Aspects of Aqueous Ruthenium(II) Chemistry

by **Pascal V. Grundler**, **Gabor Laurenczy**, and **André E. Merbach***

Institut de Chimie Minérale et Analytique, Université de Lausanne, BCH-Dorigny, CH-1015 Lausanne

Dedicated to the memory of Professor *Luigi M. Venanzi*

Since the first facile synthesis of $[Ru(H_2O)_6](tos)_2$ was published at the beginning of the eighties, several Ru^{II} aqueous inorganic and organometallic complexes were described, showing the increasing interest in this kind of compound due to potential applications in catalysis and medicine. To understand what governs the reactivity of the ligands in the first coordination sphere of the Ru^{II} center, we discuss its solution behavior, starting with the simplest aqueous species $[Ru(H_2O)_6]^{2+}$ and moving progressively in complexity with selected examples. In addition, we present variable-pressure measurements with two objectives: to determine activation volumes for mechanistic assignments, and to shift equilibria by increasing the solubility of gaseous molecules.

1. Introduction. – Interest in aqua complexes of Ru^{II} has increased over the past few years. First, from a synthetic viewpoint, Ru^{II} shows an ideal compromise between 'softness and acidity' of complexed H_2O, and back-bonding into π^* orbitals of carbon π ligands. This property allows us to envisage promising research in organometallic chemistry of Ru^{II} in H_2O. Since its facile synthesis, $[Ru(H_2O)_6](tos)_2$ is an ideal starting material for a series of new aqua complexes with ligands as varied as N-heterocycles, phosphines, arenes, and olefins, and small gaseous molecules such as H_2, N_2, CO, and $H_2C{=}CH_2$.

Second, Ru^{II} aqua complexes are key intermediates in the metabolic processes associated with the antitumor reactivity of Ru^{II} compounds. Aqua complexes of Ru^{II} have also an important catalytic activity for the polymerization and isomerization of olefins.

To understand what governs the reactivity of the ligands in the first coordination sphere of the Ru^{II} center, we will discuss its solution behavior starting with the simplest aqueous species $[Ru(H_2O)_6]^{2+}$ and moving progressively in complexity with selected examples.

In addition, we will present variable-pressure measurements with two objectives: to determine activation volumes for mechanistic assignments, and to shift equilibria by increasing the solubility of gaseous molecules.

2. $[Ru(H_2O)_6)]^{2+}$: H_2O Exchange and Complex Formation. – The mechanism of H_2O exchange ($k_{ex} = 1.8 \times 10^{-2}\ s^{-1}$) has been subject of controversy. First kinetic studies at variable temperature and pressure for the solvent exchange on $[Ru(H_2O)_6]^{2+}$ and $[Ru(MeCN)_6]^{2+}$ lead to activation volumes close to 0 cm³ mol⁻¹ ($-0.4 \pm 0.7\ cm^3\ mol^{-1}$ and $+0.4 \pm 0.6\ cm^3\ mol^{-1}$, resp., indicating equal contributions from bond forming and bond breaking in the formation of the transition state [1]. The conclusion was that the solvent exchange on Ru^{2+} proceeds *via* an interchange mechanism, *I*.

Five years later, *Aebischer et al.* reported the rate constants for the mono-complex formation between $[Ru(H_2O)_6]^{2+}$ and several ligands [2]. They observed that, for identically charged ligands, the second-order rate constants were almost independent of the nature of the ligand. This indicates that the entering group has little influence on the transition state. For a comparison between the H_2O-exchange rate on $[Ru(H_2O)_6]^{2+}$ and the second-order complex-formation rate constants with various ligands, the model proposed by *Wilkins* and *Eigen* [3] is used. This model describes the ligand exchange on octahedral complexes by considering the complex formation in two steps, the first being the fast formation of an outer-sphere complex, which is quantified by the equilibrium constant K_{os}. The second, rate-determining step, is the interchange of ligands between the first and the second coordination spheres and is described by a first-order rate constant, k_I. The second-order complex formation rate, k_f, is then given by *Eqn. 1.*

$$k_f = k_I \cdot K_{os} \tag{1}$$

The H_2O exchange rate constant, k_{ex}, of the hexaaqua complex cannot be directly compared to k_I because they are not defined in the same way. k_{ex} is defined as the exchange of a particular H_2O molecule but k_I is the rate constant for the substitution of any equivalent H_2O molecule in the first coordination sphere. To achieve compliance, one has to take into account probability factors. These are the number of molecules in the second coordination sphere, which will be called f (usually 12), and the number of directly coordinated H_2O molecules, n_c. From these definitions, the following equation (*Eqn. 2*) must be applied to transform the complex formation constant k_f to a first-order rate constant, k_I', which can now directly be compared to k_{ex}.

$$k_I' = \frac{k_f}{K_{os}} f \frac{1}{n_c} = k_I f \frac{1}{n_c} \tag{2}$$

Two observations can be made from *Table 1.* First, the inner-sphere interchange constants, k_I', as defined above are similar, and, second, their values are close to the H_2O-exchange constant on $[Ru(H_2O)_6]^{2+}$. This indicates a similar mechanism, I_d, for these reactions with a dissociative activation mode related to the rate-determining rupture of the $Ru-OH_2$ bond at the transition state.

The conclusion is different from the I mechanisms assigned from the variable-pressure study for H_2O exchange on $[Ru(H_2O)_6]^{2+}$. It has been suggested that the near-zero $\Delta V^{\neq}$ value could be due to a bond contraction of the five spectator ligands in the transition state of the I_d.

To solve this controversy, quantum-chemical calculations were performed [4]. These showed that the transition states for interchange or associative mechanism are unlikely to be formed for $[Ru(H_2O)_6]^{2+}$. Instead, the model used allowed us to calculate the transition state for a dissociative mechanism. The reaction pathway for this reaction is illustrated in *Fig. 1.* More elaborate calculations involving a second coordination sphere may lead to the transition state also for the I_d mechanism.

3. $[RuL(H_2O)_5]^{2+}$ Complexes: Synthesis and Reactivity. – Although the formation rates of the various complexes from the aqua ion are analogous (I_d mechanism), the

Table 1. *Reaction between* $[Ru(H_2O)_6]^{2+}$ *and Monodentate Ligands: Second-Order Monocomplex Formation Rate Constants,* k_f*, Outer-Sphere Equilibrium Constant,* K_{os} *and First-Order Rate Constants,* k'_I*, Obtained from* Eqn. 2 *with* $n_c = 6$ *and* $f = 12$

Ligand	$10^3 \times k_f^{298}$ [a] [kg mol^{-1} s^{-1}]	K_{os} [b] [kg mol^{-1}]	$10^3 \times k'^{298}_I$ [s^{-1}]
Cl^-	8.5	1	17
Br^-	10.2	1	20
I^-	9.8	1	20
(Oxalate)H^-	26	2	26
H_2O	–	–	18[c]
MeCN	2.07	0.16	26
Me_2SO	1.31	0.16	16
1,4-Thioxane	2.2	0.16	28
Tetrahydrothiophene	2.4	0.16	30
Maleic acid	2.18	0.16	27
Fumaric acid	1.72	0.16	22
2,5-Dihydrofuran	1.06	0.16	13
$H_2C{=}CH_2$	1.22[d]	0.16	15
DMF	0.82[e]	0.16	10
H_2	1.7	0.16	21
N-Methylpyrazinium$^+$	0.73	0.02	73

[a] From [2] and refs. cit. therein. [b] K_{os} calculated with the *Eigen-Fuoss* relation for the reaction of $[Ni(H_2O)_6]^{2+}$ with similar ligands ([11] and refs. cit. therein). [c] Rate constant, k_{ex}, for the exchange of a particular H_2O molecule [1]. [d] From [18]. [e] From [19].

species formed exhibit a rich and varied chemistry. All complexes with gaseous ligands such as CO [5], C_2H_4 [6], H_2 [7], and N_2 [8] were prepared and studied by the NMR sapphire-tube technique [9], which allows one to follow *in situ* reactions under pressure up to 10 MPa by multinuclear NMR spectroscopy. Comparison between $[Ru(N_2)H_2O)_5]^{2+}$ and $[Ru(H_2)(H_2O)_5]^{2+}$ shows that, although in both cases a diatomic molecule is bound to the metal center, the geometry is different, as demonstrated by ^{1}H-, ^{15}N-, and ^{17}O-NMR (see *Figs. 2* and *3*). The N_2 binds end-on, as demonstratead by the two ^{15}N *doublets* ($^1J(N,N) = 3.4$ Hz): the N-atom adjacent to the metal at -82.9 ppm and the distal N-atom at -24.3 ppm. The ^{17}O-NMR spectrum shows the expected 1:4 ratio for the axial and equatorial H_2O molecules. However, H_2 is bound side-on, and the H,D coupling constant of 31.2 Hz is characteristic of a dihydrogen complex [10]. The complex becomes, after some time, enriched in HD although the H_2 was used as the pressurizing gas. The only source of D is the solvent D_2O. The D enrichment probably takes place through deprotonation ($-H^+$) of the dihydrogen complex, followed by reprotonation ($+D^+$).

The substitution of a H_2O molecule, with merely σ-donating properties, by ligands with widespread donating and accepting properties strongly influences the reactivity of the remaining five H_2O molecules in $[RuL(H_2O)_5]^{2+}$. The H_2O ^{17}O-NMR chemical shifts are easily accessible and indicative of the electron distribution in the complex. In all monocomplexes, the H_2O molecules are more deshielded than in $[Ru(H_2O)_6]^{2+}$ (*Table 2*). Therefore, all ligands produce a stronger electron-withdrawing effect than H_2O and, consequently, increase the redox potential of the metal center [11]. Chemical shift for axial and equatorial H_2O molecules are clearly contrasted and span from

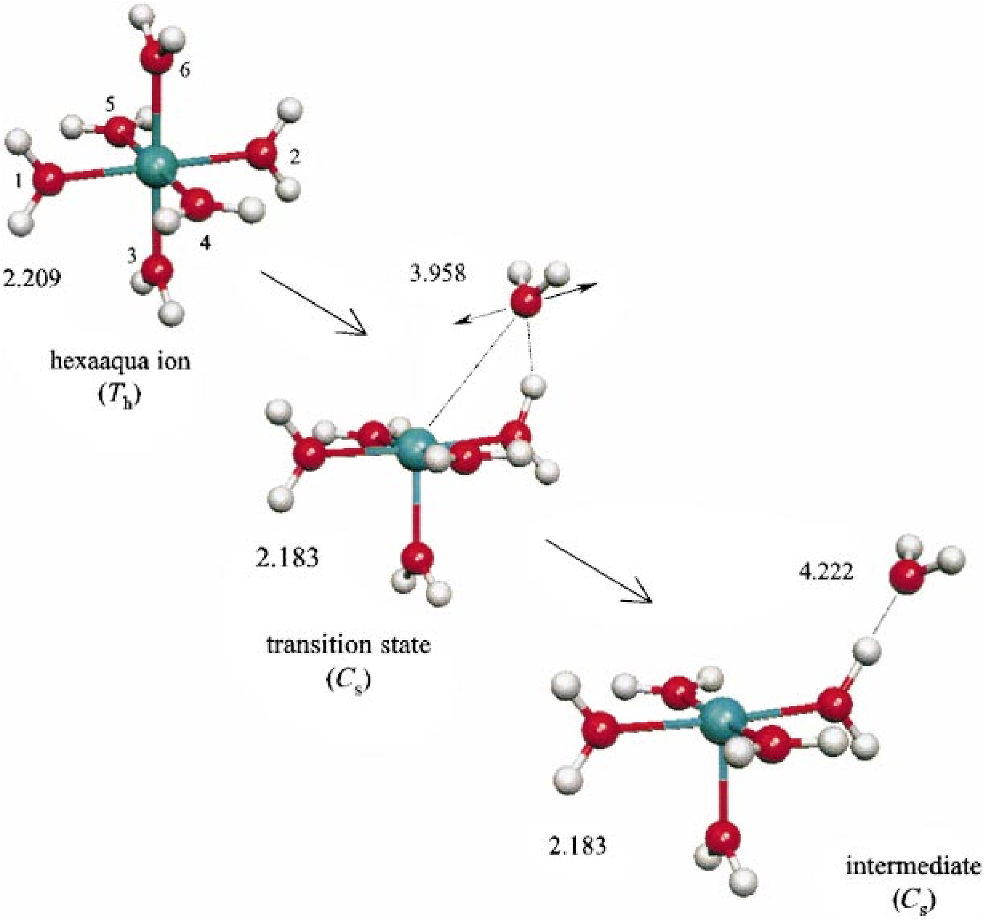


Fig. 1. *Reaction pathway for the dissociative* D *mechanism*. The imaginary mode for the transition state is indicated by arrows.

-192 ppm in $[RuCO(H_2O)_5]^{2+}$ up to -29 ppm in $[RuCO(H_2O_5)]^{2+}$, and for the equatorial ones up to -147 ppm in $[Ru(F_2C{=}CH_2)(H_2O)_5]^{2+}$ (*Table 2*). This demonstrates that the electron withdrawing is mainly experienced by the H_2O molecule *trans* to the ligand and can be correlated to the π-back-bonding capabilities of the ligands.

Results obtained by DFT calculations allow us to better understand these results. They showed that the π-back-bonding is more or less proportional to the $Ru-L$ bond energy and inversely proportional to the $Ru-O_{ax}$ bond energy (*Table 3*). The $Ru-O_{ax}$ bond energy is also proportional to the free energies of activation, $\Delta G^{\neq}$, for the H_2O exchange, which is itself inversely proportional to the $Ru-O_{ax}$ bond length. Therefore, geometric, kinetic, and electronic parameters are strongly correlated and allow predictions about the reactivity of complexes that are, at the moment, not fully characterized.

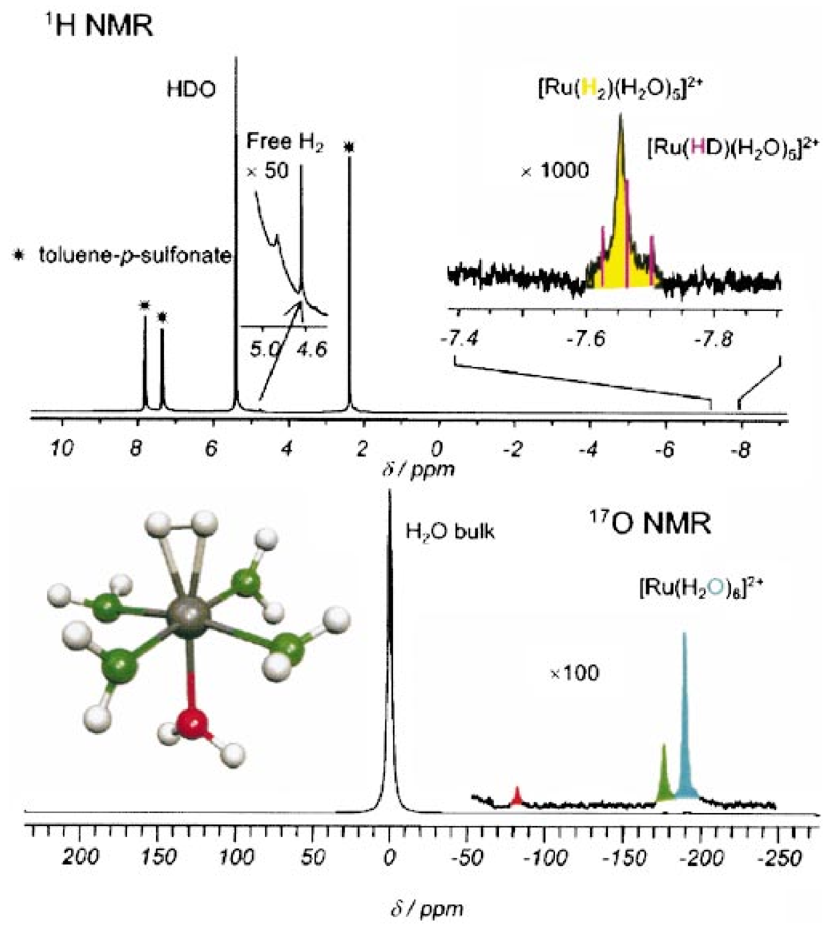


Fig. 2. Top: *400-MHz ¹H-NMR Spectrum of a solution containing initially* $[Ru(H_2O)_6]^{2+}$ (0.094 mol kg^{-1}), *toluene-4-sulfonic acid* (0.95 mol kg^{-1}) *in 99.95%* D_2O *at 298.1 K, 3 h after pressurization with 4.9 MPa of* H_2. Bottom: *54-MHz* ^{17}*O-NMR Spectrum of a solution at 297.0 K containing initially* $[Ru(H_2O)_6]^{2+}$ (0.099 mol kg^{-1}), *toluene-4-sulfonic acid* (0.56 mol kg^{-1}) *in 10%* $H_2{}^{17}O$*-enriched water at 297.0 K, 40 min after pressurization with 54.0 MPa of* H_2.

The ligands can be classified according to their *trans* and *cis* effects as shown in the following series.

Effect of L on the reactivity of the axial H_2O *molecule:*

	N_2	≪	MeCN	<	H_2O	<	CO	<	Me_2SO	<	$H_2C{=}CH_2$	<	$CF_2{=}CH_2$
k_{ax}/k_{ex}	0.0015		0.3		1		2.5		45		173		373

Effect of L on the reactivity of the equatorial H_2O *molecules:*

	$F_2C{=}CH_2$	≈	CO	<	Me_2SO	<	N_2	<	$H_2C{=}CH_2$	<	MeCN	<	H_2O
k_{eq}/k_{ex}	0.0002		0.0002		0.001		0.0016		0.02		0.08		1

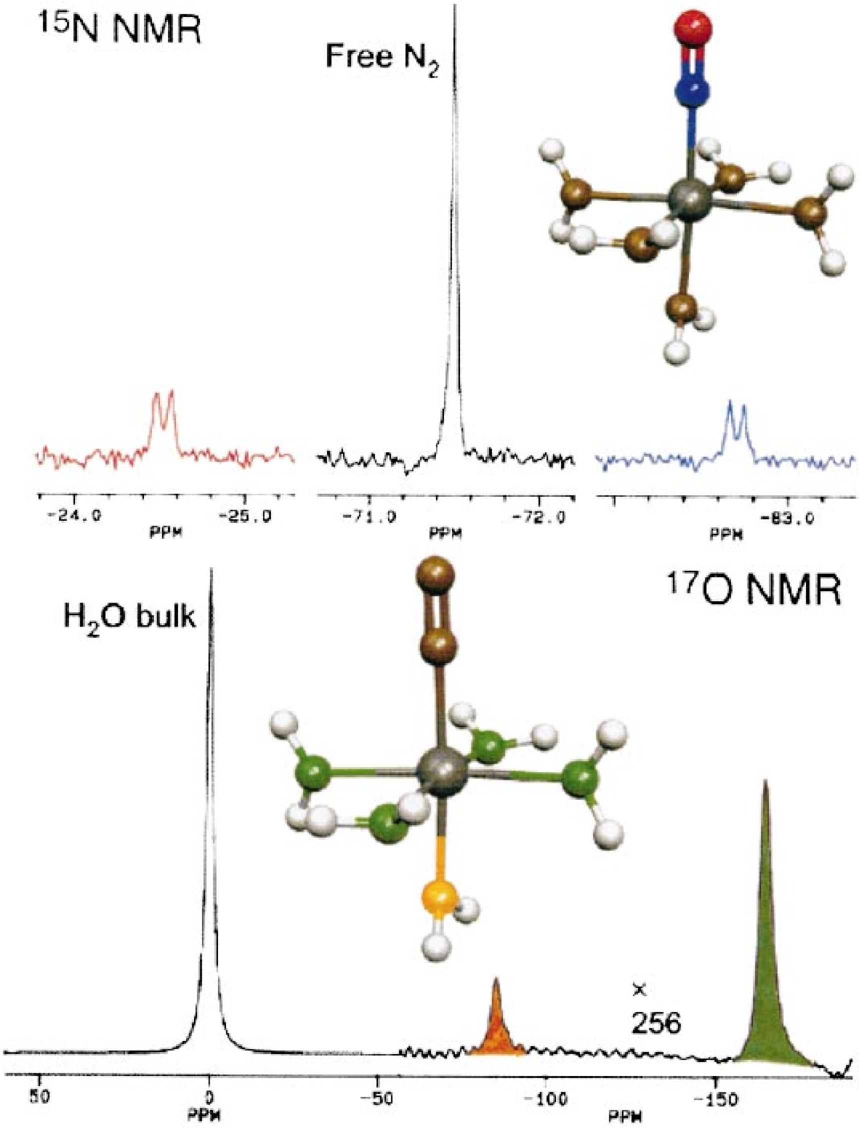


Fig. 3. *NMR Spectra of a 0.029 mol kg^{-1} $[Ru(N_2)(H_2O)_5]^{2+}$ aqueous solution* (10% $H_2{}^{17}O$-enriched) *under 5.0 MPa of dinitrogen* (7.4% ^{15}N) *at 298 K. Top:* 40.6-MHz ^{15}N-NMR, *bottom:* 54-MHZ ^{17}O-NMR.

$[Ru(N_2)(H_2O)_5]^{2+}$ exhibits a peculiar behavior in connection with the H_2O exchange. In this complex, the Ru–N bond is weaker than the Ru–O bonds. This means that the loss of N_2 is favored towards the loss of a H_2O molecule, and, therefore, the H_2O exchange proceeds *via* the substitution of N_2 [11].

4. Carbonyl Complexes. – Aquaruthenium(II) complexes with one, two (*cis*) and three (*fac*) CO (the *π* acceptor properties of CO strongly disfavor the formation of

Table 2. *Comparison of ^{17}O-NMR Chemical Shifts and Redox Potentials for the Complexes of* $[RuL(H_2O)_5]^{2+}$

Ligand	δ (^{17}O) [ppm]		$E^{0'}$ a) [V]
	ax	eq	
H_2O	– 192	– 192	0.20
MeCN	– 115	– 179	0.46
N_2	– 86	– 165	0.92
H_2	– 80	– 177	–
Me_2SO	– 58	– 164	0.81
$H_2C{=}CH_2$	– 47	– 160	0.83
CO	– 29	– 155	1.09
$F_2C{=}CH_2$	– 31	– 147	1.16

a) From [11].

Table 3. *Comparison of Calculated Properties of the Ru–O$_{ax}$ and Ru–L Bonds*

Ligand	Ru–H_2O_{ax} bond			Ru–L bond	
	kJ mol^{-1}		Å	kJ mol^{-1}	e^{-}
	E_b	$\Delta G^{\neq}$ a)	d(Ru–O)	E_b	π-Back-bonding
N_2	208.5	99.1	2.090	188.3	0.02
CO	182.5	81	2.151	286.4	0.12
H_2O	179.4	83	2.095	179.4	0
H_2 b)	174.8		2.166	172.8	0.10
$H_2C{=}CH_2$	166.2	70.4	2.188	248.6	0.32
Me_2SO b)	128.4		2.245	308.0	0.86

a) Free energy of activation for the exchange of the axial H_2O molecule. b) *H. Sidorenkova* (Institut de Chimie Minérale et Analytique, CH-1015 Lausanne), personal communication.

trans complexes even if the *trans*-located H_2O molecule is the most labile) have been investigated to determine the reactivity of the bound H_2O molecules [12]. For both mono and dicarbonyl complexes, the reactivity of the *cis*-located H_2O molecules strongly decreases compared to $[Ru(H_2O)_6]^{2+}$, which is well-documented by the H_2O exchange rates and the bond lengths as shown in *Fig. 4*. The behavior of the tricarbonyl complex is more complicated due to hydrolysis ($pK_a = -0.14$, with formation of $[Ru(CO)_3(OH)(H_2O)_2]^{+}$) even in very acidic conditions. The H_2O-exchange rate on the monohydroxo species is $k_{OH} = 0.053 \pm 0.006$ s^{-1} at 262 K. The three CO ligands with their strong π-accepting capabilities virtually transform the Ru^{II} to a +3 metal center, and, therefore, the pK_a value of the complex is lowered. The H_2O-exchange rate on $[Ru(CO)_3(H_2O)_3]^{2+}$ is too small to be determined experimentally in the presence of even small amounts of the much more reactive monohydroxo species. However, an estimation of the exchange rate can be achieved from a comparison of the ^{17}O-NMR chemical shifts and Ru–O bond lengths of the other CO complexes.

The H_2O-exchange measurements performed with ^{17}O-enriched water also showed an enrichment in ^{17}O of the CO in $[Ru(CO)_3(H_2O)_3]^{2+}$. This observation is explained by the formation of a ruthenacarboxylic acid, which is the result of the nucleophilic attack of an O-atom from water on the C-atom of the CO.

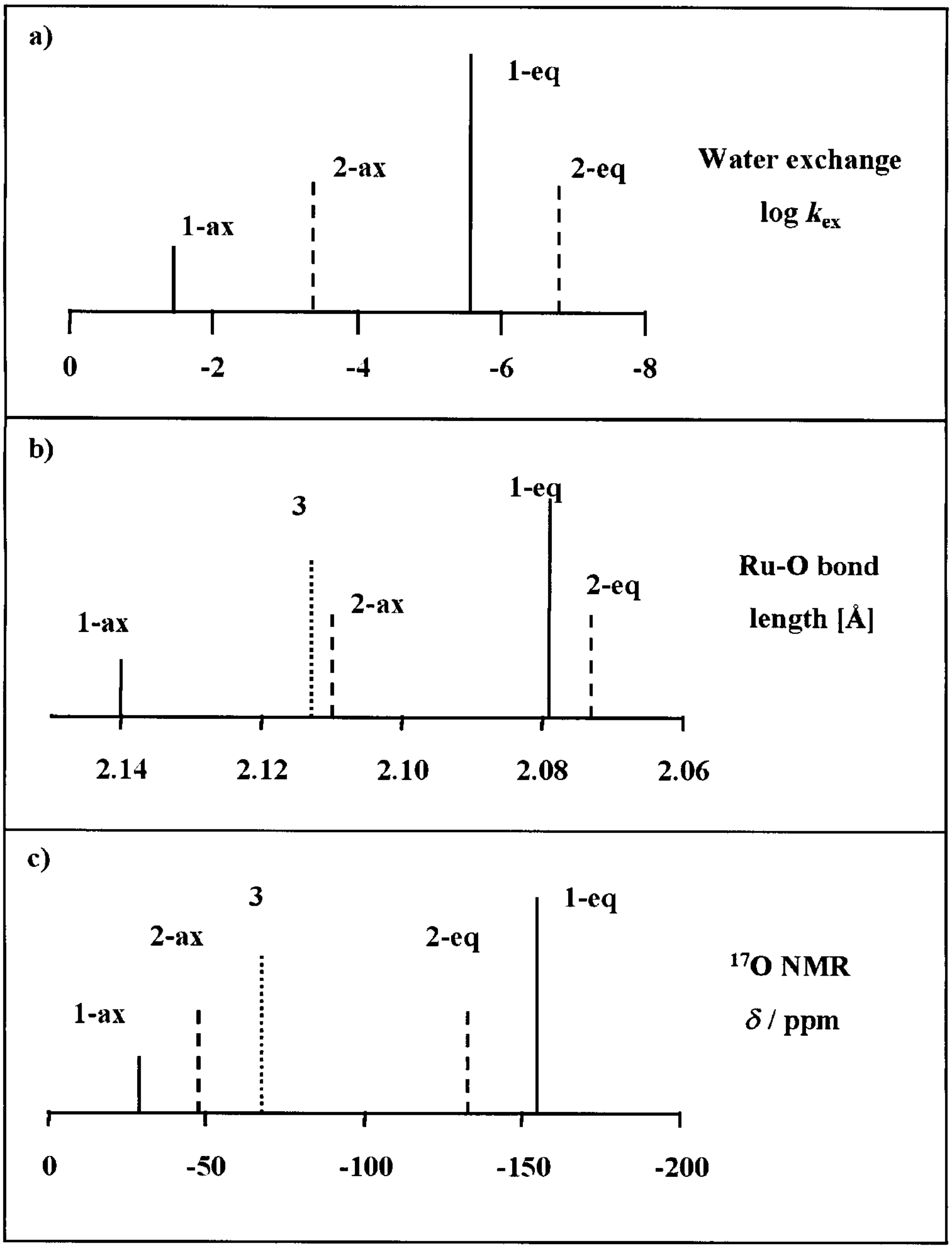


Fig. 4. *Graphical representation of* a) *rate constants,* k_{ex}, *for the* H_2O *exchange,* b) *Ru–O bond lengths, and* c) *^{17}O-NMR chemical shifts of* $[Ru(CO)(H_2Oeq)_4(H_2Oax)](tos)_2$ (–), cis-$[Ru(CO)_2(H_2O_{eq})_2(H_2O_{ax})_2](tos)_2$ (– – –), *and* fac-$[Ru(CO)_3(H_2O)_3](tos)_2$ (····)

At higher pH and temperature, $[Ru(CO)_3(H_2O)_3]^{2+}$ decomposes to CO_2 and to an hydride *fac*-$[RuH(CO)_2(H_2O)_3]^+$ [13]. The stability of this hydride in acidic solution is also a consequence of the strong π-accepting capabilities of the CO.

5. Ethylene Complexes. – Several reports have been published about the catalytic properties of $[Ru(H_2O)_6]^{2+}$ in reactions with olefins [14]. The dimerization of ethylene will be discussed here. The reaction can easily be followed by ^1H-,^{13}C-, and ^{17}O-NMR spectroscopy, and *Fig. 5* shows the ^{17}O-NMR spectra of the mono- and bis-ethylene complexes, with 1:4 and 2:2 ratios for the bound H_2O molecules, respectively. These two complexes are the two steps towards the dimerization (*Fig. 6*). As in the case of CO, the bis-complex has the *cis*-geometry, because the *trans*-geometry is disfavored with strong π-acceptors. The reaction is relatively slow at ambient temperature and not stereoselective. All isomers of butene are found except isobutene (*Fig. 6*). They form an organic layer on the aqueous Ru^{II} solution, which evaporates when the pressure is released; the removal of the dimerization products is then easily performed. The stereochemistry can be kinetically controlled, if one of the isomers is preferentially produced but subsequently isomerized.

6. Mixed Complexes. – An acidic aqueous solution of $[Ru(H_2O)_6]^{2+}$ pressurized with a mixture of H_2 and C_2H_4 produces, besides the butenes described previously, ethane, which is the hydrogenation product of ethylene. Unfortunately, no intermediate for this reaction has been observed so far. However, from the information available about the behavior of $[Ru(H_2)(H_2O)_5]^{2+}$, the occurrence of an hydride in this catalytic process is likely.

The reactions of $[Ru(H_2O)_6]^{2+}$ with a mixture of CO and C_2H_4 produce several complexes as illustrated in the *Scheme*. Formation of $[RuCO(H_2O)_5]^{2+}$ and $[Ru(C_2H_4)(H_2O)_5]^{2+}$ are almost simultaneous (I_d mechanism, *vide supra*); but $[RuCO(H_2O)_5]^{2+}$ is kinetically a dead-end compared to the ethylene complex (see H_2O-exchange rates in *Table 2*) that can undergo substitution of the *trans*- and *cis*-located H_2O molecules. If the *trans*-position is occupied by a CO, both π-accepting ligands will be competing, leading to the dissociation of one of the ligands. Due to the weak lability of $[RuCO(H_2O)_5]^{2+}$, this complex will accumulate in solution to the prejudice of $[Ru(C_2H_4)(H_2O)_5]^{2+}$. This last complex can also be substituted in *cis*-position by CO or C_2H_4. In the second case, the bis-ethylene complex is formed, which is well-known from the dimerization of ethylene. One expects that the H_2O molecules should be very labile in this complex and are, therefore, easily substituted by another ligand. If it is CO, the mixed complex *cis*-$[Ru(C_2H_4)(CO)(H_2O)_4]^{2+}$ is formed. Like the other complexes containing C_2H_4, rapid substitution of the H_2O in *trans*-position to C_2H_4 leads to *cis*-$[Ru(CO)_2(H_2O)_4]^{2+}$. These observations are a nice illustration of the *cis* and *trans* effects for octahedral aqua complexes. In this case, ethylene acts like a catalyst and accelerates the formation of $[Ru(CO)_2(H_2O)_4]^{2+}$, which would be otherwise very slow.

7. Hydrides. – Several Ru^{II} complexes derived from the aqua ion by substitution with H_2O-soluble tertiary phosphine ligands are used as catalyst in aqueous solutions for hydrogenation of CO_2 and bicarbonate [15].

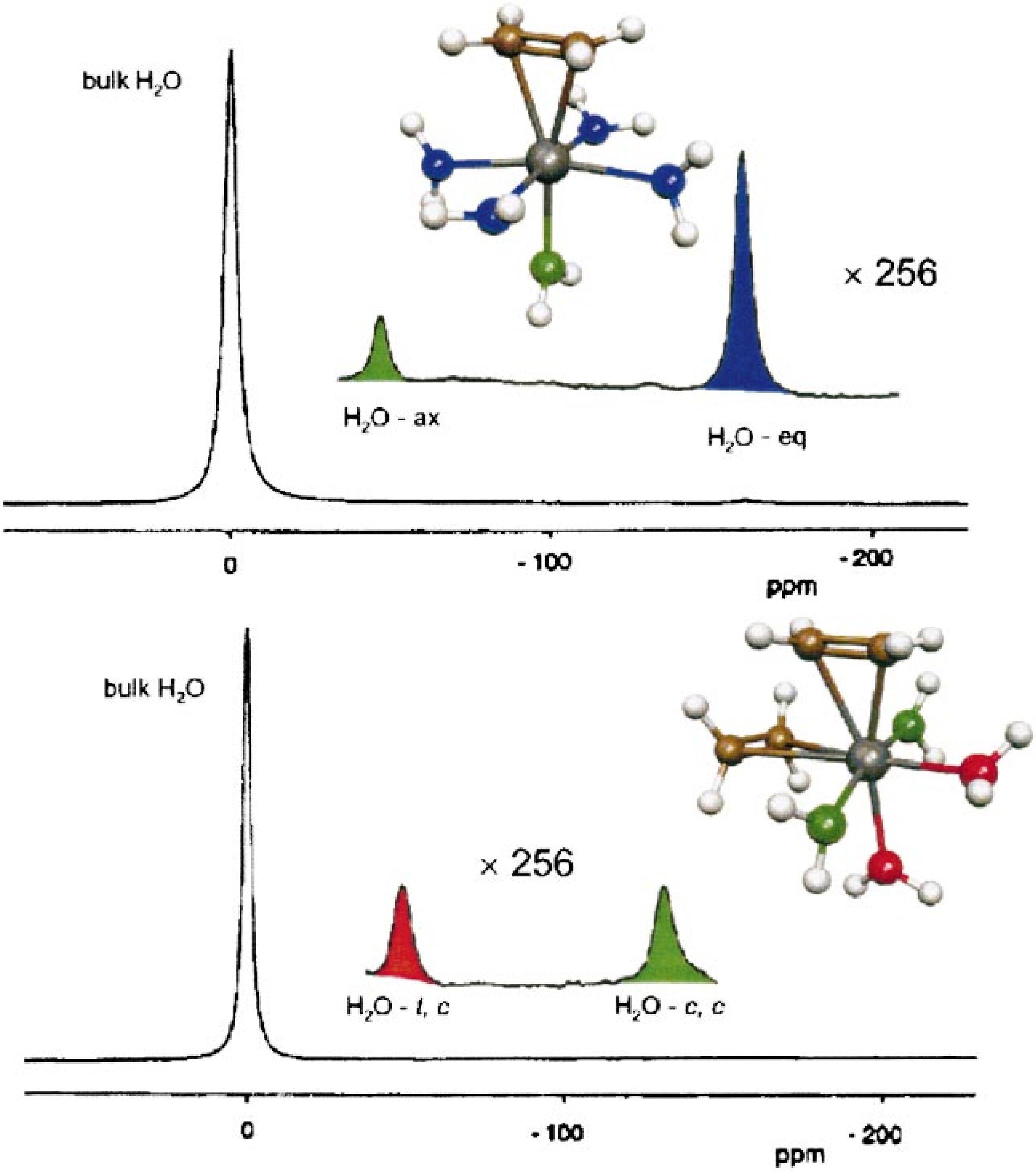


Fig. 5. *54-MHz ^{17}O-NMR Spectrum of a solution containing initially $[Ru(H_2O)_6]^{2+}$* (0.10 mol kg^{-1}) *in 10% $H_2{}^{17}O$ kept at 298 K, 6 h after pressurization with 6 MPa of C_2H_4.* 54-MHz ^{17}O-NMR Spectrum of the same solution, but 18 h after pressurization.

If an aqueous solution of $[RuCl_2(pta)_4]$ (pta = 1,3,5-triaza-7-phosphaadamantane) – or $[Ru(H_2O)_6]^{2+}$ with fourfold excess of pta – is pressurized with H_2, the originally yellow solution turns almost colorless and, depending on the experimental conditions, several new hydride signals appear in the ^{1}H-NMR spectra [16]. Under 60 bar of H_2

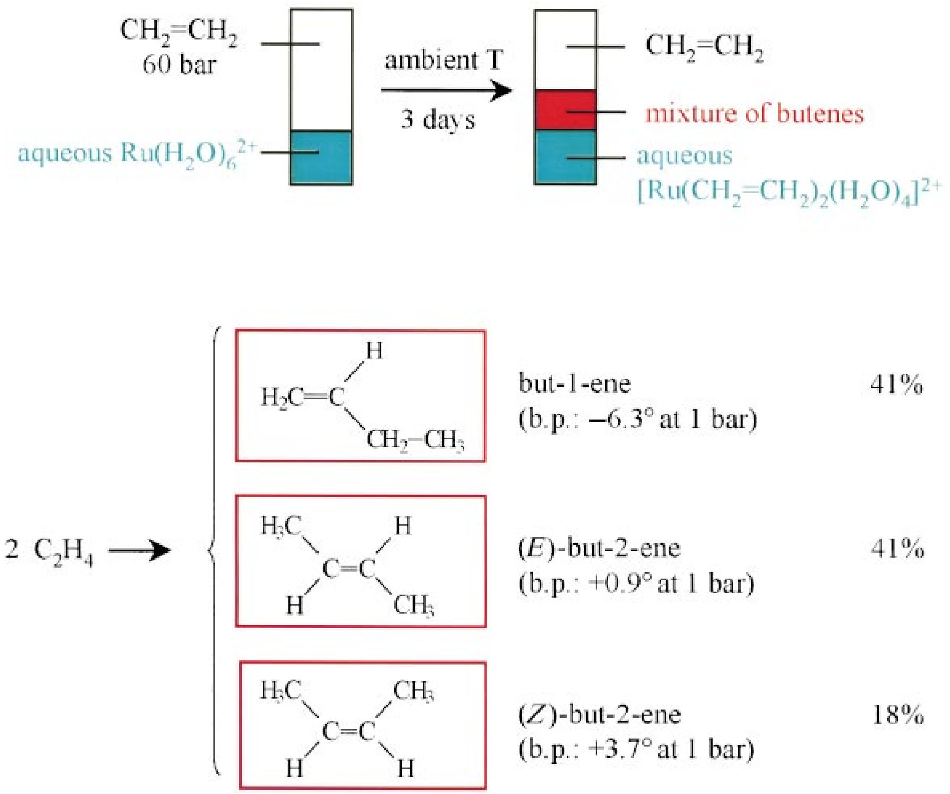


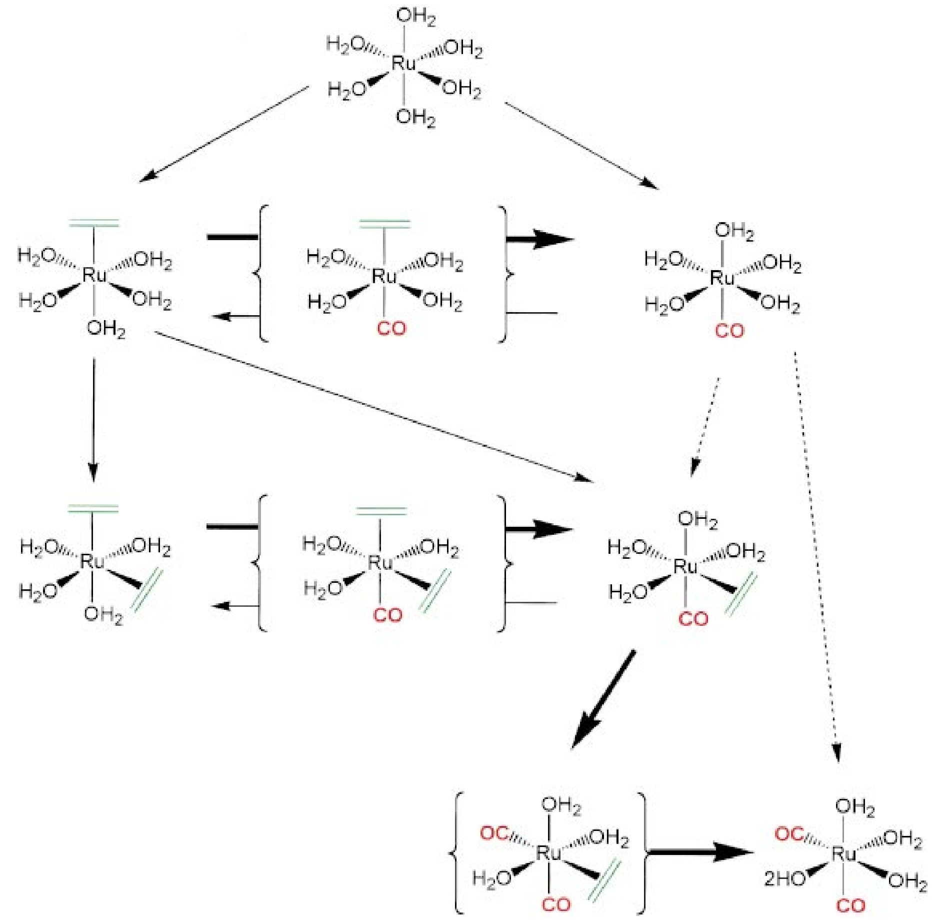
Fig. 6. *$[Ru(H_2O)_6]^{2+}$ catalyzes the dimerization of ethylene under mild experimental conditions.* The reaction shows no stereoselectivity.

pressure at pH 12.0 $[RuH_2(pta)_4]$ forms and at pH 2.0 $[RuH(pta)_4X]$ ($X = Cl^-$ or H_2O). Interestingly, when a fivefold excess of pta is used, the formation of $[RuH(PTA)_5]^+$ is detected. The structure of this unparalleled cationic pentakis-phosphino species, $[RuH(pta)_5]^+$, was unambiguously established by ^1H- and ^{31}P-NMR measurements (*Fig. 7*).

The formation of $[RuH(pta)_4X]$ and $[RuH_2(pta)_4]$ could be expected by analogy to similar complexes with Ph_3P, tppms, or tppts (tppts = 3,3′,3″-phosphanetriylbenzene-sulfonic acid, tppms: diphenylphosphanylbenzene-3-sulfonic acid) ligands, while the existence of a pentakis-phosphino derivative $[RuH(pta)_5]^+$ is completely unprecedented in aqueous organometallic chemistry. In contrast to the bulky sulfonated Ph_3P derivatives, the pta ligand proved to be small enough entering five of it to the first coordination sphere of the Ru^{II}, to form $[RuH(pta)_5]^+$.

8. Conclusions and Perspectives. – The aqueous Ru^{II} chemistry deserves much attention from both theoretical and practical points of view, due to raising applications in medicine and catalysis [17].

Scheme. *Reactions Occurring in a Solution Containing Initially* $[Ru(H_2O)_6]^{2+}$ *and Pressurised with a Mixture of CO and Ethylene.* The thickness of the arrows symbolizes the relative rates of the different steps (– – –): $3 \times 10^{-6}\ s^{-1}$, —: $3 \times 10^{-4}\ s^{-1}$, ▬ : $2 \times 10^{-3}\ s^{-1}$).



Several Ru-organometallic compounds are stable in protic media. Interest is increasing to use H_2O in biphasic systems in industrial catalytic reactions for economical and ecological reasons (easy product separation and catalyst recycling). Structural information on the catalysts leads to the better understanding of the reaction mechanism, to improve yield and selectivity. Nondestructive analytical methods play a key role in this respect, and multinuclear NMR occupies a predominant part in this field.

Higher gas pressures increase the dissolved gas concentrations according to *Henry*'s law, having both thermodynamic and kinetic effects: the higher concentrations shift equilibria towards product formations, and accelerate the second-order reactions, in the case of parallel reactions mounting the yield of the desired product. New organometallic aqua ions have been synthesized, isolated, and characterized (*e.g.*,

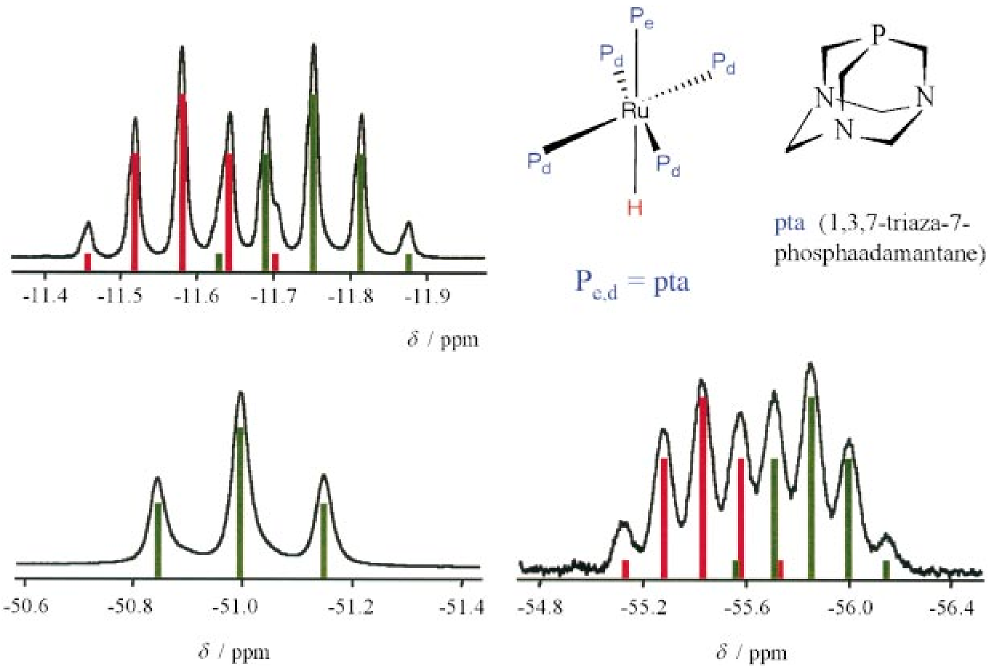


Fig. 7. *400-MHz ^{1}H-NMR Spectrum* (top, left) *of the hydride region of* $[RuH(pta)_5]^+$, *and 161-MHz* ^{31}*P-NMR spectra of the equatorial* (P_d, bottom, left), *and the axial pta ligands* (P_e, bottom, right) *in* $[RuH(pta)_5]^+$ (^{1}H-NMR: *doublet* of *quintuplet* at −11.62 ppm, $J(H,P_d) = 24.2$ Hz, $J(H,P_e) = 68.5$ Hz; ^{31}P-NMR: pseudo-*triplet*, *doublet* of *doublets at* −51.00 ppm (P_d), $J(P_d,P_e) = 24.7$ Hz, *doublet* of *quintuplets* at −55.63 ppm (P_e))

$[Ru(CH_2{=}CH_2)(H_2O)_5]^{2+}$, $[Ru(CH_2{=}CH_2)_2(H_2O)_4]^{2+}$, $[Ru(CO)(H_2O)_5]^{2+}$, and $[Ru(CO)_2(H_2O)_4]^{2+}$).

The apparent contradiction of the mechanism of the complex formation reactions involving Ru^{II} has been resolved. It was shown that the ligand substitution reactions on Ru^{II} have a dissociative character, the rate-determining step being the Ru−ligand bond breaking.

We thank the *Swiss National Science Foundation* for financial support (Grants 20-59117.99 A.M. and 2100-061653.01 G.L.), and *Helena Sidorenkova* for useful discussions and her assistance in the figure preparations.

REFERENCES

[1] I. Rapaport, L. Helm, A. E. Merbach, P. Bernhard, A. Ludi, *Inorg. Chem.* **1988**, *27*, 873.
[2] N. Aebischer, G. Laurenczy, A. Ludi, A. E. Merbach, *Inorg. Chem*. **1993**, *32*, 2810.
[3] R. G. Wilkins, M. Eigen, *Adv. Chem. Ser*. **1965**, *49*, 55.
[4] D. De Vito, H. Sidorenkova, F. P. Rotzinger, J. Weber, A. E. Merbach, *Inorg. Chem.* **2000**, *39*, 5547.
[5] G. Laurenczy, L. Helm, A. Ludi, A. E. Merbach, *Helv. Chim. Acta* **1991**, *74*, 1236.
[6] G. Laurenczy, A. E. Merbach, *J. Chem. Soc., Chem. Commun*. **1993**, 187.
[7] N. Aebischer, U. Frey, A. E. Merbach, *Chem. Commun.* **1998**, 2303.
[8] G. Laurenczy, L. Helm, A. E. Merbach, A. Ludi, *Inorg. Chim. Acta* **1991**, *189*, 131.
[9] A. Cusanelli, U. Frey, D. T. Richens, A. E. Merbach, *J. Am. Chem. Soc*. **1996**, *118*, 5265.

[10] G. J. Kubas, *Acc. Chem. Res.* **1988**, *21*, 120.
[11] N. Aebischer, E. Sidorenkova, M. Ravera, G. Laurenczy, D. Osella, J. Weber, A. E. Merbach, *Inorg. Chem.* **1997**, *36*, 6009.
[12] U. C. Meier, R. Scopelliti, E. Solari, A. E. Merbach, *Inorg. Chem.* **2000**, *39*, 3816.
[13] T. Funaioli, C. Cavazza, F. Marchetti, G. Fachinetti, *Inorg. Chem.* **1999**, *38*, 3361.
[14] D. V. McGrath, R. H. Grubbs, *Organometallics* **1994**, *13*, 224; T. Karlen, A. Ludi, *J. Am. Chem. Soc.* **1994**, *116*, 11375.
[15] F. Joó, G. Laurenczy, L. Nádasdi, J. Elek, *Chem. Commun.* **1999**, 971.
[16] G. Laurenczy, F. Joó, L. Nádasdi, *Inorg. Chem.* **2000**, *39*, 5083.
[17] 'Aqueous-Phase Organometallic Catalysis', Eds. B. Cornils, W. A. Herrmann, Wiley-VCH, Weinheim, 1998.
[18] N. Aebischer, R. Churlaud, L. Dolci, U. Frey, A. E. Merbach, *Inorg. Chem.* **1998**, *37*, 5915.
[19] N. Aebischer, A. E. Merbach, *Inorg. React. Mech.* **1999**, *1*, 233.

Received June 5, 2001