

Organometallic Aqua Complexes, III^[◇]

Olefin Aqua Complexes of Rhodium(I)

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Dehalogenation of halide precursors [(olefin)RhCl]₂ [olefin = ethylene, 1,5-cyclooctadiene (COD), norbornadiene (NBD), 2,3-dimethylbutadiene (DMB)] in water gave the respective *cis*-diolefin aqua ions, characterized by NMR spectroscopy in solution. Attempted isolation of the tosylate salt [(COD)Rh(H₂O)₂]OTs yielded crystals of (COD)Rh(H₂O)(η¹-OTs) characterized by X-ray structural analysis. [(NBD)Rh(H₂O)₂]SbF₆

in the presence of adventitious toluene decomposed into [(NBD)Rh(η⁶-toluene)]SbF₆ and [(NBD)₂Rh]SbF₆, both complexes were isolated and structurally characterized. Ethylene exchange in [(C₂H₄)₂Rh(H₂O)₂]⁺ is fast with *k*₂ of the order of 10⁴–10⁵ s⁻¹ · M⁻¹. The rate constant for water exchange in [CODRh(H₂O)₂]⁺ is estimated as 10⁴ s⁻¹ (Δ*G*_{‡73}⁺ ≈ 25 kJ/mol) at 173 K.

The known coordination chemistry of Rh(I)^[2] is confined to complexes stabilized by π-acceptor ligands. No single molecular compound where Rh(I) is coordinated solely to σ-donor ligands has been prepared to date. In general, at least two of the four coordination sites of a square-planar Rh(I) center must be occupied by π-acceptor ligands where σ-donor ligands frequently form the bridges in e.g. [(diolefin)RhX]₂ or [(PR₃)₂RhX]₂. A variety of anionic complexes [L₂RhX₂]⁻ where X is halide^[2] or e.g. acetate^[3], likewise represent the donor/acceptor combination typical of a broad class of Rh(I) complexes.

One example where delineation is somewhat arbitrary is the anionic complex [RhCl(SnCl₃)₂]₂⁴⁻^[2]; a chloro complex of analogous composition has, however, apparently not been prepared. Note also the non-existence of binary halides RhX. A step towards pure σ-donor ligand stabilized Rh(I) can be seen in a recently prepared anionic hydrido complex Li₃[RhH₄]^[4], a solid featuring square-planar [RhH₄]⁴⁻ units which, however, does not appear to exist in solution.

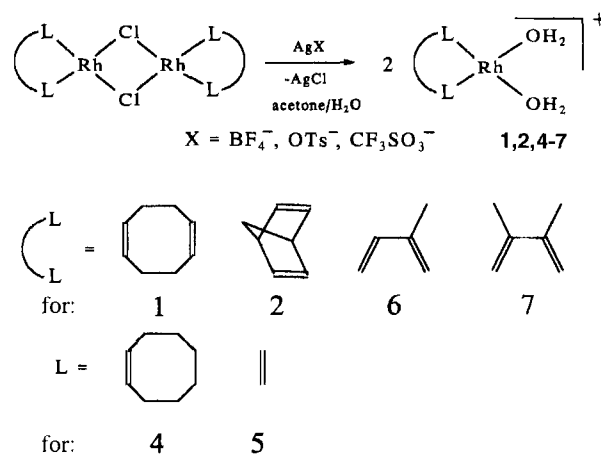
More closely related examples are methoxy- and hydroxo-bridged dimers [(COD)Rh(μ-OR)]₂, R = H, Me^[5], water-insoluble molecular compounds prepared from halide complexes by exchange of halide for OH or OMe respectively.

Monomeric diammine complexes [(COD, NBD)Rh(NH₃)₂]⁺ have recently been generated in solution and were stabilized and structurally characterized as crown ether inclusion complexes^[6]. Dehalogenation of Rh(PPh₃)₂(CO)Cl by various Ag⁺ salts in the presence of a trace amount of water has led to isolation and structural characterization of

the monoqua ion [Rh(PPh₃)₂(CO)(H₂O)]⁺ independently in two laboratories^[7,8].

The characterization of a variety of arene- and olefin-water complexes^[9], in particular (arene)Ru(H₂O)₃²⁺^[10], Cp* (Co,Rh,Ir)(H₂O)₃²⁺^[11,12], (diolefin)Ru(H₂O)₄²⁺^[13], and (olefin)Ru(H₂O)₄²⁺^[14] in recent time has stimulated our interest in possible organometallic Rh(I) aqua species. Since a Rh(I) aqua ion is neither known nor can its existence be expected the question arises: what is the minimal number and nature of π acceptor ligands necessary to stabilize Rh(I) in aqueous solution? The simple and straightforward strategy to answer this question is to perform dehalogenation of chloro complexes, e.g. [(diolefin)RhCl]₂, in water or water solvent mixtures and study the properties of the resulting solutions.

Scheme 1

**Dehalogenation of Olefin Chloro Complexes**

Treatment of [(COD)RhCl]₂ with AgOTs in water, water/acetone, or water/ethanol gave almost instantaneously a

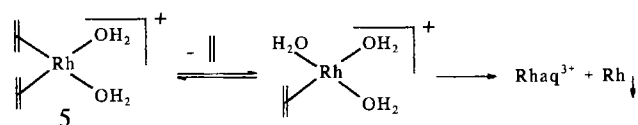
[◇] Part II: Ref.^[1].

precipitate of AgCl and a yellow solution which after evaporation of the solvent left a yellow solid. NMR spectroscopy ($[D_6]$ acetone) of the solid, apart from a water signal at $\delta = 3.7$ integrating as about 4 protons, showed the presence of coordinated COD with one signal for the olefinic ($\delta = 4.07$), a multiplet at $\delta = 2.27$ (4H) and an AB-like pattern for aliphatic protons of the diolefin ligand, showing the same symmetry as the starting chloride. Apart from coordination shifts a coupling of the olefinic carbon ^{13}C signal ($\delta = 77.5$) to Rh ($J = 15.4$ Hz) is indicative of coordinated COD.

The NMR spectrum of a sample obtained by precipitating the solid from acetone with ether and recorded in CD_2Cl_2 showed a water signal at $\delta = 2.50$ which could be eliminated by shaking with D_2O and integrated as about four protons or two molecules of water per COD and per tosylate respectively. Appearance of the olefinic COD protons as a slightly broadened (by coupling) singlet at $\delta = 4.2$ further confirmed C_{2v} symmetry of the complex. Though it is difficult to definitively assess the exact water content of the solution species due to fast water exchange (see below) we believe that the primary species formed in water and water/solvent mixtures is the diaqua ion **1**. The tosylate salt could be liberated from solvent in high vacuo and redissolved in water or acetone without changing its properties.

Similar results were obtained when the analogous NBD complex was treated in the same manner. Spectra taken after dehalogenation are in accordance with the *bis*-aqua complex **2**. In this case, however, the sample after having crystallized from acetone/ether showed in $[D_6]$ acetone a signal intensity indicative of only one coordinated water molecule according to the composition (NBD)Rh(H_2O)(OTs) (**3**) (vide infra).

Scheme 2



Besides to chelating diolefin complexes the dehalogenation procedure has also been applied to *bis*-monoolefin complexes. Treatment of a suspension of complexes [(cyclooctene) $_2$ RhCl] $_2$ and [(ethylene) $_2$ RhCl] $_2$ in acetone containing a trace of water ($\approx 1-2\%$) with AgBF $_4$, AgOTs or AgTf (Tf = CF $_3$ SO $_3$) caused rapid dissolution of the solid to give clear orange to yellow solutions after removal of AgCl by filtration. 1H -NMR spectra showed the presence of coordinated olefin with a signal at $\delta = 2.67$ for olefinic protons of cyclooctene in **4** and about 3.0 ppm ($[D_6]$ acetone) for ethylene in **5** respectively. Generated that way the complex ion [(C $_2$ H $_4$) $_2$ Rh(H_2O) $_2$] $^+$ is stable in solution for days at ambient temperature. However, when solutions were evaporated to dryness they turned dark and only part of the material redissolved to refurnish the original NMR spectrum, leaving some Rh metal. Obviously, partial loss of ethylene occurs during evaporation which causes decompo-

sition with disproportionation into Rh(III) and elementary Rh.

Analogous complexes could be obtained with the dienes 2-methylbutadiene (isoprene) and 2,3-dimethylbutadiene. A solution of **5** in acetone/water treated with an excess of isoprene gave, according to NMR, the respective isoprene complex [(isoprene)Rh(H_2O) $_2$] $^+$ (**6**). If the mixture was heated with an excess of isoprene under pressure to 60°C for some hours a toluene soluble isoprene polymer could be extracted leaving an aqueous solution of **6**. The 2,3-dimethylbutadiene (DMB) complex [(DMB)Rh(H_2O) $_2$] $^+$ (**7**) was prepared by dehalogenation of the respective chloro complex [(DMB)RhCl] $_2$.

Ethylene Exchange

The ethylene 1H -NMR signal in **5**, dissolved in $[D_6]$ acetone, splits on cooling into a symmetrical AB pattern with $\Delta\delta = 0.84$. From the coalescence temperature of 232 K at 500 MHz proton frequency a value of $\Delta G^\ddagger = 43$ kJ/mol was calculated for the barrier to equilibration. An Arrhenius plot in the temperature range 128–238 K yielded activation parameters $\Delta H^\ddagger \approx 20$ kJ/mol and $\Delta S^\ddagger \approx -100$ J/mol · K. The splitting of ethylene protons into two signals of equal intensity is only compatible with a *cis*-bis-olefin complex in analogy to the complexes formed from chelating diolefins.

With ethylene being present in the amount as given by the starting chloro complex the observed process can be either an inner rotation or ethylene exchange depending on which is faster. Applying an ethylene pressure of 2 bar, which results in about one equivalent of excess ethylene as shown by integration, we observe only one signal for free and coordinated ethylene at $\delta = 4$ (intermediate between coordinated and free ethylene at $\delta = 5.3$) at ambient and low temperature, indicating rapid intermolecular exchange. The ethylene ^{13}C signal under these conditions was coalesced. If only a slight excess of ethylene was added to the NMR sample of **5** coalescence could be still observed but the coalescence temperature for proton equilibration dropped by at least 40 K. This observation points to ethylene exchange as the process responsible for equilibration. From line widths at 213 K first-order rate constants for ethylene exchange could be estimated as $3.5 \cdot 10^3$ and $2 \cdot 10^2$ s $^{-1}$ for the two cases with and without excess ethylene respectively. Evaluation of the second-order rate constant requires the concentration of free ethylene. In experiments where this concentration is in a range measurable by NMR integration exchange is too fast to be monitored. An order of magnitude for k_2 can be estimated as follows: since in the experiment where a small amount of additional ethylene was applied neither integration nor chemical shift changed within the limits of accuracy, a maximum excess of $\leq 5\%$ ethylene is inferred. The concentration of the complex was 0.15 M, which means excess ethylene is ≤ 0.0075 M which leads to a second-order rate constant $k_2 \geq 2.6 \cdot 10^5$ M $^{-1}$ s $^{-1}$ (since the proportion of free ethylene is very small, the lifetime τ derived from the NMR line width above the coalescence temperature when only one broadened line is present

can still be equated to τ_{compl} , i.e. the lifetime of ethylene within the complex). This conclusion implies that **5** dissociates to a small extent in solution into a monoethylene complex. Such dissociation is clearly obvious also from $^1\text{H-NMR}$ spectra of **4**, where signals of coordinated olefinic protons at $\delta = 2.23$ and 2.76 are broadened at ambient temperature and become sharp on cooling to 213 K along with the appearance of the signal set for about 10% of free olefin. Proton equilibration in **5** could then occur either by dissociation or alternatively by liberation of a small quantity of ethylene that exchanges for coordinated ethylene in a second-order process. Acceleration of ethylene exchange by excess ethylene as well as a negative entropy of activation strongly argue in favor of the latter mechanism.

Water Exchange

Applying the above procedure, we prepared a sample of **5** in $[\text{D}_6]\text{acetone}/\text{H}_2\text{O}$ where the water signal integrated as twice the amount of water required by the formula $[(\text{ethylene})_2\text{Rh}(\text{H}_2\text{O})_2]^+$. This water signal did not split down to -95°C . Thus, water or water proton exchange between coordinated and bulk water contained in the acetone is still fast at this temperature.

Water exchange was further studied with **1**. In an experiment performed as above using 23% enriched H_2^{17}O a relatively sharp ^{17}O signal ($\Delta\nu \approx 200\text{ Hz}$) at $\delta = -11\text{ ppm}$ (relative to acetone at $\delta = 573$) was observed at ambient temperature. This water signal is shifted from the position of water in acetone by not more than a few ppm. Complexed ^{17}O water of **1** as the BF_4^- salt appears in THF at $\delta = -17$ and in CD_2Cl_2 at $\delta = -15.7$. Since the sample in CD_2Cl_2 does not contain any extra water beyond the coordinated one it is concluded that the water coordination shift exerted by the (olefin)Rh(I) moiety at ambient temperature is much less than observed for other comparable aqua-ions^[15].

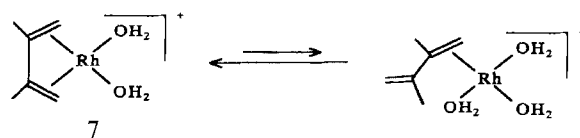
On cooling the acetone solution, the water signal started to broaden below -60°C and exhibited a line width of 9030 Hz at -100°C . However, coalescence or separation into two lines could not be reached at the lowest possible temperature (ca. -110°C). A similar experiment was performed in THF containing $10\ \mu\text{l H}_2^{17}\text{O}$ in 0.5 ml solvent with a molar ratio $\text{Rh}:\text{H}_2^{17}\text{O}$ as about 1:4. Broadening of the water signal again started around -60°C reaching a linewidth of 7090 Hz at -100°C . This linewidth is much greater than the viscosity broadening of the same amount of water in THF which is 1320 Hz at -90°C . Moreover, it was noticed that at this temperature in the pure THF/water mixture most of the water was frozen out, whereas the solution containing the Rh complex was clear down to -100°C . From line broadening and solubility behavior it is concluded that water is coordinated to the (olefin)Rh moiety in acetone and THF respectively even at this low water content, at least at the lower temperatures. Line broadening at lower temperatures, moreover, suggests that the shift difference between free and coordinated water must be much greater at low temperature than at ambient temperature, in particular greater than the line width of the signal at low

temperature. Taking ca. 100 ppm (6770 Hz) as a mean value for the shift difference between metal-coordinated and bulk water in these types of aqua ions^[15], we estimated a first order rate constant for water exchange at this temperature of $k \approx 10^4\text{ s}^{-1}$ ($\Delta G_{173}^\ddagger \approx 25\text{ kJ/mol}$) from the line broadening at 173 K . More reliable values for water exchange rates can possibly be obtained in future experiments using the paramagnetic line broadening technique.

Internal Mobility in $[(\text{DMB})\text{Rh}(\text{H}_2\text{O})_2]^+$

The relatively high thermal stability of $[(\text{DMB})\text{Rh}(\text{H}_2\text{O})_2]^+$ (**7**) in water allowed the exchange of binding sites in this complex to be studied. The $^1\text{H-NMR}$ spectrum in D_2O at 25°C is consistent with a symmetrical η^4 structure, showing a singlet for Me protons and signals at $\delta = -0.18$ and 1.84 for *syn* and *anti* protons of the coordinated diene respectively with chemical shifts comparable to e.g. those of the chloro complex. On heating, these latter signals broadened and coalesced at about 65°C . Above this temperature, up to 95°C , a new pattern appeared consisting of a virtually unchanged Me signal along with two broad signals at $\delta = 0.9$ and 2.8 intermediate between shifts of the *syn* and *anti* protons and the corresponding positions in the free olefin ($\delta \approx 5.1$ and 5.2). The high-temperature spectrum thus indicates the presence of a species with partly decomplexed diene in a dynamic equilibrium as shown in Scheme 3. From the observed chemical shifts at 363 K a ratio of about 70% of η^4 to 30% of η^2 -form may be derived. From the fact that the change in NMR spectra is fully reversible on lowering the temperature and that no sizeable decomposition was noticed during the experiment we strongly conclude that only one double bond can be decomplexed at the time, otherwise, rapid formation of metallic Rh would be expected.

Scheme 3



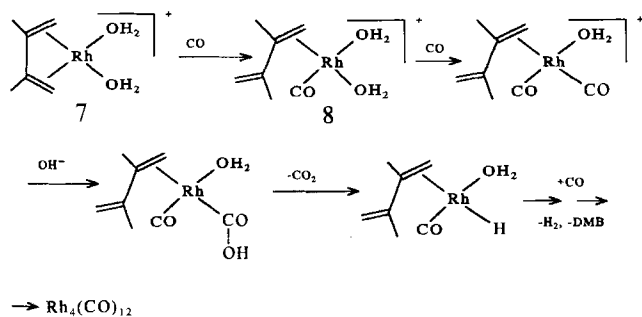
When **7(OTs)** was recrystallized from acetone and the NMR spectrum taken in CD_2Cl_2 a pattern very similar to the high-temperature spectrum in water was encountered. Moreover, the water content by integration again corresponds to the composition $(\text{DMB})\text{Rh}(\text{H}_2\text{O})(\text{OTs})$. Obviously, also under these conditions an equilibrium featuring a fraction of monodentate DMB, and possibly bidentate OTs, is present in solution.

Carbonylation

Attempted dehalogenation of the analogous chlorocarbonyl $[(\text{CO})_2\text{RhCl}]_2$ under the same conditions as used in the above experiments led to spontaneous decomposition with precipitation of metallic Rh. If, instead, a slight pressure (2–4 bar) of CO was applied to a solution of one of the olefin-aqua complexes, it turned red and eventually a red precipitate separated. Reaction of CO with solutions of

7 was studied in more detail. When 2 bar CO were admitted to an orange solution of **7** in water/MeOH rapid decolorization to faint yellow was observed. An IR spectrum taken from this solution showed a single CO band at 2049 cm^{-1} indicating a monocarbonyl **8**. After some time the solution turned bright red as previously observed and two new CO bands appeared at 2075 and 2000 cm^{-1} at the expense of the former. The final IR spectrum was that of $\text{Rh}_4(\text{CO})_{12}$. Note that in this instance no Rh(III) was formed. Thus Rh(I) was obviously reduced to Rh(0) by CO in a watergas shift-like reaction. Accordingly, the rate is considerably reduced in acidic solution. At pH 1 intermediates of the reaction could be detected by NMR. The faint yellow solution showed a new ^{13}C signal as a doublet at $\delta = 182$ ppm ($J_{\text{Rh-C}} = 76.3$ Hz) and a doubled signal set for singly coordinated DMB confirming the presence of monocarbonyl **8**. The lack of Rh-C coupling in the ^{13}C resonances of coordinated olefinic carbon is attributed to the relatively slow exchange between coordinated and uncoordinated sites in this system too. Concomitantly with the formation of the red $\text{Rh}_4(\text{CO})_{12}$ solution signals of free DMB were observed. The reaction course is depicted in Scheme 4. Formation of $\text{Rh}_4(\text{CO})_{12}$ has been observed previously in a variety of reactions of Rh(I)carbonyl compounds, particularly under basic conditions, an example being the aqueous hydrolysis of the dimeric methoxycarbonyl $[(\text{CO})_2\text{Rh}(\mu\text{-OMe})_2]$ which likewise led to the formation of $\text{Rh}_4(\text{CO})_{12}$ ^[16].

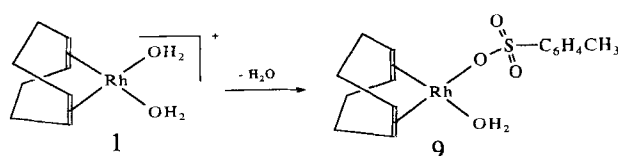
Scheme 4



Crystal Structures

Attempts to obtain the diaqua ions present in solution in a crystalline form failed and led to the isolation of different species. In contrast to monoaqua complexes $\text{RhL}_3(\text{H}_2\text{O})^+$ the diaqua complexes did not precipitate from the solution with large anions such as PF_6^- .

Scheme 5



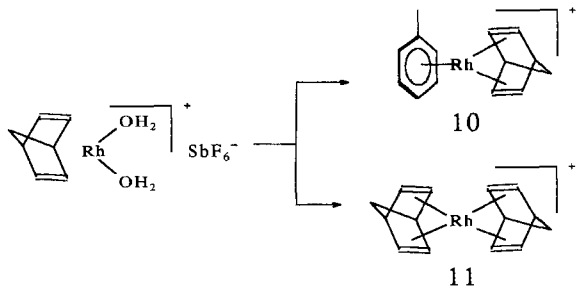
Crystallization of OTs salts from acetone/ether and inspection of the crystalline products by NMR indicated the composition (diolenin)Rh(H₂O)(OTs) in all cases but for the

ethylene complex. Yellow crystals of $[(\text{COD})\text{Rh}(\text{H}_2\text{O})\text{OTs}]$ (**9**) obtained from acetone/ether were found suitable for X-ray analysis. Parameters for structure determination of **9** together with those for **10** and **11** are collected in Table 1. The molecular model (Figure 1) shows the metal coordinated to COD, one water molecule and one oxygen atom of the OTs counterion in a square-planar arrangement. Two such units are bridged via hydrogen bonds between this water molecule and one non-coordinating SO_3 oxygen atom from an adjacent molecule to form dimers in the crystal. The angle O3-Rh-O4 is $92.4(1)^\circ$, i.e. close to an ideal square. Rh-O distances to water [2.106(3) Å] and sulfonate oxygen [2.102(3) Å] are equal within the limits of error. These distances may be compared with Rh-OH₂ distances in *trans*- $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})]^+$ from two independent determinations^[7,8] where Rh-O is cited as 2.115(5)/2.130(6)^[7] in the complex $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})]\text{BF}_4 \cdot 1/2 \text{H}_2\text{O} \cdot 1/4 \text{C}_6\text{H}_{12}$ and 2.316(12) in $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})] \text{O}_3\text{SCF}_3$ ^[8]. Even though the error seems to be an order of magnitude larger in the second example the difference is outside standard deviation and quite remarkable. A related example is provided by the five-coordinate complex $\text{Rh}(\text{triphos})\text{-}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})\text{BF}_4$ with a water ligand *trans* to phosphane and a Ru-O distance of 2.215 Å^[17]. The value found for **9** compares with the smaller distance of the $[\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{H}_2\text{O})]^+$ aqua ion. The variation within the series is quite remarkable and suggests that Rh-O distances in these aqua ions are sensitive not only to the *trans* counter ligand but also to the mode of hydrogen bonding to anions present. Rh-C_{COD} distances in **9** on the other hand averaging 2.075(4) Å appear to be short in comparison with corresponding distances in known (COD)RhX₂ structures, which typically amount to values 2.11–2.13 Å whatever the complex charge^[6,18–21]. It may be too early to draw conclusions from the limited set of data available at present but since from the above examples the thiolate-bridged complex $[\text{CODRh}(\mu\text{-SR})]_2$ has Ru-C distances at the long end (2.135 Å)^[22] it may be expected that a shorter *trans* olefinic bond is found along with the harder σ -ligands in these (COD)Rh complexes. A similar trend has recently been observed for Ru-C_{Cp} distances in dependency of the σ -counterligands in $\text{Cp}^*\text{RuL}_n^\sigma$ complexes^[23].

In a further attempt to obtain crystalline diaqua complexes the chloro complex $[(\text{NBD})\text{RhCl}]_2$ was dehalogenated with AgSbF_6 under the same conditions as above. In the Ru series we observed that NBD in comparison to COD decreases the solubility of olefin aqua complexes. SbF_6^- was chosen as a large non-hydrolyzing and non-coordinating anion. The reaction proceeded as above giving solutions of $[(\text{NBD})\text{Rh}(\text{H}_2\text{O})_2]\text{SbF}_6$ in aqueous acetone. From an acetone solution obtained by evaporation of water in high vacuo and redissolution of the residue which was overlaid with ether, after some time two different kinds of yellow and red crystals respectively separated. The yellow compound turned out to be $[(\text{NBD})\text{Rh}(\eta^6\text{-toluene})]\text{SbF}_6$ (**10**) and the red compound $[(\text{NBD})_2\text{Rh}]\text{SbF}_6$ (**11**). The formation of **11** can be understood as a reaction of $[(\text{NBD})\text{Rh}(\text{H}_2\text{O})_2]^+$ with excess NBD present in the reac-

tion medium or stemming from decomposition. The formation of the toluene complex **10** may be due to some adventitious toluene present in the ether.

Scheme 6



Both complexes are known compounds. In particular **11** is an important precursor of Rh(I) hydrogenation and hydrosilylation catalysts but the crystal structure has not been determined so far. Moreover, structural information on complexes $[(\text{diene})\text{Rh}(\text{arene})]^+$ is limited. Since the compounds were formed as suitable crystals we took the opportunity of determining the molecular structures.

Molecular models are depicted in Figures 2 and 3. The salt **11** crystallizes in the space group $C2/c$ with Rh located on an inversion center and SbF_6^- on a twofold axis. The most interesting parameter in the structure of **11** and **10** are Rh–C distances. In **11** these are on an average 2.205(8) Å and thus are longer by about 0.1 Å in comparison with complexes $(\text{NBD})\text{RhX}_2$ and $(\text{COD})\text{RhX}_2$ ^[6,24] (note that Ru–C distances in analogous NBD and COD complexes are equal^[6]). In **10** the average distance of Rh to the four olefinic carbon atoms in two independent molecules is 2.12 Å which is much closer to the normal value. Rh–C_{olefin} distances in **10** can be compared with those in two arene benzobarrelene structures which are 2.14(1)^[25] and 2.12(1)^[26] Å respectively and thus close to the value observed with the simpler prototype complex **10**. Rh–C_{arene} distances average 2.28(2) Å and seem to be located at the short end of the scale of examples presently known $[\text{Rh}(\text{durene})(\text{benzobarrelene})]^+$ 2.30(1)^[25], $[\text{Rh}(\text{toluene})(\text{P}(\text{OPh})_3)_2]^+$ 2.333(6)^[27], and $(\text{Rh}(\text{C}_2\text{H}_4)_2)(\eta^6\text{-C}_6\text{H}_5)_2\text{BPh}_2$ 2.30(1)^[28] Å).

Discussion

Complexes of the composition $[(\text{olefin})_2\text{Rh}(\text{H}_2\text{O})_2]^+$ where the olefinic ligand can be a monoolefin, diolefin or diene are generated in organic/aqueous solution by dehalogenation of the respective chloro dimers. A symmetrical pattern for the olefin part in the ¹H-NMR spectrum is taken as evidence for a symmetry plane as required by a *cis* diaqua structure. Due to its high substitutional lability it is, however, difficult to prove this solution structure unambiguously. In the solid state a *cis* combination of one tosylate and one water ligand seems to be the preferred coordination mode which implies ready loss of one water molecule on evaporation of the solvent in conjunction with this anion. If the complex cation is deprived of this kind of stabilization in nonaqueous solution, additional π -ligands are

Figure 1. ORTEP plot of $(\text{COD})\text{Rh}(\text{H}_2\text{O})(\text{OTs})$ (**9**). Bond lengths [Å] and angles [°]: Rh–OH₂ 2.106(3), Rh–O'SO₂ 2.102(3), 2.075(4)av., C=C_{COD} 1.386(5); O–Rh–O' 92.4(1), midpoint C=C–Ru–midpoint C=C 88.7

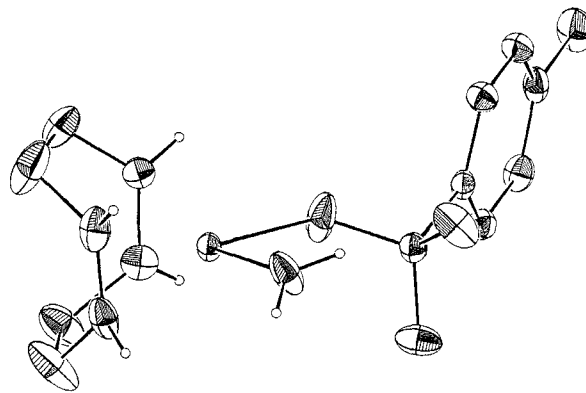


Figure 2. ORTEP plot of the cation of $[(\text{NBD})(\text{tol})\text{Rh}]\text{SbF}_6$ (**10**). Bond lengths [Å]: Rh–C_{NBD} 2.11(1)/2.12(1) av., Rh–C_{tol} 2.28(1)/2.28(2) av., C=C_{tol} 1.35(2)/1.38(2)av.

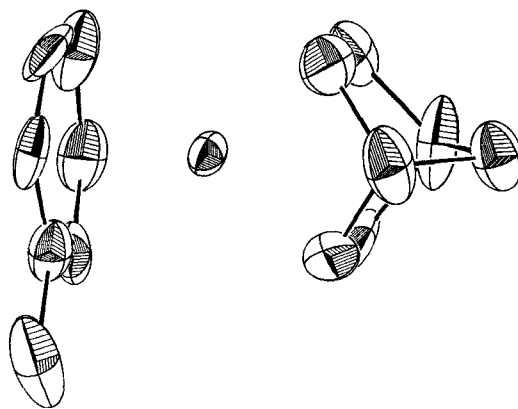
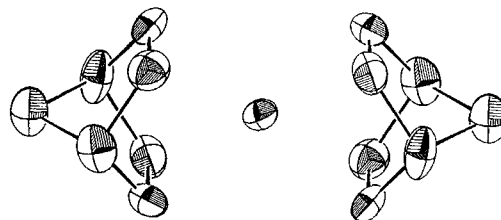


Figure 3. ORTEP plot of the cation of $[(\text{NBD})_2\text{Rh}]\text{SbF}_6$ (**11**). Bond length [Å]: Rh–C 2.205(7)



easily complexed as is shown by the formation of **11** and **12**. The stability of aqueous solutions, however, do not seem to depend on the anion (PF_6^- , SbF_6^- , BF_4^- , CF_3COO^-). Thus, in water, the anion appears not to contribute measurably to coordination.

A most remarkable feature of these aqua complexes is their high lability to undergo substitution reactions. Ready exchange of ethylene in $[(\text{C}_2\text{H}_4)_2\text{RhCl}]$ (Cramer's complex) has been noted from the beginning and has since been utilized extensively for the preparation of analogs featuring other olefinic ligands. Quantitative measurements of the kinetics are thwarted by the relative insolubility of Cramer's complex. Ethylene exchange in $[(\text{C}_2\text{H}_4)_2\text{Rh}(\text{acac})]$ has re-

cently been quantified by Åkermark and coworkers^[29]. If their activation data ($\Delta H^\ddagger = 9.7$ kJ/mol, $\Delta S^\ddagger = -145$ J/mol · K) are extrapolated to 213 K, the temperature for which the second-order rate constant of ethylene exchange in **5** was estimated, about 40 kJ/mol for ΔG_{213}^\ddagger is calculated and must be compared with $\Delta G_{213}^\ddagger \approx 30$ kJ/mol for ethylene exchange in **5**. (Note that the estimate for k_2 as given above was an upper limit, more precise values would require the use of enriched $^{13}\text{C}_2\text{H}_4$). Apart from the preliminary nature of the kinetic data ethylene exchange in the aqua complex is again more facile than in related molecular complexes. On the other hand, ^{17}O measurements have shown that also water exchange with $\Delta G_{173}^\ddagger \approx 28$ kJ/mol is much faster than any ligand exchange at square-planar Rh(I) known so far which range from 10^{-5} ^[30] to 10^4 $\text{M}^{-1} \cdot \text{s}^{-1}$ ^[31]. The low limit refers to exchange of PPh_3 for hexene in $\text{Rh}(\text{COD})\text{Cl}(\text{PPh}_3)$ where separate kinetics could be followed for the formation of the five-coordinate intermediate and its decomposition to the final product. The more rapid reactions pertain to substitution of COD for $\text{P}(\text{OPh})_3$ in $(\text{COD})\text{Rh}(\text{Racac})$. In this latter study an increase in the substitution rate by three orders of magnitude was noted if acac was successively replaced by higher fluorinated derivatives. Fluorination of the acac makes the ligand harder which leads to faster substitution. It is thus conceivable that a water complex will show even faster substitution kinetics of the coligands. Focussing on water exchange, an example has recently been found, where it could be shown by using the ^{17}O paramagnetic line broadening technique that exchange of water *trans* to an olefinic double bond as opposed to exchange of water *trans* to another water ligand in the same molecule ($[(\text{COD})\text{Ru}(\text{H}_2\text{O})_4]^{2+}$) was faster by five orders of magnitude^[32]. A similar *trans* effect may be operative in the square-planar Rh(I) complexes leading to fast water exchange in these compounds.

Second-order ethylene exchange in **5** in the absence of excess ethylene requires dissociative formation of some monoolefin complex. The analogous species shows up in the static NMR spectrum of **4** and in the dynamic equilibrium of **7** at elevated temperature. This means that monoolefinic triaqua complexes have a finite lifetime and do not decompose instantaneously. Lowering the ethylene concentration below the ratio required for a diolefin complex by e.g. concentration of the solution, on the other hand, leads to partial decomposition, indicating the limit of stability of these species.

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Experimental

Experiments were conducted under nitrogen with deaerated solvents. NMR spectra were recorded with Bruker WP 80 and Varian Unity 500 instruments at 80 and 500 MHz proton frequency respectively.

$[(\text{COD})\text{Rh}(\text{H}_2\text{O})\text{OTs}]$ (**1**): In 10 ml of water/ethanol were suspended 197 mg (0.40 mmol) of $[(\text{COD})\text{RhCl}]_2$ and 223 mg (0.80 mmol) of silver *p*-toluenesulfonate and the suspension was ultrasonicated for 3 min. A precipitate of AgCl and an orange solution formed. After filtration the solution was evaporated to dryness in high vacuo leaving 307 mg (quantitative) of crude product. Slow diffusion of ether into an acetone solution gave 195 mg (63%) of yellow prisms. – ^1H NMR ($[\text{D}_6]$ acetone): $\delta = \text{COD } 4.07$ (4H, CH), 2.45 (4H, CH_2), 1.695, 1.668 (ABq, $J_{\text{AB}} = 7.2$ Hz, 4H, CH_2); OTs 7.66, 7.25 (ABq, 4H), 2.37 (CH_3), H_2O 3.83. – ^{13}C NMR: COD 77.5 (CH, $J_{\text{H-Rh}} 15.4$ Hz), 30.9 (CH_2); OTs 143.2, 141.1 (C_{ipso}), 129.5, 126.8 (C_{arene}), 21.2 (CH_3). – $\text{C}_{15}\text{H}_{22}\text{O}_4\text{RhS}$ (401.3): calcd. C 45.01, H 5.29; found C 44.90, H 5.35.

$[(\text{NBD})\text{Rh}(\text{H}_2\text{O})\text{OTs}]$ (**2**): $[(\text{NBD})\text{RhCl}]_2$ was treated in the same way as described for the COD complex and crystallized from acetone/ether. – ^1H NMR ($[\text{D}_6]$ acetone): $\delta = 3.97$ (m, 4H, CH_{olef}), 3.89 (m, 2H, bridgehead), 3.13 (s, $\approx 2\text{H}$, H_2O), 1.1 (t, 2H, bridge).

Solution of $[(\text{C}_8\text{H}_{14})_2\text{Rh}(\text{H}_2\text{O})_2\text{OTs}]$ (**4**): From $[(\text{C}_8\text{H}_{14})_2\text{RhCl}]_2$ treated as above with silver *p*-toluenesulfonate. – ^1H NMR ($[\text{D}_6]$ acetone, 213 K): $\delta = 1.2, 1.33, 1.55$ (3 m, 12H, CH_2), 2.18 (br. d, 2H, $J = 10.7$ Hz, CH_2), 2.67 (br. s, 2H, CH).

Solution of $[(\text{C}_2\text{H}_4)_2\text{Rh}(\text{H}_2\text{O})_2\text{OTs}]$ (**5**): $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ was treated as above with silver *p*-toluenesulfonate. – ^1H NMR ($[\text{D}_6]$ acetone): $\delta = 2.91$. – ^{13}C NMR: $\delta = 60.5$.

Solution of $[(\text{isoprene})\text{Rh}(\text{H}_2\text{O})_2\text{OTs}]$ (**6**): To a solution of 0.13 mmol of **5** in 10 ml of acetone and 1 ml of water was added 3 ml of freshly distilled isoprene. The mixture was stirred at 60 °C for 3 d in a pressure Schlenk. Polyisoprene was extracted with toluene and the residual clear solution evaporated to dryness. – ^1H NMR ($[\text{D}_6]$ acetone): $\delta = 5.04$ (ps. t, 1H, H^3 , 3.28 (br. m, 2H, *syn*-H), 2.1–1.5 (br. m, 2H, *anti*-H), 1.89 (s, 3H, Me).

$[(\text{DMB})\text{Rh}(\text{H}_2\text{O})\text{OTs}]$ (**7**): In a mixture of 20 ml of acetone and 1 ml of water 85 mg (0.19 mmol) of $[(\text{DBM})\text{RhCl}]_2$ was dissolved. Addition of 108 mg (0.38 mmol) of silver *p*-toluenesulfonate and ultrasonication of the mixture led to precipitation of AgCl . Filtration and drying of the filtrate afforded 66 mg (90%) of spectroscopically pure material. – ^1H NMR (CD_3OD): $\delta = \text{DBM } 1.84$ (br. s, 8H, Me and *syn*-H), -0.18 (2H, *anti*-H). – ^{13}C NMR: $\delta = 27.6$ (d, $J_{\text{Rh-C}} = 8.8$ Hz, terminal C), 92.5 (d, $J_{\text{Rh-C}} = 13$ Hz, inner C), 17.6 (Me).

Carbonylation of 7: As described above 280 mg (0.633 mmol) of $[(\text{DBM})\text{RhCl}]_2$ was dehalogenated in 15 ml of MeOH/water, 1:1. After filtration the solution was subjected to 3 bar CO in a pressure-resistant Schlenk vessel. Admission of CO effected a rapid color change from orange to yellow and after some time a reddish brown precipitate separated. This was extracted with pentane, the solvent evaporated and the residue dried to yield 170 mg (72%) of $\text{Rh}_4(\text{CO})_{12}$ identified by IR spectroscopy (ν_{CO} , pentane, 2075, 2069, 2061, 2044, 1886 cm^{-1}).

$[(\text{DMB})\text{Rh}(\text{H}_2\text{O})(\text{CO})]^+$ (**8**): 147 mg (0.33 mmol) of $[(\text{DMB})\text{RhCl}]_2$ was dehalogenated with 186 mg (0.667 mmol) silver *p*-toluenesulfonate in 3 ml D_2O . After filtration of AgCl the pH of the solution was adjusted to 1 by the addition of one drop of D_2SO_4 . Me_4NNO_3 was added as an NMR standard [$\delta(^1\text{H}) = 3.18$, $\delta(^{13}\text{C}) = 54.3$]. The solution was filtered into a pressure NMR tube (Wilmad PV) and the filtrate subjected to 2 bar CO. – ^1H NMR (D_2O , D_2SO_4): $\delta = 1.64, 1.88$ (two s, 6H, Me), 2.16 (m, 2H, coord. *anti*, uncoord. *syn*), 3.18 (d, $^2J = 0.6$ Hz, 1H, coord. *syn*), 3.22 (d, $^2J = 1.8$ Hz, 1H, uncoord. *anti*). – ^{13}C NMR: $\delta = 182.6$ (d, $J_{\text{Rh-C}} = 76.3$ Hz, CO), 117.1, 114.6 ($\text{C}^{2,3}$), 63.3, 64.3, ($\text{C}^{1,4}$), 20.0, 18.6 (Me).

X-ray Structure Determination of 9, 10, and 11: For all compounds geometry and intensity data were collected by means of Enraf-Nonius CAD4 diffractometers equipped with graphite monochromators. The structures were solved and refined with the SDP package^[33]. All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were treated as riding with idealized geometry [C–H = 0.98 Å, B(H) = 1.3 · B_{iso}(C)]. For **9** all hydrogen atoms in interesting positions (coordinating water molecule, coordinating double bonds of the COD ligand) were refined isotropically. A statistical weighting scheme $w^{-1} = \sigma^2(F_o)$ was used for all reflections. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-401817 (**9**), CSD-401818 (**10**), CSD-401819 (**11**).

Table 1. Crystal data and parameters of structural refinement

	9	10	11
Formula	C ₁₅ H ₂₁ O ₂ RhS	C ₁₄ H ₁₆ F ₅ RhSb	C ₁₄ H ₁₆ F ₅ RhSb
Formula weight	400.30	522.93	522.93
Space group (No.)	P1(2)	P2 ₁ /n(14)	C2/c(15)
a / Å	11.600(3)	13.506(5)	16.947(3)
b	11.826(5)	11.087(3)	9.984(2)
c	8.340(7)	22.38(2)	10.087(2)
α / °	79.60(5)		
β	81.18(5)	108.23(3)	114.930(9)
γ	65.58(3)		
V [Å ³]	775(1)	3217(5)	1548(1)
Z	2	8	4
d _{calc} /g cm ⁻³	1.715	2.159	2.244
μ / cm ⁻¹	12.25	14.31	28.62
Temp. °C	25	25	-10
Radiation	Mo-K _α	Ag-K _α	Mo-K _α
λ / Å	0.7107	0.5609	0.7107
Crystal dimensions / mm ³	0.2 × 0.2 × 0.4	0.4 × 0.4 × 0.6	0.3 × 0.4 × 0.4
Measured reflections	2549	11119	1833
Scan range	3° ≤ θ ≤ 24°	0° ≤ θ ≤ 24°	3° ≤ θ ≤ 27°
Ewald sphere	(h, ±k, ±l)	(h, k, ±l)	(-h, k, ±l)
Absorption correction	none	none	emp. PSI-scans ^[34] (99.66%/73.16%)
(max./min. transmission)			
Sec. ext. coeff.	not refined	E = 1.22 × 10 ⁻⁶	not refined
Observed indep. refl.	2196	3221	1042
>	2s(l)	1.5σ(l)	3σ(l)
Parameters refined	214	398	102
Agreement fact. R	0.025	0.083	0.041
R _w	0.030	0.065	0.049
GOF	1.711	1.763	1.499
Res. el. density e ⁻ / Å ³	0.54	1.45	0.65

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