh_2(H_2O)_8^{4+}$. $Cuaq^+$ is a transient species in water but in the absence of Cu^{2+} disproportionation is kinetically slow. The coordination number in all cases appears to be 6 (4+2 for Cu^{2+}), with the exception of Pd^{2+} and Pt^{2+}, which are four-coordinated, in accordance with the known coordination chemistry of these ions [7,8].

Simple aqua ions are confined, in general, to oxidation states 2 and 3. Lower oxidation states are too strongly reducing or tend to disproportionate into the metal and higher valence ions or oxides. Aqua ions of charge higher than +3 in most cases are too strong acids to exist even in acidic aqueous solution. The monomeric $Ti(H_2O)_6^{4+}$ is found in very low concentrations in a strong perchloric acid solution of $TiOaq^{2+}$ [9]. However, the chemistry of the lower oxidation states of the heavier early transition metals is dominated by metal–metal bonding, leading to dimers or M_6 octahedral clusters.

When moving to the right in the transition series, the oxidation states +2 and +3 are less strongly reducing for 4d and 5d metals, and the tendency for metal–metal bonding decreases with increasing number of d electrons, giving way to the existence of aqua ions. The principal difficulty for preparing these species results from the high substitutional inertness of the low-spin d^5 and d^6 configurations in octahedral and d^8 configuration in square planar coordination geometries, which makes it difficult to remove the initial ligands which are mostly halides. The example is cited of the chloro complex $RuCl(H_2O)_5^{2+}$, which is totally resistant to hydrolysis to the aqua ion [10]. Therefore, all preparations of $Ru(H_2O)_6^{3+}$ have to start from halide-free precursors, such as RuO_4 or H_2RuO_4 [11].

This inertness may be responsible for the lack of as yet unaccessed $Os(H_2O)_6^{3+}$ or $Os(H_2O)_6^{2+}$. A further point is the exceptional acidity of the +2 aqua ions of Hg, Pd and Pt, which, even on a qualitative basis, is much higher than that predicted on the grounds of charge density. Therefore, Pd and Pt can be kept only in fairly acidic solutions (2.5 M perchloric acid) and tend to hydrolyse at higher pH values [7,8].

3. ORGANOMETALLIC AQUA IONS AND MODEL COMPLEXES

The known organometallic aqua ions, as defined in the Introduction, are listed in Table 2. Apart from the entries in Table 2, scattered reports on organometallic complexes containing one water (or hydroxo) ligand among a set of carbon or heteroatom π and σ ligands can be found in the literature. These will not be treated systematically in this account but will be mentioned when appropriate.

As a model mimicking a "triaqua" group, the tripodal oxygen ligand depicted in Fig. 1 has been used extensively in our group. This "tripod" combines a weak ligand field parameter with high formation constants for mono and bis tripod complexes which have been prepared and studied for many elements in the periodic

TABLE 2

Organometallic aqua ions

Compound		Ref.
$[Cp_2Ti(H_2O)_2]^{2+}$	xxx	12
$[Cp^*_2Ti(H_2O)_2]^{2+}$	xxx	13
$[Cp_2Zr(H_2O)_3]^{2+}$	xxx	14
$[CpCr(H_2O)_3]^{2+}$	s	15
$[Cp^*Cr(H_2O)_3]^{2+}$	s	16
$[(C_6H_6)Ru(H_2O)_3]^{2+}$	xxx	1, 17
$[(TMT)Ru(H_2O)_3]^{2+}$	xxx	18
$[(C_6H_6)Os(H_2O)_3]^{2+}$		1
$[(COD)Ru(H_2O)_4]^{2+}$	xxx	19
$[(CO)Ru(H_2O)_5]^{2+}$	s	19
$[Cp^*Co(H_2O)_3]^{2+}$	s	20
$[Cp^*Rh(H_2O)_3]^{2+}$	s	5, 21–23
$[Cp^*Ir(H_2O)_3]^{2+}$	—	5
$[(COD)Pt(CH_2Ph)(H_2O)]^+$	xxx	16

TMT = tetramethylthiophene; COD = 1,5-cyclooctadiene; xxx, X-ray structure of the solid; s, solid salt prepared.

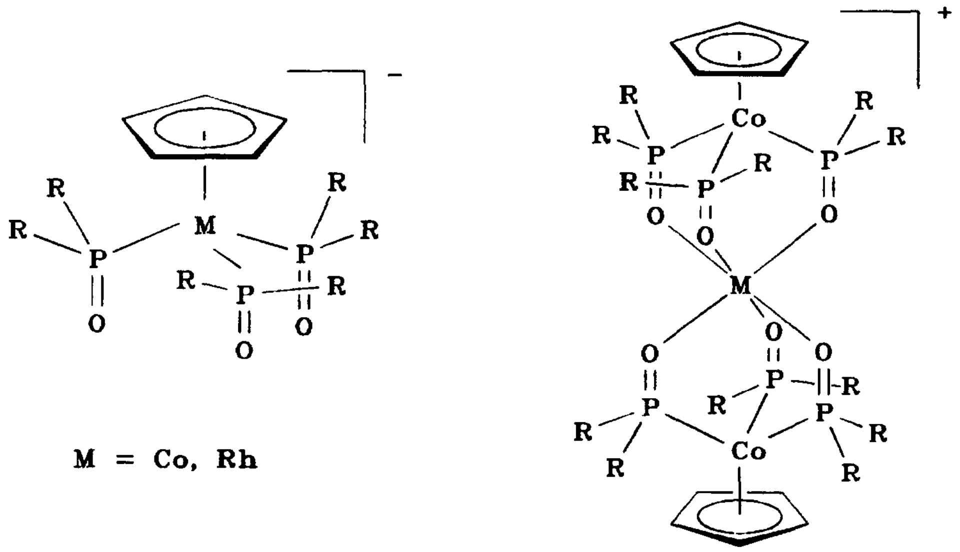


Fig. 1. "Tripod" ligand as a model for a tri(aqua) group.

table [24]. The tripod ligand has been assigned a nephelauxetic parameter similar to that of water, by evaluating d–d spectra.

Tripod complexes are formed simply by the reaction of the respective aqua ion with the tripod-Na salt in water. We never observed decomplexation of an arene or olefin by the tripod, but frequently observed substitution of three water ligands. In contrast to aqua complexes, which in many cases are difficult to isolate and crystallize from aqueous solutions, the analogous tripod complexes $L_\pi M(\text{tripod})^{q+}$ are neutral or monocations that are either insoluble or easily precipitated as, for example, hexafluorophosphates from water. Furthermore, they are conveniently purified by recrystallization from organic solvents.

4. METHODS OF PREPARATION

The most straightforward access to organometallic aqua ions is through dehalogenation of the respective halide complexes

$$L_mMX_n + nAg^+ \xrightarrow[-AgX]{H_2O} L_mM(H_2O)_n^{n+} \qquad (1)$$

This may be accomplished by precipitation of the halide by Ag^+ or Tl^+, by ion exchange or, in some cases (*vide infra*), by mere hydrolysis in water. It is found that these dehalogenation reactions proceed generally much more readily if the metal bears a π cyclic acceptor ligand than is the case with simple binary halides, such as $RuCl_3$.

Another possibility is the acid hydrolysis of an organic ligand, such as a π-allyl group, or direct reaction of the aqua ion with either the organic ligand or some precursor thereof.

5. Ti GROUP IONS

The best characterized examples for this group are the bis(cyclopentadienyl) aqua cations Cp_2Maq^{2+}. In the very first investigations of the dichlorides Cp_2MCl_2 (M = Ti, Zr, Hf) in 1953 [25], water solubility of the compounds — most uncommon for organometallic complexes — was observed. The halides could then be regenerated from aqueous solutions by the addition of strong HCl. Nuclear magnetic resonance (NMR) spectral investigation led Döppert [26] to conclude that these solutions are ionic and contain three species, as shown in Scheme 2.

$$Cp_2TiCl_2 \xrightleftharpoons{H_2O} \underset{\mathbf{1}}{[Cp_2Ti(H_2O)_2]^{2+}} \xrightleftharpoons{-H^+} \underset{\mathbf{2}}{[Cp_2Ti(H_2O)(OH)]^+}$$

$$2[Cp_2Ti(H_2O)(OH)]^+ \xrightleftharpoons{-H_2O} [Cp_2Ti(H_2O){-}O{-}Ti(H_2O)Cp_2]^{2+} \qquad (2)$$

Scheme 2. Hydrolysis of Cp_2TiCl_2.

The sequence of Scheme 2 comprises all three important reactions of the halide and aqua complexes, i.e. hydrolysis to form the aqua complex, prototropic equilibria and condensation of the hydroxo species at higher pH values. With the unsubstituted Cp ligand, hydrolysis occurred at pH values above 3.5 to insoluble compounds.

By controlled hydrolysis of the permethylated derivatives $Cp^*_2TiCl_2$, Thewalt and Honold [12] were able to obtain crystalline salts of $[Cp^*_2Ti(H_2O)_2]^{2+}$ (**1**) and $[Cp^*_2Ti(H_2O)(OH)]^+$ (**2**). X-ray structural determination gave Ti—O distances of 2.077 Å (mean) for **1**, and 2.10–2.12 Å for Ti—OH_2 and 1.88 Å for Ti—OH in **2**. **1** and its congeners are Bronsted acids in water, but the exact pK value for the first deprotonation seems not to have been determined. From the report that **2** crystallizes from 2.5×10^{-2} M solutions of **1** in a 60% yield, a pK_a value of approximately 0 can be extrapolated — a value still much higher than that estimated for the very acidic $Tiaq^{4+}$ ion [9]. Apart from the aqua ion, a variety of mono and polynuclear oxo and caboxylato complexes of the $Cp^{(*)}Ti(IV)$ residue have been prepared and characterized.

6. Cp(*)Cr, Cp*Co, Cp*Rh AND Cp*Ir COMPLEXES

Owing to the similarities of the d^3 and low-spin d^6 configuration in transition metal σ-donor complexes, the chemistries of Cr(III) and Co(III) have much in common and, for this reason, the respective aqua ions are treated in the same paragraph, along with the heavier congeners. Examples of higher oxidation state $Cp^{(*)}Cr$ complexes comprise the tetrameric oxide $[Cp^{(*)}CrO]_4$ [27] and the dimeric dioxo complex $[Cp^*CrO_2]_2$ [28]. The halide complex $[CpCrCl_2]_2$, available through the reaction of Cp_2Cr with CCl_4 [29], readily hydrolyses in water. Alternatively, chloride-free solutions are obtained by acid hydrolysis of chromocene [15]. Evolution of hydrogen gas and the formation of an organic polymer suggest a reaction such as reaction (3) in Scheme 3, with oxidation to chromocenium ions in the first step. These chromocenium ions are known to be susceptible to hydrolysis.

$$Cp_2Cr + H^+ \xrightarrow{HBF_4/H_2O} [Cp_2Cr]^+ + \tfrac{1}{2}H_2$$

$$[Cp_2Cr]^+ + H^+ \xrightarrow{H_2O} [CpCr(H_2O)_3]^{2+} + C_5H_6 \xrightarrow{polym.} \tag{3}$$

$$[CpCrCl(H_2O)_2 \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} [CpCr(H_2O)_3]^{2+} \tag{4}$$

Scheme 3. Hydrolysis of Cp_2Cr and anation of $CpCr(H_2O)^{2+}$ (3).

Aquation as well as anation of aqua and chloro complexes, respectively, were studied spectrophotometrically [15]. The aquation of a presumed monochloro complex showed a rate constant $k_2 \approx 10\ M^{-1}\ s^{-1}$ (3.5×10^{-3} M [Cl^-] and [Cr]), which is unusually fast kinetics for a Cr(III) complex. This observation has been reproduced frequently in the meantime, with other electron configurations known to be substitutionally inert (*vide infra*).

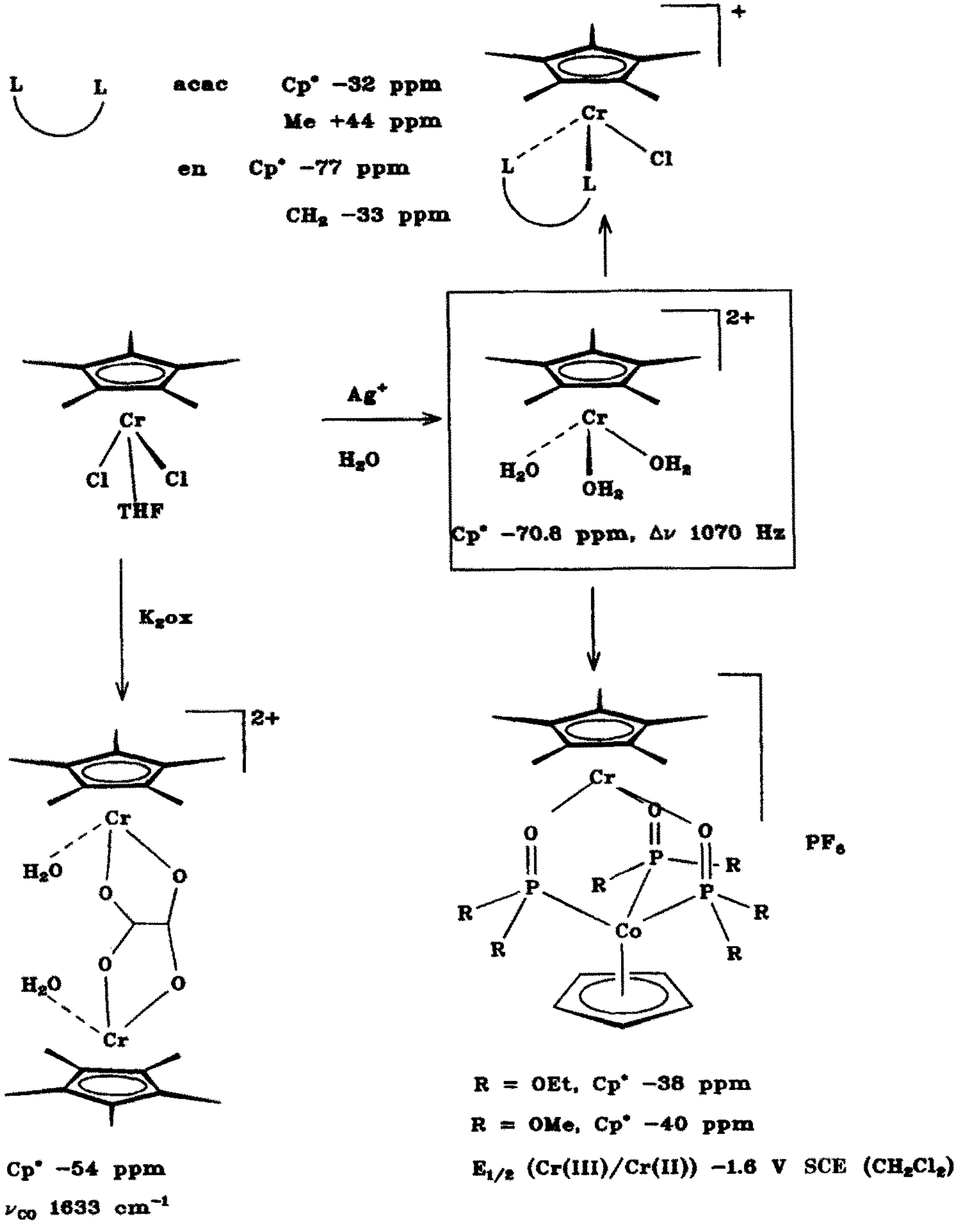
The study of the $CpCr(H_2O)_3^{2+}$ ion (**3**) was hampered by its limited stability, even in acidic solutions. Though samples with a reasonable analytical composition for $[CpCr(H_2O)_3](BF_4)_2$ were obtained by freeze drying a solution of $CpCr(H_2O)_3^{2+}$ containing HBF_4, the rate for hydrolytic cleavage of the Cp ligand in solution was still estimated as about $10^{-2}\ s^{-1}$.

The pentamethyl (Cp*) derivative (**4**) which is more stable to hydrolysis was recently prepared in our laboratory by hydrolysis of $Cp^*CrCl_2 \cdot THF$ [5]. This precursor is readily prepared from $CrCl_3 \cdot THF$ and Cp*Li in a yield of 57% [30]. The aqua ion **4** is obtained by dehalogenation of $Cp^*CrCl_2 \cdot THF$ with Ag^+ in water (or other solvent), and can be isolated as a sulfate, tetrafluoroborate or hexafluorophosphate. The solid remaining after precipitation with $AgBF_4$ in water, filtration of AgCl and drying correctly analyses as $[Cp^*Cr(H_2O)_3](BF_4)_2$. It is characterized by a paramagnetically shifted broad singlet at δ −70.8 ppm for Cp* and a water signal (in acetone-d_6) at δ +10 ppm. Though the electron transfer redox stability of **4** in the absence of air is very reasonable (irreversible reduction at −0.86 V and irreversible oxidation at +0.8 V vs. SCE), solutions (especially at higher pH values) are air sensitive, owing most probably to ready oxidation to the known Cr(V) species $(Cp^*CrO_2)_n$ [28]. No signs of hydrolytic cleavage of the Cp* ligand were found in acidic solutions in an oxygen-free atmosphere.

The tripod complex $Cp^*Cr(tripod)^+$ (tripod = $CpCo(P(OEt)_2O)_3^-$, *vide supra*) (**5**) was prepared as a model for the triaqua cation and structurally characterized as the hexafluorophosphate. As a result of the regularly polyhedral shape of the molecule, it shows extended disorder in the crystal in the Cp as well as in the $[P(OEt)_2]_3$ part [31]. Notably, the tripod complex is not observed to be oxidized in the cyclic voltammogram and, owing to the chelating character of the tripod ligand, it is completely air stable as a solid and in solution.

A number of derivatives related to the aqua ion were prepared by the reaction of either **4** or the precursor $Cp^*CrCl_2 \cdot THF$. Thus, a dimeric aqua oxalate, from the reaction of $Cp^*CrCl_2 \cdot THF$ with $K_2C_2O_4$, and an aqua acetylacetonate, by the hydrolysis of Cp*CrCl(acac), were obtained. Chelating nitrogen ligands such as bipy gave the corresponding bipy complex depicted in Scheme 4.

Indication of a Co aqua ion $[Cp^*Co(H_2O)_3]^{2+}$ (**5**) was obtained first in 1982, when it was found that halides $[Cp^*CoX_2]_2$ (X = Cl, Br) prepared from the paramagnetic Co(II) complexes $[Cp^*CoX]_2$ [32] were water soluble and did not spontaneously hydrolyse to $Coaq^{2+}$ [20]. The reaction sequence most conveniently leading to the aqua ion is depicted as follows, starting from readily available



Scheme 4. Hydrolysis and derivatives of $Cp^*CrCl_2/Cp^*Cr(H_2O)_3^{2+}$.

$[Cp^*CoCl]_2$:

$$[Cp^*Co^{II}Cl]_2 \xrightarrow[-C_2Cl_4]{C_2Cl_6} [Cp^*Co^{III}Cl_2]_2 \underset{HCl}{\overset{H_2O}{\rightleftharpoons}} [Cp^*Co(H_2O)_3]^{2+} \overset{OH^-}{\rightleftharpoons} [Cp^*Co(\mu\text{-}OH)_3CoCp]^+ \tag{5}$$

The stability of these Cp*Co(III) aqua complexes in acidic solutions is somewhat less than that for CpCr(III). Therefore, no aqua ion or similar hard oxygen-donor ligand CpCo complex was ever isolated with the unsubstituted Cp ligand [33]. Hydrolysis of $(CpCoI_2)_n$ instead only gives $Coaq^{2+}$ and Cp_2Co^+ (even $CpCo(NCCH_3)_3^{2+}$ spontaneously disproportionates in the presence of SO_4^{2-} or CH_3COO^-).

Similarly, as in the Cr case, the absorption spectrum of an aqueous solution of $[Cp^*CoCl_2]_2$ does not change when Cl^- is precipitated by Ag^+ ions, indicating complete hydrolysis in dilute (0.1 M) aqueous solutions. With strong HCl, a chloro complex is reformed that can be extracted with CH_2Cl_2 from the acidic aqueous phase. Solutions of $Cp^*Co(H_2O)_3^{2+}$ with HBF_4 freeze dried, again gave correct analysis as $[Cp^*Co(H_2O)_3](BF_4)_2$ [20].

The acidity of $[Cp^*Co(H_2O)_3]^{2+}$ was determined by potentiometric titration with a first pK_a value of 5.9. In alkaline solution, the tris(μ-OH) cation $[Cp^*Co(\mu\text{-}HO)_3CoCp^*]^+$ is formed and some intermediate species were detected from pH-dependent polarographic reduction [20]. A number of $CpCoX_n$ complexes (with $X = NCS^-$, N_3^-, acac$^-$, $S_2C_2(CN)_2^{2-}$, o-NH_2-phenol, NO_2^- and CN^-) were obtained from the aqueous solution. In contrast to the triaqua ion, the monoaqua ion $[Cp^*Co(bipy)(H_2O)]^{2+}$ exhibits complete long-term stability to hydrolysis of the Cp* ligand, and could be used for spectrophotometric determination of the anation rate constants for a variety of anionic and neutral ligands [34]. Again, these substitutions showing $k = 1.05 \pm 0.02$ and $0.192 \pm 0.004\ M^{-1}\ s^{-1}$ at 20°C for SCN^- and thiourea anation, respectively [34], proceed orders of magnitude faster than similar reactions at Co(III) coordination centers.

The aqua Rh ion $Cp^*Rh(H_2O)_3^{2+}$ (**6**) seems to have been observed first by Maitlis and co-workers [21], who, when isolating a Cp*Rh sulfate complex, remarked that "it seems likely the aqueous solutions of this sulphate complex contains the triaqua cation $Cp^*Rh(H_2O)_3^{2+}$". These authors noted the identity of the absorption spectra of aqueous solutions obtained through dehalogenation of $[Cp^*RhCl_2]_2$ with those obtained by acid cleavage of $[Cp^*Rh(\mu\text{-}OH)_3RhCp^*]^+$ ($\lambda_{max} = 375$ nm, $\varepsilon = 3130\ M^{-1}\ cm^{-1}$). Differently from the Co complexes, the presence of Cl^- in this case does affect the spectra and PF_6^- precipitates the $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]^+$ cation from aqueous solutions of the sparingly soluble $[Cp^*RhCl_2]_2$ [22].

A reinvestigation of the $Cp^*Rh(H_2O)_3$–sulfate system in our laboratory [5,22], with the aim of crystallizing the tris aqua ion, eventually yielded from an acetone + chloroform mixture a crystalline material of composition $Cp^*Rh(SO_4)(H_2O)_{1.5}$ (NMR integration, $Cp^*:H_2O = 15:3$). The material remaining after dehalogenation of $[Cp^*RhCl_2]_2$ with Ag_2SO_4 has a very peculiar solubility behavior. Being sparingly soluble in a 4:1 acetone:chloroform mixture at ambient temperature, the solubility increases at low temperature. Thus, crystals were obtained by warming a clear solution from −50°C to room temperature. The broad NMR water signal at ambient temperature splits at low temperature (−50°C in acetone-d_6)

into two resonances (δ 5.84 and 6.39) with intensity ratio 2:1, but one single Cp* singlet (δ 1.71). These observations are best accounted for by the assumption of a monoaqua complex with one bidentate sulfate ligand and one additional water molecule bridging between two sulfate ligands, as shown in Fig. 2. It can be anticipated that this complex has a better solubility in an unpolar solvent mixture than do the ionic or more polar constituents **6** and SO_4^{2-}. A higher stability at low temperature and dissociation at higher temperature satisfactorily explain the unusual solubility behavior of the compound.

Bidentate sulfate had already been suggested by Maitlis and co-workers on the basis of sulfate IR bands and elementary analysis (indicating, however, the formula $Cp^*Rh(SO_4)(H_2O)_2$). Substitution of tosylate for sulfate gave the composition $Cp^*Rh(OTs)_2(H_2O)_{1.5}$, with probably one complexed and one bridging water molecule. These results show the high tendency of Rh(III) for complexing hard oxygen ligands.

Other anions that were investigated by us in connection with **6** were BF_4^- and SbF_6^-. After drying of the solution at a high vacuum in a non-aqueous solvent, salts with either anion showed by ^1H NMR the composition $Cp^*Rh(H_2O)_3X_2$. In the case of BF_4^-, separate signals were seen for coordinated and free water protons at low temperature; however, the salt had no tendency to crystallize. The SbF_6^- salt has a higher tendency for crystallization and could eventually furnish the crystalline aqua ion.

The pK_a values of **6** have been determined as 3.8, 5.7 and 9.3 ± 0.1 [35], which have to be compared with the values 3.2 and 4.0 given for the hexa-aqua ion [36]. Whereas the third pK_a value of $Cp^*Rh(H_2O)_3^{2+}$ does not necessarily belong to a mononuclear species, the first two seem to be quite comparable. Obviously, the organometallic aqua ion is less acidic, which can be expected from the lower charge. However, the difference of only 0.6 pK units between the hexa-aqua and the Cp* triaqua ion for Rh as compared with Co, where the same difference amounts to about 5 (or at least 3.5, depending on the value accepted for $Co(H_2O)_6^{3+}$) units, a special effect must be operative in the case of Rh (for Ir, figures are not yet complete but are expected to be around the same). The relative increase in the acidity of the Cp* over the bare aqua ion can be qualitatively traced back to the stronger covalency of the Rh–Cp* as compared with the Co–Cp* bond also responsible for the much

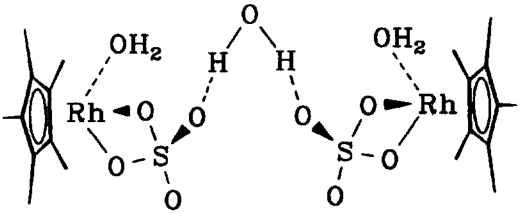


Fig. 2. Proposed structure for binuclear aqua sulfato Rh complex from water in the presence of SO_4^{2-}.

higher hydrolytic stability of **6** compared to **5**. The softer Brønsted acids with equal ionic charges generally show a tendency for the formation of more acidic aqua ions.

The Ir congener $Cp^*Ir(H_2O)_3^{2+}$ (**7**) can be prepared [5] as an aqueous sulfate solution or solid salt, in much the same way as given for Rh, though detailed composition studies of the solid have not yet been performed.

Parameters for the water exchange kinetics, which were expected to be slowest for Ir in the Co triad, were determined for **6** and **7** from ^{17}O NMR data, including high pressure measurements [37] and are given in Table 3. As can be seen from Table 3, coordinated water is slightly more mobile at Rh than at Ir, as expected. However, the faster exchange rate at ambient temperature at Rh is due entirely to a much higher entropy of activation. From this, one would conclude a mostly dissociative I_d mechanism for Rh and a more symmetrical interchange for Ir. A different explanation, which better accounts for the more positive activation volume for the Ir complex, is a higher ordered ground state for Rh, with possible anion participation, as indicated by the NMR data cited above. Unfortunately, the water exchange kinetics in $Ir(H_2O)_6^{3+}$ seem still to await determination. However, since the kinetics should not be faster than in $Rh(H_2O)_6^{3+}$, the value found for **7** also signifies a dramatic increase in exchange rate of some six orders of magnitude for the organometallic ion **7** over typical values for Ir(III) coordination compounds.

7. Rh(I) COMPLEXES

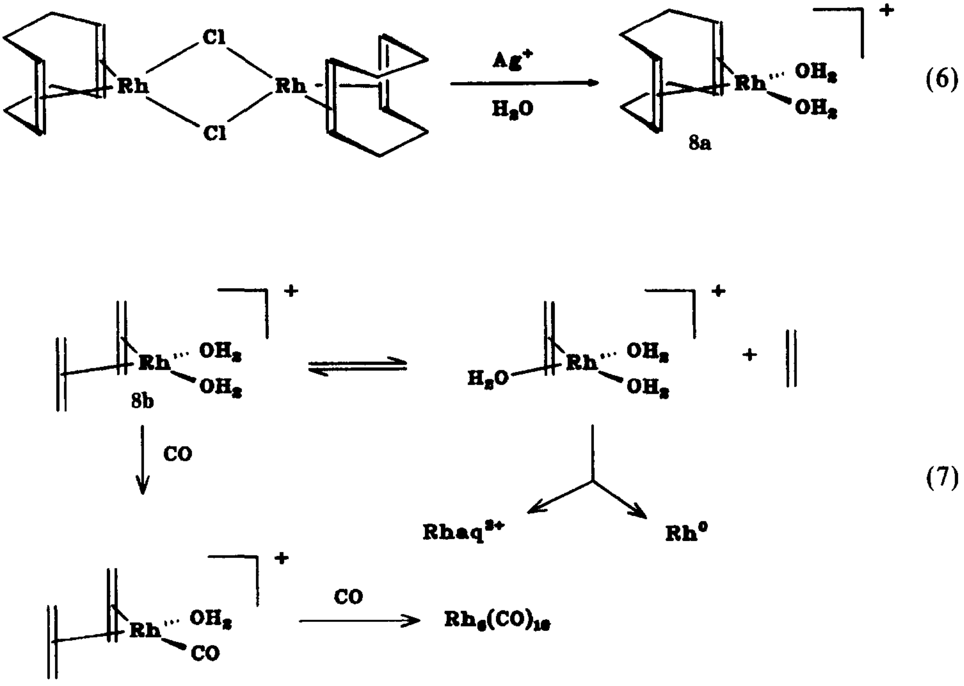
Virtually no aqueous chemistry of Rh(I) has been published to date. The electrochemical reduction of $Cp^*Rh(H_2O)_3^{2+}$ in methanol has revealed a transient signal assigned to a $Cp^*Rh(H_2O)_n$ species [23] but, on electrolysis, mostly metallic Rh was deposited. In contrast, dehalogenation of $[(COD)RhCl]_2$ in water with Ag^+, as in reaction (6) in Scheme 5, has recently produced the first aqua Rh(I) (**8a**) species in our laboratory [38].

A complex that crystallized from aqueous tosylate solution was shown by X-ray structure determination to be an OTs coordinated monoaqua complex, as depicted in Fig. 3. Surprisingly, in the case of the much softer Rh(I) and, as has been discussed for **6** above, the tendency of sulfate ligands to complex to the metal

TABLE 3

Water exchange parameters for $[Cp^*M(H_2O)_3]^{2+}$ from ^{17}O NMR

	M = Rh (**6**)	M = Ir (7)
k^{298} (s^{-1})	$(1.6 \pm 0.3) \times 10^5$	$(2.53 \pm 0.08) \times 10^4$
ΔH ($kJ\ mol^{-1}$)	65.6 ± 7	54.9 ± 3
ΔS ($J\ mol^{-1}\ K^{-1}$)	75.3 ± 24	23.6 ± 11
ΔV_{ex} ($cm^3\ mol^{-1}$)	0.6 ± 0.6	2.4 ± 0.6



Scheme 5. (COD)Rh$(H_2O)_3^+$ and (ethylene)Rh$(H_2O)_3^+$.

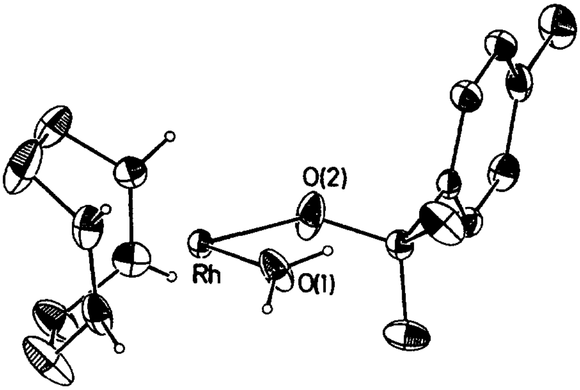


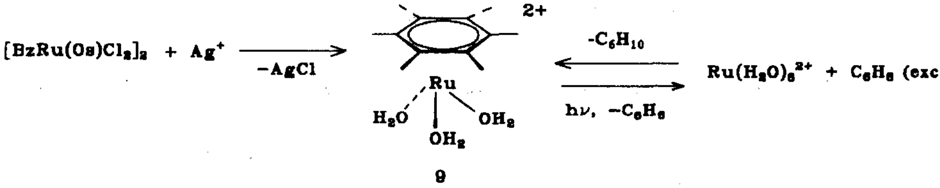
Fig. 3. ORTEP plot of (COD)Rh(OTs)(H_2O). Rh–O(1). 2.106(3), Rh–O(2) 2.102(3), Rh–C(COD) 2.079(3), 2.071(4), 2.080(4), 2.070(3)8. Ru(Os) arene complexes.

prevents crystallization of an aqua ion, even if this was the predominant species in solution.

A dehalogenation analogous to reaction (6), performed with the ethylene complex $[(C_2H_4)_2RhCl]_2$, yielded a solution which exhibits NMR signals (1H 2.93, ^{13}C 60.6 ppm) characteristic for complexed ethylene, indicating the presence of an ethylene aqua complex (**8b**). Ethylene exchange and/or rotation is fast on the NMR timescale. This species is stable only in the presence of excess ethylene (reaction (7)) and, if ethylene is removed under vacuum, the solution starts depositing metallic Rh by disproportionation. This is a clear indication that a plain aqua ion of Rh(I) such as $Rh(H_2O)_4^+$ will not exist at ambient temperature as a stable entity and will inevitably require some acceptor ligands for its stabilization. Treatment of **8b** with CO under pressure in methanol/water gives a transient aqua carbonyl species which finally converts into the cluster carbonyl $Rh_4(CO)_{12}$ of Rh^0 [38].

The first report on the possible aqua ions $BzRu(H_2O)_3^{2+}$ and $BzOs(H_2O)_3^{2+}$ by Taube and co-workers [1] appeared at the same time but independent of the observations on $CpCr(H_2O)_3^{2+}$ [15]. Evidence for aqua ions ("there is a good prospect then that species such as $[C_6H_6Os]^{2+}(aq)$ can be characterized...") was gained from the chemical and spectroscopic behavior of solutions prepared by Ag^+ ion dechlorination of the chloro complexes $Bz(Ru,Os)Cl_2$ in water. All the species were presumed at the time to be triaqua complexes in agreement with the canonical coordination chemistry of Ru and Os^{2+} (as well as Cr^{3+}), though definitive proof was lacking, because no aqua complexes were isolated. In particular, the great resistance of the arene ligand to hydrolytic cleavage in acidic solutions was noted. As with Rh^I the Os compound is an example of an organometallic water complex where the parent aqua ion is (still) not known. The dipositive charge was inferred from the ion exchange behavior, in analogy to related triammine ions $Bz(Ru,Os)(NH_3)_3^{2+}$. Attempts to determine the pK_a values of coordinated water through potentiometric titration were thwarted by intervening condensation. The first equivalence point required 1.5 mol base per metal, and the formation of the tris-μ-hydroxy ion $[BzRu(\mu\text{-}OH)_3RuBz]^+$ [39] (cf. also Cp*Rh and Cp*Ir [21]) was indicated by the titration. This result requires condensation and, since mechanistically a condensation of M–OH groups is conceived as a substitution of water for metal-bound OH, the reaction indicates ligand substitution to be fast on the preparative timescale. This could be taken as an indication of water exchange being much more facile than in the parent aqua ions (where figures had not been determined at the time).

New routes to $BzRu(H_2O)_3^{2+}$ (**9**) were found in the reaction of $Ru(H_2O)_6^{2+}$ with cyclohexadiene (either 1,3- or 1,4-) which gave the aqua ion with a rate constant of about $5 \times 10^{-4}\,s^{-1}$ at 303 K [17] (Scheme 6). In their detailed study of $Bz(Ru,Os)(H_2O)_3^{2+}$, Ludi and co-workers were able to isolate a tosylate and a sulfate



9

Scheme 6. Synthesis and transformation of $BzRu(H_2O)_3^{2+}$.

in crystalline form. Careful single-crystal X-ray structure determinations at three different temperatures indeed confirmed the species as triaqua ions, with an approximately staggered conformation of the benzene rings vs. the water tripod. However, the observed mean Ru–O bond length (Table 4) of 2.117(11) Å was not very different from that found by the same group for the tosylate of $Ru(H_2O)_6^{2+}$ (2.122(16) Å mean) [11].

An apparent pK_a value of 3.5 was determined for **9** by alkalimetric titration — a value that is much closer to the value found for $Ru(H_2O)_6^{3+}$ (2.4) than to the value estimated for $Ru(H_2O)_6^{2+}$ (6–8). A most significant result of the study was the water exchange rate constant of $11.5 \pm 3.2\ s^{-1}$ at 25°C, which is three orders of magnitude faster than water exchange in $Ru(H_2O)_6^{2+}$ ($1.8 \times 10^{-2}\ s^{-1}$ [40]) and was attributed to a kinetic trans effect of the benzene ligand.

An aqua ion closely related to the above is the triaqua tetramethylthiophene (TMT) complex of Ru (**10**), prepared by dehalogenation of the respective chloride $(TMT)RuCl_2$ and characterized structurally by Rauchfuss and co-workers [18]. Dehalogenation of the chloride by AgTf ($Tf = CF_3SO_3^-$) in methylene chloride gave a triflate with probably several differently coordinated (TMT)Ru species, as indicated by a complex methyl pattern in the NMR spectrum. However, in a polar solvent (CD_3NO_2), the spectrum simplifies to that expected for one TMT ligand π-coordinated to a symmetrical ML_n fragment; similarly, ^{19}F NMR showed the presence of one single, possibly uncoordinated, Tf anion. When exposed to atmospheric moisture, the triflate converted to the tris aqua ion **10** with uncoordinated triflate (ν_{SO} shifting from over 1300 cm^{-1} to 1268 cm^{-1}). X-ray structural determination revealed a tris aqua ion with a piano-stool arrangement of the water ligands and Ru–O distances 2.16(1) and 2.17(1) Å (Table 4), which now are sizeably longer than those in $Ru(H_2O)_6^{2+}$. Complex **10** is stable to hydrolysis up to 100°C or more and decomposes at 150°C to yield $Ru(TMT)_2^{2+}$ — also obtained from $(TMT)Ru(H_2O)_3^{2+}$ and TMT at 100°C. The stable ammine derivative $(TMT)Ru(NH_3)_3^{2+}$ is formed in aqueous ammonia. Remarkably, **10** can be bound on alumina without decomplexation. The intact (TMT)Ru residue was proven by ^{13}C CP/MAS NMR as well as liberation of the aqua complex by washing alumina loaded with (TMT)Ru with water, whence the aqua ion reappeared in solution.

8. Ru OLEFIN COMPLEXES

The formation of mono-olefin complexes derived from $Ru(H_2O)_6^{2+}$ has been recently reported by different laboratories. Steed and Tocher [41] isolated and characterized $[(C_{12}H_{18})RuCl((H_2O)]BF_4$, where $C_{12}H_{18}$ is η^2-, η^3-, η^2-coordinated dodecatetraene. Counting the allylic moieties as anionic, they assigned a +IV oxidation state to Ru. The Ru–O bond length in this complex was found from X-ray structure to be 2.165(5) (Table 4), which shows the assignment as Ru(IV) to be rather formal.

In a study of the Ru-induced, ring-opening polymerization (ROMP) [42], Grubbs reacted $RuCl_3$ with functionalized olefins in water or alcohol, and observed spectroscopically the formation of mono-olefin complexes derived from functionalized olefins such as allylethers [43]. It was shown that the efficient catalyst for ROMP of some 7-oxanorbornenes was in fact a 7-oxanorbornene-Ruaq complex which had been formed under the conditions from $RuCl_3$. Subsequently, Ru complexes of allylethers and similarly functionalized olefins were isolated and characterized by NMR spectra and electrochemical redox potentials. A complex containing two water ligands and two molecules of 3-pentenoate complexed through carboxylato groups and the olefinic double bond to Ru was characterized by X-ray structure determination (Table 4) [44].

These experiments first started from Ru halide or halide complexes but, subsequently, it was observed that the $Ru(H_2O)_3^{2+}$ ion also can effect the chemistry. Previously, it had been found in Ludi's group [45] and later in the author's laboratory that $Ru(H_2O)_6^{2+}$ could react directly with olefins in ethanol. The Swiss workers isolated dienyl or arene sandwich complexes in high yields, where a π-complexed tosylate group had completed the coordination shell, e.g. $(\eta^5\text{-}C_8H_{11})Ru(\eta^6\text{-}p\text{-}MeC_6H_4SO_3)$, from the reaction of $Ru(H_2O)_6(OTs)_2$ and 1,3-cyclooctadiene.

We developed as a convenient source of the somewhat difficult to access $Ru(H_2O)_6^{2+}$ — a photochemical route [46] that starts from $BzRuCl_2$ (Scheme 7) and obtained exclusively from the reaction of 1,5-cyclooctadiene (COD) with $Ru(H_2O)_6^{2+}$ in ethanol the aqua complex $(COD)Ru(H_2O)_4^{2+}$ (**11**) [19]. The novel compound showed extraordinary thermal (up to at least 100°C in water) and redox stability (no redox transition between $+1.5$ and -2 V in the cyclic voltammogram), and appears to be much more stable than $Ru(H_2O)_6^{2+}$ itself, which disproportionates on gentle heating, a result which nicely complements the observations given above for Rh(I). Substitution in **11** led to a variety of (COD)Ru complexes, where between one (CO) and four (salen) water ligands could be displaced without removing the

TABLE 4

$Ru{-}OH_2$ distances (ångströms) in Ru and Pt aqua complexes

$[Ru(H_2O)_6](OTs)_2$	2.107(2), 2.121(2), 2.139(2) [11]
$[BzRu(H_2O)_3](SO_4)$	2.151(2), 2.114(2), 2.116(3) [17]
$[(TMT)Ru(H_2O)_3](Tf)_2$	2.16(1), 2.17(1) [18]
$[(COD)Ru(H_2O)_4](OTs)_2$	2.095(2), 2.158(1) [19]
$[(NBD)Ru(H_2O)_4]SO_4$	2.077(2), 2.085(2), 2.156(2), 2.158(2) [38]
$[(COD)Ru(H_2O)_2(bipy)](PF_6)_2$	2.117(2), 2.136(2) [38]
$[(C_{12}H_{18})RuCl(H_2O)]BF_4$	2.165(5) [41]
$Ru(OCOCH_2CO{=}CHCH_3)_2(H_2O)_2$	2.115(3), 2.141(3), 2.080(3), 2.065(3)(carboxylate) [45]
$[(COD)Pt(CH_2Ph)(H_2O)]BF_4$	2.07(1) [16]

COD ligand (Scheme 8). Halide ions, such as Br^-, form the polymeric halide complexes, which in this case cannot be dehalogenated to the aqua ion.

$$RuCl_3aq \xrightarrow[EtOH]{1,3-C_6H_8} [Ru(C_6H_6)Cl_2]_2 \xrightarrow[H_2O]{AgOTs}$$

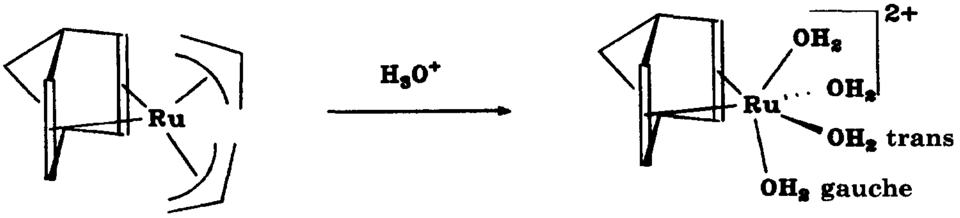
$$Ru(C_6H_6)aq^{2+} \xrightarrow[H_2O,\ 10^\circ C]{h\nu} Ruaq^{2+}\ (TsO^-, SO_4^{2-})$$

$$Ruaq^{2+} \xrightarrow[EtOH]{1,3-COD} (\eta^5-C_8H_{11})Ru(\eta^6-p-MeC_6H_4SO_3)$$

$$Ruaq^{2+} \xrightarrow[EtOH]{1,5-COD} \underset{\mathbf{11}}{(1,5-COD)Ruaq^{2+}}$$

Scheme 7. Photochemical preparation of $Ru(H_2O)_6^{2+}$ and reaction with COD.

The analogous NBD complex could not be prepared in the same way, owing to rapid polymerization and ROMP of NBD in the presence of $Ru(H_2O)_6^{2+}$. The

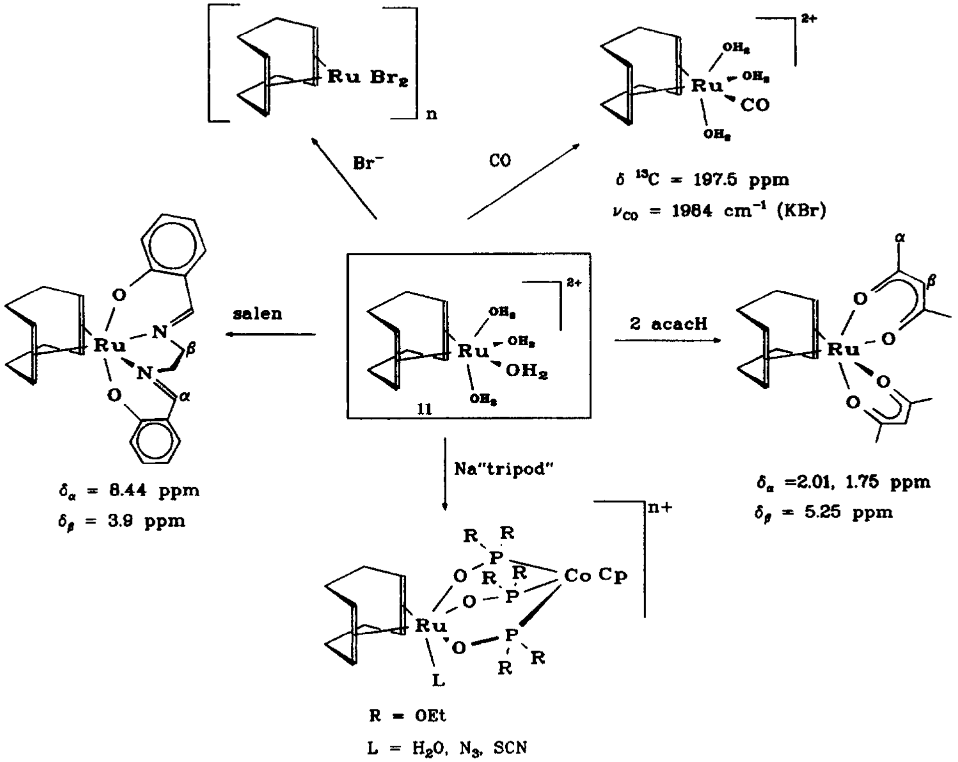


(8)

acid cleavage of allyl complexes (NBD, COD) Ru $(\pi-C_3H_5)_3$ was found to be a convenient high-yield route to either olefin aqua cation by a suitable non-coordinating acid.

Crystals of $[(COD)Ru(H_2O)_4](OTs)_2$ and $[(NBD)Ru(H_2O)_4]SO_4$ were obtained, suitable for X-ray structure determination, from acetone + water. In the crystals, water ligands are linked through tosylate or sulfate, respectively, by hydrogen bridges, forming symmetric double strands in the case of $[(COD)Ru(H_2O)_4](OTs)_2$ (Fig. 4) with each water hydrogen bound to one tosylate oxygen and a less symmetrical arrangement for $[(NBD)Ru(H_2O)_4]SO_4$ where all the water hydrogens are also involved in hydrogen bonding. Both structures show two distinct sets of Ru–O water distances, as given in Table 4 — a longer distance for H_2O trans to the olefinic double bond and a shorter distance for H_2O mutually trans to each other (>O–Ru–O 155°). These Ru–O distances, differing by about 0.08 Å (i.e. 4%), are succinct, structural proof for the trans effect of the olefinic double bonds.

The water exchange kinetics at **11** were determined quite recently [47] and results are given in Table 5. As can be seen, the difference in exchange rate between H_2O_{trans} and H_2O_{gauche} is dramatic and results from the higher enthalpy as well as entropy of activation for exchange of the "classical", i.e. trans-water. To the best of our



Scheme 8. Substitution reactions at $[(COD)Ru(H_2O_4]^{2+}$.

TABLE 5

Water exchange parameters for H_2O_{trans} and H_2O_{gauche} in $[(COD)Ru(H_2O)_4]^{2+}$ from ^{17}O NMR

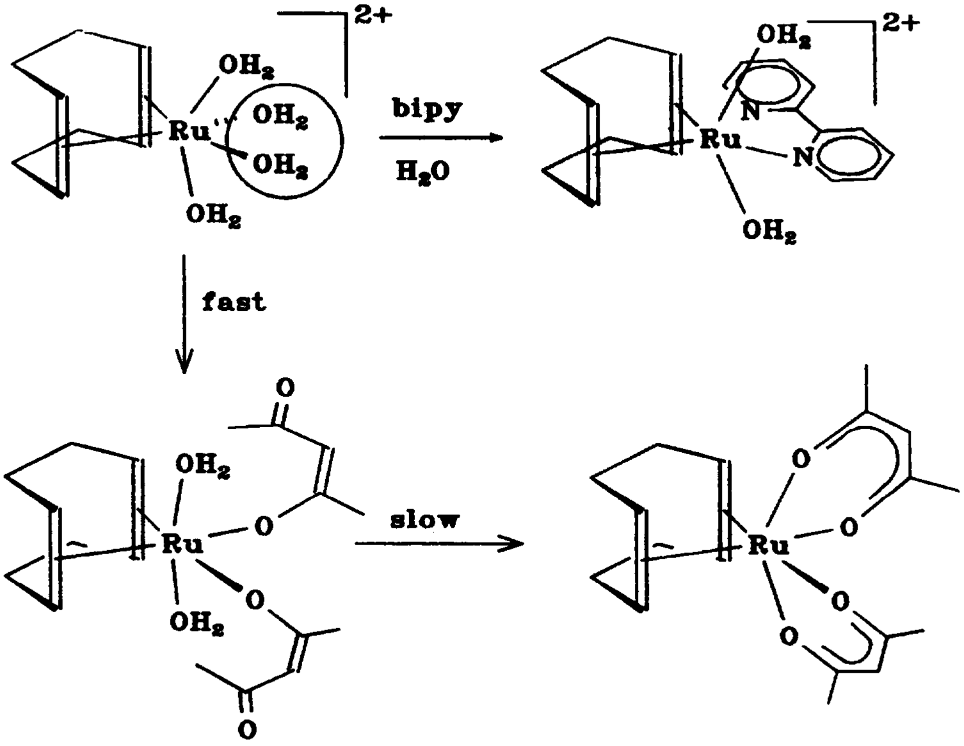
	H_2O_{gauche}	H_2O_{trans}
k^{298} (s^{-1})	$(1.5 \pm 0.3) \times 10^{-5}$	0.51 ± 0.03
ΔH (kJ mol^{-1})	135.9 ± 7	85.4 ± 0.9
ΔS (J mol^{-1} K^{-1})	118.6 ± 21	35.7 ± 3.0

knowledge, this is the first case where different exchange kinetics of the same substituent at a molecule can be directly correlated to bond lengths of this ligand.

The tripod derivative $(COD)Ru(tripod)(H_2O)PF_6$ was also characterized by a single-crystal, X-ray structural determination. Here, Ru–O distances to the tripod oxygen atoms are nearly equal (2.09(2), 2.10(2), 2.10(2) Å) and are close to that characteristic for H_2O_{gauche}.

To demonstrate the consequence of different exchange or substitution rates for the different water positions, the substitution of **11** with acacH and with

2,2′-bipyridine (Scheme 9) is illustrative. Whereas pentanedionate, applied in excess, formed only the *bis*-pentanedionato complex (Scheme 8), a *mono*-bipy-*di*-aqua complex with bipy trans to the olefinic bonds (substituting H_2O_{trans}, Scheme 9) was obtained with bipy. In a second, much slower reaction, a *bis*-bipy complex analogous to the acac derivative is formed. The reason for this different behavior is not likely to be the different O—O distances between H_2O_{trans} (2.95 Å) and H_2O_{trans}–H_2O_{gauche} (2.75 Å), but rather the different substitution rates. For an acac molecule, which can function as a bidentate but also as a monodentate ligand, at least in an intermediate stage, rapid substitution of both H_2O_{trans} positions by two acac molecules, followed by slower substitution of the H_2O_{gauche} water seems a plausible hypothesis. In the case of bipyridine, which can only enter in a bidentate fashion, substitution of both trans sites blocks further substitution of the gauche positions. The Ru—O distances for the remaining water molecules in $(COD)Ru(bipy)(H_2O_{gauche})_2(PF_6)_2$ are 2.12–2.13 Å from X-ray crystallography, i.e. longer than in the olefin aqua ion. In a preliminary kinetic study, the rate constant for substitution of two water ligands for bipyridine, was $k_2 = 3.0 \pm 0.03\ M^{-1}\ s^{-1}$ at 295 K under pseudo-first-order conditions



Scheme 9. Substitution of specific water positions in $[(COD)Ru(H_2O)_4]^{2+}$.

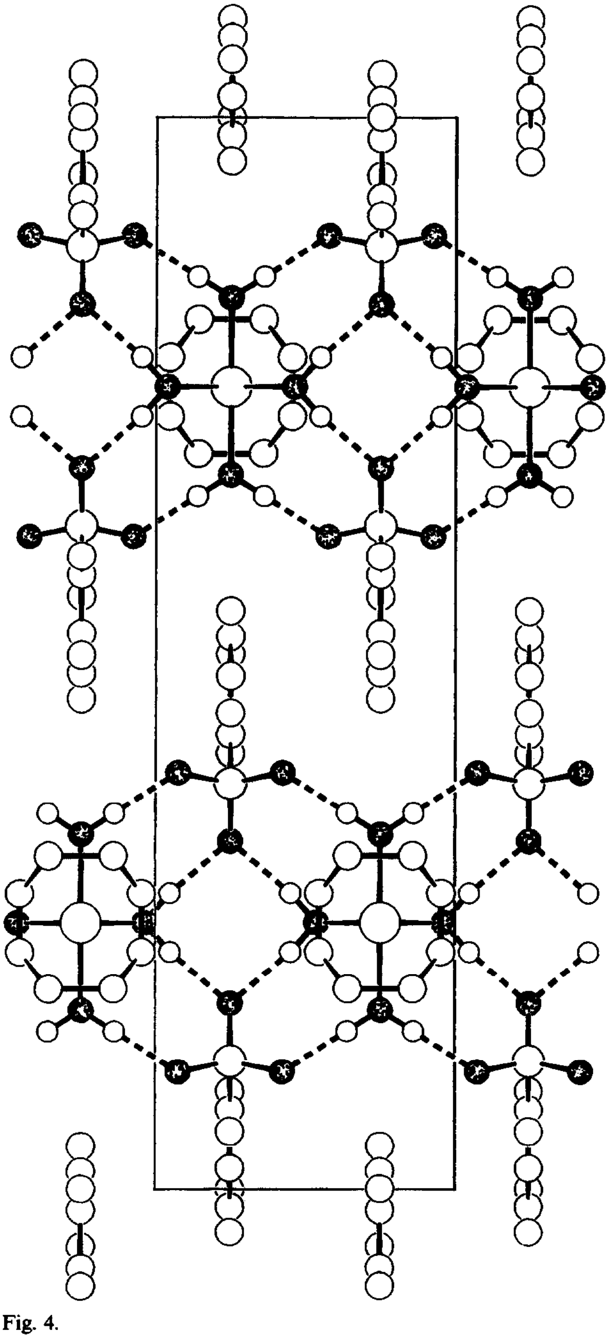


Fig. 4.

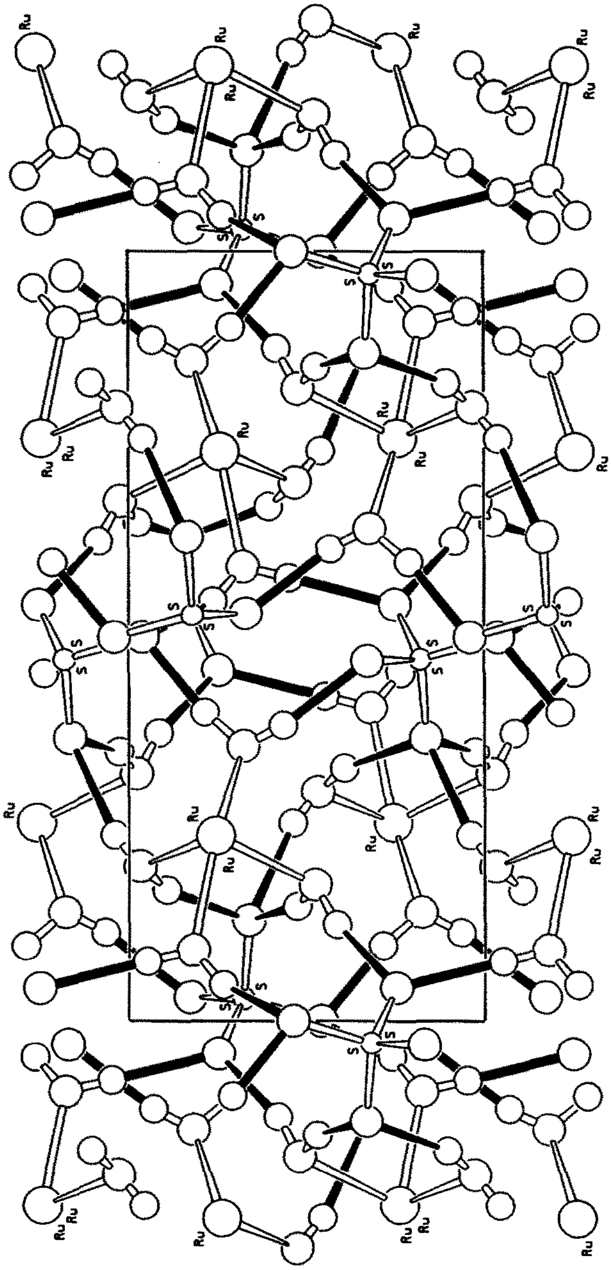
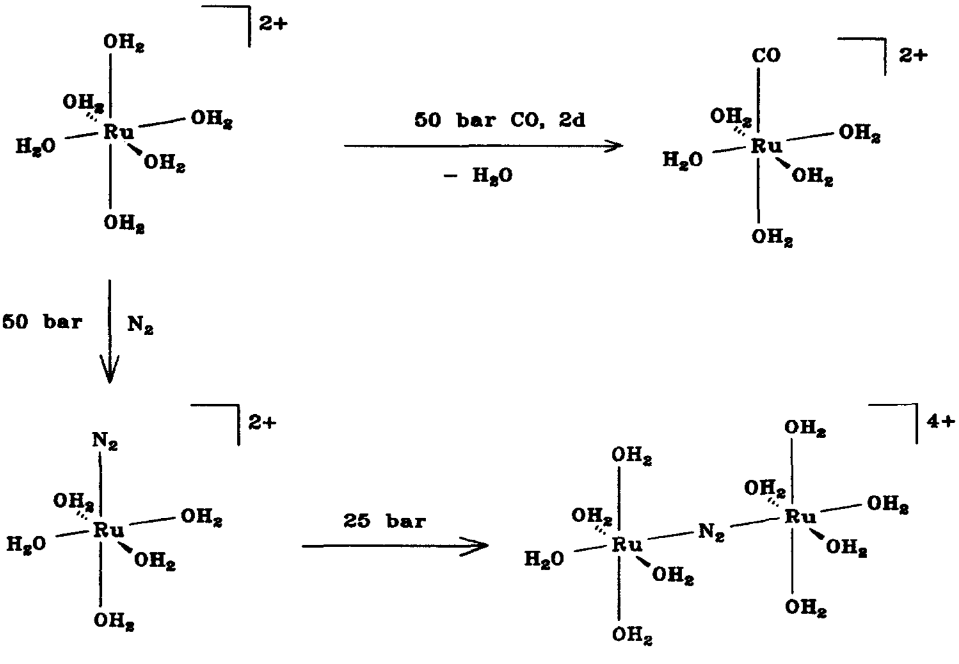


Fig. 4 (continued). Hydrogen bonding network in the crystal structure of $[(COD)Ru(H_2O)_4](OTs)_2$ and $[(NBD)Ru(H_2O)_4]SO_4$.

([Ru] = 1.04 × 10^{-3} M, [bipy] = 12.4 × 10^{-3} M), which is the same order of magnitude as that for water exchange for H_2O_{trans} (Table 5).

Binding of two-electron acceptor ligands L to $Ru(H_2O)_6^{2+}$ was demonstrated elegantly by ^{17}O NMR spectroscopy for L = CO [48] and L = N_2 [49]. In the case of CO, the ^{17}O signal from $Ru(H_2O)_6^{2+}$ (10% ^{17}O enriched) splits into two lines at δ −155 and −29 ppm, with relative intensities 1:4 assigned to cis and trans water ligands, respectively, when an aqueous solution of $Ru(H_2O)_6^{2+}$ was pressurized with 2 bar of CO. There concomitantly appeared two CO signals, i.e. δ 205 and 187 ppm, for coordinated and free CO, respectively, in the ^{13}C NMR spectrum.

The spectrum obtained in the presence of (7.4% ^{15}N enriched) dinitrogen depends on the nitrogen pressure. At 50 bar, the water signals at −165 and −86 ppm are assigned to cis and trans water of a mono-N_2 complex (Scheme 10), the ^{15}N NMR signal of which consists of two doublets ($^1J_{NN}$ = 3.4 Hz) assigned to the coordinated (−83 ppm) and uncoordinated (−24 ppm) nitrogen atom of an end-on bound N_2 molecule.



Scheme 10. Substitution at $Ru(H_2O)_6^{2+}$ by CO and N_2.

Most remarkably, at half the nitrogen pressure and a higher Ru^{2+} concentration, an additional signal with chemical shift to higher field (−98 ppm) appeared as a singlet in the ^{15}N spectrum, along with an additional ^{17}O signal close to the cis water signal of the mono-N_2-adduct. This obviously symmetrical complex was assigned to the dinuclear N_2-bridged complex, as shown in Scheme 10. The substitution of water by the acceptor ligands was slow (several days), and the complexes, once formed, were stable and did not revert to the hexa-aqua ion when excess water was evaporated *in vacuo*. To close this section, the recently achieved coordination of ethylene, pressurized (100 bar) onto an aqueous solution of $Ru(H_2O)_6^{2+}$ to form successively the mono and bis-ethylene complexes $Ru(H_2O)_5(C_2H_4)^{2+}$ and *cis*-$Ru(H_2O)_4(C_2H_4)_2^{2+}$ respectively, should be mentioned [55]. From the latter a mixture of 1- and *cis*/*trans*-2-butenes was liberated. Thus, the aqua ion $Ru(H_2O)_6^{2+}$ functions as a catalyst for ethylene dimerization in water at ambient temperature.

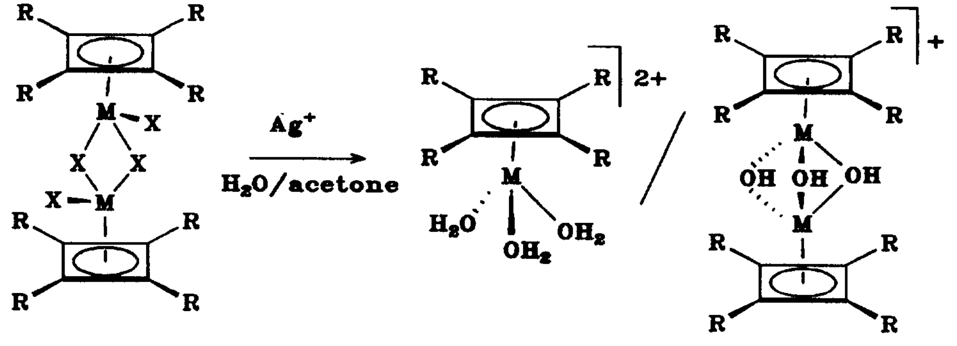
9. Ni, Pd AND Pt COMPLEXES

A logical extension into Group 10, in the present context, is given by cyclobutadiene (Cbd) complexes of Ni, Pd and Pt [5]. In fact, whereas the chemistry with arene and Cp ligands of these elements is rather limited, in particular for Pd and Pt, a variety of alkyl- and phenyl-substituted cyclobutadiene halide derivatives of formula $[(C_4R_4)MX(\mu\text{-}X)]_2$ (R = alk, Ph, X = Cl, Br, I, M = Ni, Pd, Pt), completely analogous to arene Ru(Os) and CpCo(Rh,Ir) complexes, are well-known compounds. The first example was the Ni chloro complex $[(C_4Me_4)NiCl_2]_2$, prepared by Criegee and Schröder in 1959 [50] through the reaction of 1,2-dichlorocyclobutene with $Ni(CO)_4$. In their publication, they noted the water solubility of the red complex, but implications of this phenomenon were obviously not pursued.

When the red aqueous solution of $[(C_4Me_4)NiCl_2]_2$ was treated with AgOTs, AgCl filtered and thoroughly washed with water, after drying, a material of analytical composition $[(C_4Me_4)Ni(H_2O)_3](OTs)_2$, showing an Me singlet at δ 0.90 in the NMR (D_2O), was isolated with a 96% yield. The aqua ion appears quite stable and did not show signs of decomposition in water over longer periods (Scheme 11).

Similarly, dehalogenation of the blue bromo complex $[(C_4Ph_4)NiBr_2]_2$ [51] with Ag^+ gave a red solution, most probably of the aqua ion. In this case, however, a colour change from red to mauve on evaporation of water indicates a change in coordination. Elementary analysis is in agreement with the formulae $[(C_4Ph_4)NiSO_4]$, *i.e.* water ligands are displaced by sulfate or $\{[(C_4Ph_4)Ni]_2(\mu\text{-}OH)_3\}_2SO_4$, where condensation has taken place.

With Pd, only the C_4Ph_4 derivative $[(C_4Ph_4)PdCl_2]_2$ is easy to obtain [52]. Since the compound is not soluble in water, dehalogenation using Ag_2SO_4 was performed in an acetone + water mixture. The resulting yellow solution on drying gave a yellow powder, which also was not soluble in water. NMR spectroscopy (acetone-d_6) revealed (apart from a Ph multiplet) two water signals at δ 3.27 and 3.45, which were assigned to bridging OH and free water. The NMR integration is in agreement with the formula $[(C_4Ph_4)Pd(\mu\text{-}OH)_3Pd(C_4Ph_4)]_2SO_4 \cdot H_2O$. The compound was not stable and, on repeated dissolution and reprecipitation slowly decomposed leaving small amounts of metallic Pd. These observations were repeated if AgOTs instead of Ag_2SO_4 was used for dehalogenation.



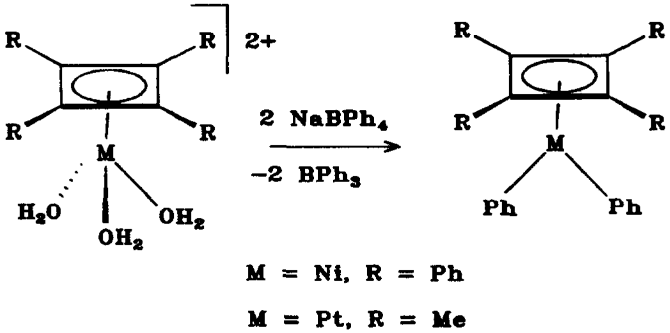
M = Ni, X = Cl, R = Me
M = Ni, X = Br, R = Ph
M = Pd, X = Cl, R = Ph
M = Pt, X = Cl, R = Me

Scheme 11. Aqua ions from the Ni triad.

Attempted dehalogenation of $[(C_4Me_4)PtCl_2]_2$ [53] under the same conditions as above resulted in complete decomposition with the deposition of metallic Pt. A solution of a presumed aqua ion can be prepared by dehalogenation of $[(C_4Me_4)PtCl_2]_2$ in 1 M sulfuric acid at 0°C. The near colorless solution is stable for about 1 h at this temperature, but slowly decomposes with the formation of a Pt mirror. ^{1}H NMR spectroscopy of the freshly prepared solution in 1 M $D_2SO_4 + D_2O$ showed an Me singlet at δ 1.56, shifted to a higher field compared with the chloride precursor and showing Pt satellites with $^3J_{Pt—H} = 21$ Hz.

Thus, when going from Ni to Pd to Pt, possible $C_4R_4M(H_2O)_3^{2+}$ ions become increasingly acidic and increasingly unstable. Interestingly, an attempt to isolate aqua complexes from aqueous solutions by precipitation with $NaBPh_4$ in two cases gave a new, hitherto unknown cyclobutadiene derivative, i.e. $(C_4Ph_4)Ni(\sigma\text{-}Ph)_2$ and $(C_4Me_4)Pt(\sigma\text{-}Ph)_2$, evidently by nucleophilic substitution of H_2O for a phenyl group of the BPh_4^- anion (Scheme 12). Whereas the NMR spectrum of the Ni complex, owing to the presence of only Ph protons, is not very conclusive, the Pt complex is easily characterized by NMR, showing an Me signal (δ 1.61, acetone-d_6) with Pt satellites ($^3J_{Pt—H} = 11.8$ Hz) and a phenyl multiplet (6.87–7.86) in the correct intensity ratio. Both complexes could be crystallized by the diffusion of pentane into an acetone solution, and gave correct CH analysis for the indicated composition.

As model complexes for the cyclobutadiene aqua ions of the Ni group, which for Pd and Pt obviously are of limited stability, a series of tripod complexes were prepared and structurally characterized. In each case, a water (or acetone + water for the Pd compound) solution was prepared as described above, to which a solution of the tripod-Na salt $[CpCo(PO(OR)_2)_3]Na$ (R = Me, Et) was added. On the addi-



Scheme 12. Formation of $(C_4R_4)Ni(Pt)Ph_2$.

tion of one equivalent of PF_6^-, the respective tripod monocationic complex precipitated from the solution. It was thoroughly washed with water, reprecipitated from acetone + pentane and finally crystallized by the diffusion of pentane into an acetone solution. Red (Ni), yellow (Pd) or pale yellow (Pt) crystals were obtained.

The crystal structures were frequently complicated by disorder of the central $(PO(OR)_2)_3$ part with respect to the cyclobutadiene or the CpCo part. Details of the structures and packing and disorder problems are given elsewhere [31]. Two representative structures are displayed in Fig. 5. In the present context, these experiments show that the aqueous solutions indeed contain unhydrolysed (with respect to the cyclobutadiene ligand) LM fragments complexed to only water or hydroxide.

The Ni–O distances in the tripod complexes are around 1.96 Å and are difficult to compare with those of related oxygen ligands. Generally, Ni–O in, for example, acetylacetonate complexes are shorter and mostly around 1.90 Å (cf. Ru–O of 2.10 Å in $(COD)Ru(tripod)(H_2O)^+$ above, with Ru–O of 2.11 Å in [Cp*Ru(acac)] [54]). Most obvious are short Ni–C distances to cyclobutadiene carbon atoms (1.986 Å mean), up to 0.012 Å shorter than those in the soft ligand cyclobutadiene Ni complexes, along with rather short intraligand C–C bonds (1.386 Å mean to be compared with 1.46–1.47 Å in halide complexes). These figures indicate a strong Ni–cyclobutadiene interaction, but one of more ionic character with less backbonding into cyclobutadiene π^* orbitals, as indicated by the very short C–C bond lengths. Similar trends were observed in the tripod complexes of Pd and Pt, where the M–O bond lengths are quite long compared with other oxo and oxy ligands, whereas the cyclobutadiene ring is less affected than in the case of Ni.

10. CONCLUDING REMARKS

Considering the results detailed above, an idea can be gained about the prerequisites for the existence and chemical behavior of organometallic aqua ions. They are notoriously unstable and will rapidly lose the carbocyclic ligand if the metal center is too hard. No indication of any Fe organometallic aqua ions has become

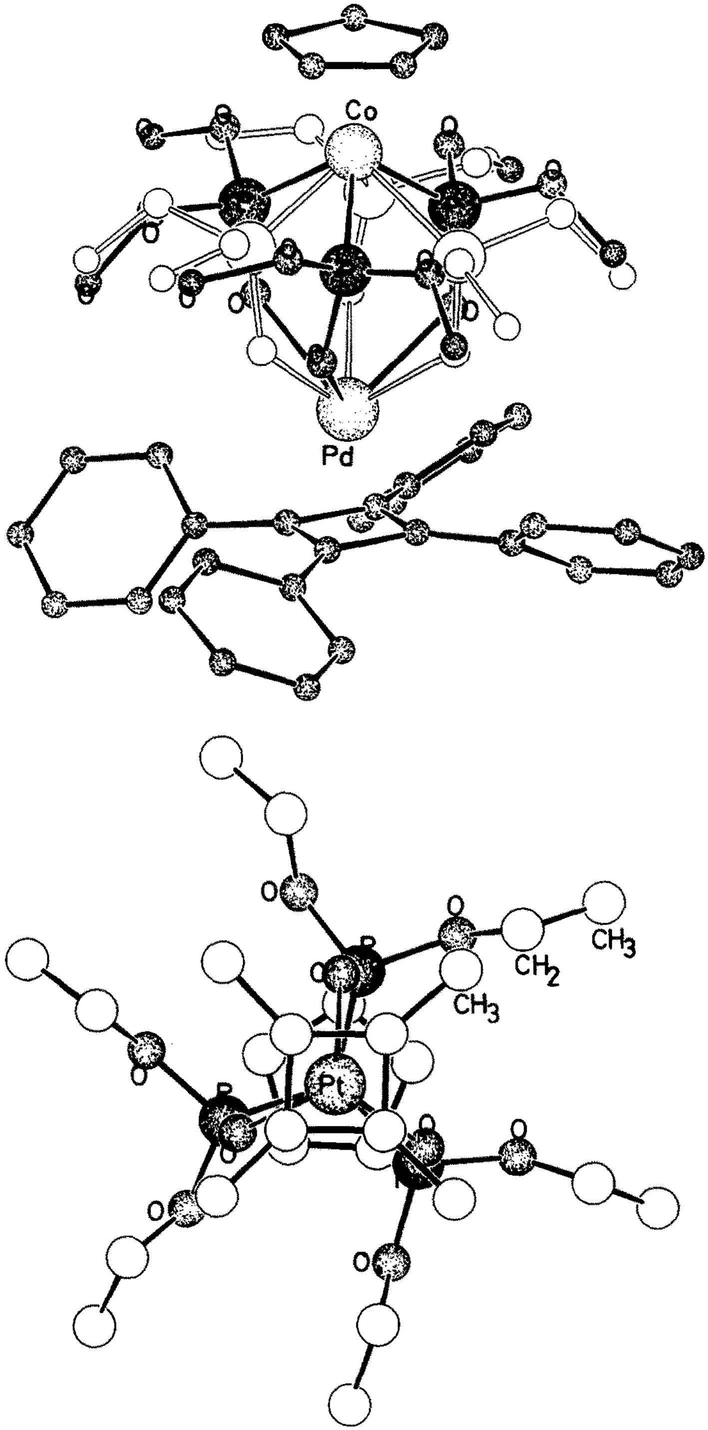


Fig. 5. SCHAKAL representation of (a) $[CpCo(OEt)_2)_3Pd(C_4Ph_4)]^+$, showing disorder of the $(PO(OEt)_2)_3$ belt, and (b) $[CpCo(PO(OEt)_2)_3Pt(C_4Me_4)]^+$, viewed down the Pt–Co axis.

apparent. Co appears at the limit of stability, isolable only with the more basic Cp* ligand. $Cp^*Co(H_2O)_3^{2+}$ has a stability comparable to that of $CpCr^{2+}$, and $CbdNi^{2+}$ is even more stable than both of these. Thus, a sequence of decreasing stability for 3d organometallic aqua ions emerges: $Ni(II) > Cr(III) > Co(III) \gg Fe(II)$. 4d and 5d transition metal aqua ions could be stable if the parent aqua ion is not too acidic, as is the case for Pd and Pt.

Considering cyclobutadiene complexes, an inherent ambiguity exists in the stereochemistry and electron count. Considering C_4R_4 as a neutral four-electron ligand would impose oxidation state II and, consequently a square planar coordination environment for Pd and Pt. The composition and stereochemistry of the $C_4R_4MX_2$ complexes with pseudo-octahedral coordination (assigning three positions to a C_4R_4 ligand, in analogy to Cp and arene complexes), corroborated by the same stereochemistry in the $(C_4R_4)M$(tripod) complexes above, implies a six-electron $C_4R_4^{2-}$ ligand with a formal oxidation state of IV for the metal. In fact, this may increase the acidity of the water ligands in the respective aqua ions beyond the value tolerable for a stable complex.

Rh(III) and Ru(II), up to the present, represent the ideal compromise between "softness and acidity" of complexed water and backbonding into π^* orbitals of carbon π ligands and, therefore, exhibit the most promising organometallic aqua chemistry. A point of paramount importance that should stimulate future research in the area is the promise for obtaining organometallic chemistry in water or at least water + alcohol mixtures. Such chemistry could make a valuable contribution to solve ecological problems of industrial production in the future.

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