Synthesis and Catalytic Properties of New Water-Soluble Ruthenium(II)−N-Heterocyclic Carbene Complexes

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Summary: The new water-soluble complexes [RuXY(1-butyl-3-methylimidazol-2-ylidene)(p-cymene)]$^{n+}$ (X = Cl$^-$, H_2O; Y = Cl$^-$, H_2O, 1,3,5-triaza-7-phosphaadamantane (pta); n = 0−2) catalyze the hydrogenation of various olefins, aldehydes, and ketones and the redox isomerization of allyl alcohol in aqueous solution under mild conditions and are suitable for the modification of lipid membranes by catalytic hydrogenation.

In the past few years the catalytic application of transition-metal complexes containing N-heterocyclic carbene (NHC) ligands has received increased attention.[1] Important examples include—among others—ring-opening and ring-closing metathesis processes,[2] hydrogenation,[3] hydrogen transfer,[4] hydrosilylation,[5] hydroformylation,[6] telomerization,[7] and various C−C coupling reactions.[8]

Organometallic catalysis in water and in aqueous−organic biphasic systems is a mature field of catalysis and serves as the basis of several industrial processes[9] best exemplified by the Ruhrchemie-Rhône-Poulenc process[9,10] of propene hydroformylation. Despite their extremely strong basicity,[11] N-heterocyclic carbenes are able to form complexes stable to water,[12] as was first observed by Taube.[13] Although the possibility of using water-soluble transition-metal−NHC complexes in aqueous-phase catalysis has been recognized earlier,[1b] surprisingly, this was not followed by systematic investigations of the synthesis, aqueous-phase coordination chemistry, and catalytic properties of these compounds. In addition to the preparation of a few water-soluble NHC complexes,[14] there are only three reports on the use of such water-soluble catalysts for hydroformylation,[6] cyclization,[15] and Suzuki cross-coupling.[16] None of these studies addressed the molecular state of the catalysts in the aqueous solutions. [$RuH_2(CO)(H_2O)$-$(IMes)_2$] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), containing a coordinated water (and a rather rare trans arrangement of the hydride ligands), has been obtained by recrystallization of [$RuH_2(CO)(AsPh_3)$-$(IMes)_2$] from undried hexane;[17] however, this complex is not soluble in water and its aqueous chemistry was not explored. Nevertheless, since N-heterocyclic carbene complexes are likely to complement or replace tertiary

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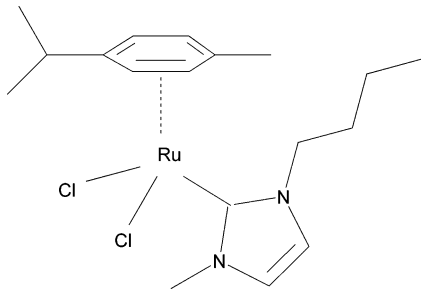
phosphine complexes as catalysts in several processes,[1–8] there is a need for their detailed study also in aqueous media.

Here we report the synthesis and properties of a new water-soluble Ru(II)−NHC complex (**1**) which—together with some of its in situ formed derivatives—catalyzes the homogeneous or biphasic hydrogenation of a variety of organic substrates. The catalysis of the redox isomerization of allyl alcohol to propanal has also been observed. Some basic findings on the coordination chemistry of the catalysts are also reported.

Results and Discussion

$[RuCl_2L(C_{10}H_{14})]$ (**1**; L = 1-butyl-3-methylimidazol-2-ylidene, $C_{10}H_{14}$ = *p*-cymene) was prepared by the carbene transfer methodology.[18] $[\{RuCl_2(p\text{-cymene})\}_2]$



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was reacted with $[AgL_2][AgCl_2]$, obtained in the reaction of 1-butyl-3-methylimidazolium chloride (bmim-Cl) and Ag_2O in CH_2Cl_2. **1** is readily soluble in CH_2Cl_2 and was isolated upon precipitation with diethyl ether as a pale orange powder. The ^1H and ^{13}C NMR spectra recorded in CD_2Cl_2 solutions display the expected resonances with a single carbene ^{13}C resonance at δ 173.7 ppm (s). The MALDI-TOF spectrum shows peaks of two ions obtained from **1** via loss of one or two chloride ligands; the signals are centered at 409 and 373 Da, respectively, and display the characteristic Ru isotopic pattern.

Interestingly, **1** dissolves well also in water. However, in a D_2O solution two singlet ^{13}C resonances are seen at 169.5 and 169.8 ppm. On addition of NaCl only the one at 169.8 ppm remains observable. These phenomena can be explained by the equilibrium

$$\underset{\mathbf{1}}{[RuCl_2L(C_{10}H_{14})]} \overset{H_2O}{\rightleftharpoons} \underset{\mathbf{2a}}{[RuCl(H_2O)L(C_{10}H_{14})]^+} + \underset{\mathbf{2b}}{[Ru(H_2O)_2L(C_{10}H_{14})]^{2+}}$$

Accordingly, the ESI-TOF mass spectra of the solutions prepared with water showed strong signals centered at 409 Da ($[\mathbf{2a} - H_2O]^+$) and 373 Da ($[\mathbf{2a} - Cl - H_2O - H]^+$ or $[\mathbf{2b} - 2H_2O - H]^+$). Conversely, in the case of the solutions containing 0.1 M KCl the intensity of the peak at 373 Da was strongly reduced and a new signal of low intensity appeared at 483 Da ($[\mathbf{1} + K]^+$) showing

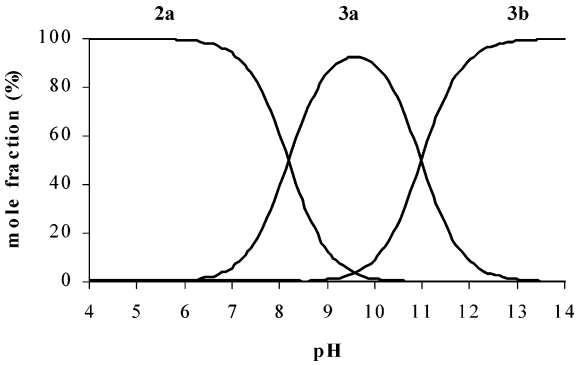

Figure 1. Mole fractions of **2a**, **3a**, and **3b** as a function of pH. [Ru] = 3.66×10^{-3} M, $[Cl^-]_{total}$ = 0.1 M, and T = 25 °C.

the shift of the equilibrium from **2b** to **2a** and, to a small extent, to **1**. In a 0.1 M aqueous KCl solution **2a** is by far the major Ru−NHC species. In 0.5 M KCl the complex is only sparingly soluble, but the relative intensity of the peak at 483 Da is increased; both phenomena are in agreement with a further shift of the equilibrium toward **1**. The ^{13}C NMR signals observed in D_2O solutions can now be assigned to the chloro−aqua species (**2a**; 169.8 ppm) and to the diaqua species (**2b**; 169.5 ppm).

In many cases the detection of a neutral compound such as **1** can be improved by the addition of potassium salts; therefore, we recorded the ESI-TOF spectra in the presence of KNO_3 and KH_2PO_4 as well; these salts contain weakly coordinating anions. In the presence of 0.1 M KNO_3 ($[K^+]/[Ru] = 100$) the signal at 483 Da ($[\mathbf{1} + K]^+$) was hardly observable, showing that in the absence of added chloride **1** was not present in the solution in significant concentration. Instead, a strong signal was observed at 436 Da, which can be assigned to $[\mathbf{2b} - 2H_2O + NO_3]^+$. Expectedly, in the solutions made with 0.01 M aqueous KNO_3 or KH_2PO_4 there were no peaks referring to the presence of **1**; however, signals were detected at 487 Da ($[\mathbf{2a} - H_2O + 2K]^+$ (both salts) and furthermore at 436 Da ($[\mathbf{2b} - 2H_2O + NO_3]^+$) and 471 Da ($[\mathbf{2b} - 2H_2O + H_2PO_4]^+$), respectively. Although the mass spectral data referring to **2b** could be interpreted by assuming chloride loss from **1** and **2a** only *in the gas phase* during the measurements, the above experiments and the low solubility of **1** in aqueous media strongly suggest that in the absence of added chloride both **2a** and **2b** (and only those) are present in the aqueous *solutions*.

Attempts were made to determine the solid-state structure of **1** by X-ray crystallography. However, due to notorious twinning of the crystals, we were as yet unable to obtain an R factor better than 12%. Nevertheless, the connectivities are clearly established and are in agreement with the results of the NMR and MS characterizations (see the Supporting Information).

According to the ^{13}C NMR spectra, the Ru−carbon bonds in these water-soluble Ru(II)−NHC complexes are stable in a wide (2−12) pH range. However, the coordinated water ligands in **2a** and **2b** undergo deprotonation with increasing pH. Our pH−potentiometric experiments showed that **2a**, formed in situ from **1** in 0.1 M aqueous chloride solutions, could be titrated as a diacid. Figure 1 shows the distribution of the resulting

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Table 1. Hydrogenation of Various Substrates Catalyzed by 1 and 4[a]

	catalyst			
	$[RuCl_2L(C_{10}H_{14})]$ (**1**)		$[RuClL(pta)(C_{10}H_{14})]^+$ (**4**)	
substrate	conversn (%)	TOF $(h^{-1})^b$	conversn (%)	TOF $(h^{-1})^b$
acetone	33.6	47	98.2	139
acetophenone	28.4	40	46.1	65
allyl alcohol[c]	85.6	121	95.6	135
benzylideneacetone	20.8	29	42.3	60
cinnamaldehyde	27.3	39	42.0	59
propanal	78.3	110	86.2	122
4-styrenesulfonic acid Na salt	3.5	5	27.4	39

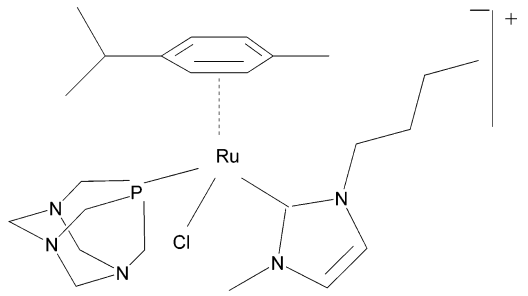
[a] Conditions: $p(H_2) = 10$ bar, $T = 80$ °C, [Ru] = 4.73 mM, [substrate] = 667 mM, $t = 1$ h, pH 6.90 (phosphate buffer). [b] In units of mol of converted substrate (mol of catalyst)$^{-1}$ (time)$^{-1}$. [c] Isomerization is included in the total conversion.

hydroxo complexes, $[RuCl(OH)L(C_{10}H_{14})]^+$ (**3a**) and $[Ru(OH)_2L(C_{10}H_{14})]$ (**3b**), as a function of the pH. Formation of insoluble polymers, clusters, or colloids from metal complex catalysts often throws doubt on the homogeneous nature of the catalytic reactions.[19] It is remarkable that no signs of such transformations were observed in highly basic solutions of **1**, despite the sterically nondemanding nature of the 1-butyl-3-methylimidazol-2-ylidene ligand. Note also that when **1** is dissolved in (unbuffered) water such deprotonation (hydrolysis) results in the lowering of the pH of the solutions. It is conceivable that, similar to the case of the water-soluble Ru(II) and Rh(I) catalysts[9,20] with the mono- and trisulfonated phosphine ligands *m*tppms and *m*tppts (*m*tppms = (diphenylphosphino)benzene-3-sulfonate), *m*tppts = tris(3-sulfonatophenyl)phosphine), the pH affects the catalytic properties of the water-soluble Ru(II)−NHC complexes; such investigations are underway in our laboratory.

Aqueous solutions of **1** react with hydrogen with a color change from orange to deep red, and the resulting solutions show considerable catalytic activity in the hydrogenation of various unsaturated substrates; representative data are shown in Table 1. It is remarkable that acetone and acetophenone are hydrogenated with TOF values of 47.4 and 40.0 h^{-1}, respectively; hydrogenation of ketones was not observed with the closely related $[RuCl_2(PR_3)(C_{10}H_{14})]$ catalysts[21] (PR_3 = pta, *m*tppts) or with the $[\{RuCl_2(m\text{tppms})_2\}_2]$ + *m*tppms (*m*tppms = (diphenylphosphino)benzene-3-sulfonate) catalyst system.[20] Both cinnamaldehyde and benzylideneacetone were preferentially hydrogenated at the C=C double bond. The homogeneous nature of catalysis was checked by the classical mercury test;[19] addition of a drop of mercury into the reaction mixtures did not affect the yields of the hydrogenations, showing them to be truly homogeneous systems.

NMR analysis of the products of allyl alcohol hydrogenation during the course of the reaction revealed that until about 90% total conversion propanol and propanal were produced in an approximately 1:1 ratio. Following that, propanol was formed at the expense of propanal. Since propanal itself undergoes fast hydrogenation (Table 1), such kinetics suggest that propanol is formed in two parallel reactions rather than exclusively through propanal. This is the first example of a redox isomerization catalyzed by a water-soluble transition-metal−NHC complex catalyst; furthermore, we are not aware of similar studies in organic solvents using such catalysts. Transposition reactions of allylic alcohols to carbonyl compounds have considerable synthetic potential as 100% atom economic processes.[1,22]

Addition of 1 equiv of 1,3,5-triaza-7-phosphaadamantane (pta) to an aqueous solution of **1** instantaneously produces a color change from orange to yellow, and a mixture of two new Ru complexes is obtained. These species are characterized by singlet ^{31}P resonances at δ −35.5 and −36.1 ppm and, furthermore, by singlets in the ^{13}C NMR spectrum at δ 165.4 and 165.6 ppm. On the basis of these spectral data, the complexes are formulated as $[RuClL(pta)(C_{10}H_{14})]^+$ (**4**) and $[Ru(H_2O)L(pta)(C_{10}H_{14})]^{2+}$ (**5**). The strong peak at 566 Da in the ESI-TOF mass spectrum showed **4** as the single species in solutions containing 0.1 M KCl.



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In general, the mixed Ru−NHC−tertiary phosphine complexes showed substantially higher activity and selectivity than **1**; the results are shown in Table 1. For example, with **4** acetone was hydrogenated with 98.1% conversion, compared to 33.6% conversion observed with **1**. Similarly, in the hydrogenation of benzylideneacetone **4** afforded 42.3% total conversion with 91.9% selectivity to 4-phenyl-2-butanone, while with **1** only 20.8% conversion and 61.7% selectivity were obtained.

Catalytic hydrogenation of biological membranes is a valuable tool for the study of important membrane-associated processes such as thermotolerance.[23] Therefore, we attempted the hydrogenation of aqueous dispersions of dioleyl-phosphatidyl choline (DOPC), a

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typical unsaturated lipid constituent of biomembranes. Under very mild conditions (37 °C, 1−10 bar of H_2, pH 6.9) both double bonds of DOPC were hydrogenated and up to 88% conversions were achieved in 3 h with **1** as catalyst. This corresponds to a turnover number of 1.2, showing the true catalytic nature of the process. Such a catalyst activity is perfectly suited for the hydrogenation of cell suspensions where the absolute amount of substrate is very small and high conversions may even be lethal.[8,9,23]

Conclusions

The new water-soluble Ru(II)−NHC complexes described in this study are readily available from the [{$RuCl_2$(*p*-cymene)}$_2$] and bmim-Cl starting materials. According to the results of pH−potentiometric measurements they are stable toward decomposition or aggregation in aqueous systems in a wide pH range and up to relatively high temperatures (80 °C); however, in basic solutions well-defined, stable hydroxo complexes are formed. The new complexes are active and selective catalysts for the hydrogenation of olefins and oxo compounds, for the redox isomerization of allyl alcohol, and for the modification of model biological membranes in aqueous solution or in biphasic media.

Experimental Section

All manipulations were carried out using standard Schlenk techniques. [$RuCl_2$(*p*-cymene)]$_2$[24] and 1-butyl-3-methylimidazolium chloride[25] were synthesized according to processes described in the literature. Dioleyl-phosphatidyl-choline was purchased from Sigma, and all other chemicals were supplied by Aldrich. Lipid dispersions were prepared using a Branson Sonifier 250 ultrasound disintegrator. Nuclear magnetic resonance spectra were recorded at ambient temperature on a Bruker DRX 360 instrument. Mass spectra were obtained on a Bruker Biflex III MALDI-TOF (for lipid samples) and a Bruker BioTOF II ESI-TOF mass spectrometer in positive ion mode. For MALDI measurements 2,5-dihydroxybenzoic acid (DHB) was used as a matrix (dissolved in $CHCl_3$/MeOH = 1/1).

Catalytic hydrogenations were performed in a Schlenk vessel or in a pressure-resistant glass tube reactor. The reactors were thermostated (Julabo 25 circulator), and the reaction mixtures were stirred magnetically. In most experiments the concentration of substrates was 667 mM, whereas in the case of lipid dispersions it was 1.27 mM. The concentration of the catalyst was 4.73 mM in the former case and 1.88 mM in the latter case. Aqueous mixtures of acetophenone, cinnamaldehyde, benzylideneacetone, and DOPC samples were extracted with chloroform after hydrogenation. These extracts were concentrated by the evaporation and analyzed by NMR or MALDI-TOF-MS techniques. The reaction mixtures with water-soluble substrates, such as allyl alcohol, were directly used for NMR analysis after the addition of D_2O as lock.

pH−potentiometric titrations were performed at 25 °C and constant ionic strength, maintained by the addition of KCl (C_{KCl} = 0.100 M). Measurements were carried out with an automatically controlled Metrohm 702 S14 titration system equipped with a Metrohm 6.0234.100 combined electrode. The concentration of **1** was about (4−7) × 10^{-3} M in each experiment. The titration data were analyzed with the PSEQUAD program, and the distributions of the various complex species were calculated and plotted by MEDUSA v. 9.

Synthesisof[Ag(1-butyl-3-methylimidazolin-2-ylidene)$_2$][$AgCl_2$]. 1-Butyl-3-methylimidazolium chloride (bmim-Cl) (0.30 g, 1.72 mmol) was dissolved in 25 mL of dichloromethane and transferred into a Schlenk vessel. Silver(I) oxide (0.24 g, 1.03 mmol) was added, and the mixture was stirred for 3 h at 50 °C under an Ar atmosphere. The unreacted Ag_2O was filtered off, and in most cases the solution was directly applied for further synthetic steps. The product can be isolated by removing the solvent in vacuo to give a yellow waxy substance, extremely sensitive to oxygen and water. Yield: 0.32 g (66%). ^{1}H NMR (360 MHz, 298 K, CD_2Cl_2): δ 0.95 (t, 6H, $NCH_2CH_2CH_2CH_3$), 1.34 (sextet, 4H, $NCH_2CH_2CH_2CH_3$), 1.81 (quintet, 4H, $NCH_2CH_2CH_2CH_3$), 3.84 (s, 6H, NCH_3), 4.12 (t, 4 H, $NCH_2CH_2CH_2CH_3$), 7.10 (s, 4 H, CH=CH). ^{13}C NMR (90 MHz, 298 K, CD_2Cl_2): δ 13.38 (CH_2CH_3), 19.59 ($NCH_2CH_2CH_2$), 33.41 (NCH_2CH_2), 38.67 (NCH_3), 51.58 (NCH_2), 121.00 (CH=CH), 122.25 (CH=CH), 179.64 (NCN).

Synthesis of 1. [$RuCl_2$(*p*-cymene)]$_2$ (0.27 g, 0.44 mmol) was taken up in 5 mL of dichloromethane and added to a solution of [Ag(1-butyl-3-methylimidazolin-2-ylidene)$_2$][$AgCl_2$] (0.25 g, 0.49 mmol in 7.5 mL CH_2Cl_2). A white precipitate (AgCl) formed, and the mixture was stirred for 2 h at 40 °C. After filtration in air, the solvent was removed in vacuo to give a brown waxy substance. The Schlenk vessel containing the raw product was immersed into liquid nitrogen, and 5 mL of diethyl ether was added. The waxy substance was triturated for a couple of minutes, and the diethyl ether was removed by a Pasteur pipet. This purification treatment was repeated five times, when a pale orange powder (**1**) was obtained. This compound is stable in air and can be kept in an aqueous solution for several days without decomposition. Yield: 0,25 g (61%). Analytically pure samples could be obtained by layering hexane on CH_2Cl_2 solutions of **1**. MS (ESI): *m/z* 373 [M − 2Cl − H]$^+$, 409 [M − Cl]$^+$. ^{1}H NMR (360 MHz, 298 K, CD_2Cl_2): δ 1.04 (t, 3H, $NCH_2CH_2CH_2CH_3$), 1.31 (d, 6H, $CHCH_3$), 1.47 (sextet, 2H, $NCH_2CH_2CH_2CH_3$), 1.74 (quintet, 2H, $NCH_2CH_2CH_2CH_3$), 2.02 (s, 3H, CCH_3), 2.97 (heptet, 1H, CH_3CHCH_3), 4.01 (s, 3H, NCH_3), 4.49 (t, 2H, $NCH_2CH_2CH_2CH_3$), 5.01−5.43 (m, 4H, −CH−), 7.11 (d, 1H, NCH=CHN), 7.16 (d, 1H, NCH=CHN). ^{13}C NMR (90 MHz, 298 K, CD_2Cl_2): δ 13.71 ($-CH_2CH_3$), 18.34 (CCH_3), 20.10 ($NCH_2CH_2CH_2$), 21.42 ($CHCH_3$), 30.72 ($CHCH_3$), 33.82 (NCH_2CH_2), 39.34 (NCH_3), 51.21 (NCH_2), 81.17, 81.74 ($CHCH$), 98.85 (CCH_3), 108.91 ($CHCH(CH_3)_2$), 121.51, 124.02 ($NCH=CHN$) 173.68 (NCN). Anal. Calcd for $C_{18}H_{28}N_2Cl_2Ru$: C, 48.65; H, 6.35; N, 6.30; Cl, 15.96. Found: C, 48.10; H, 6.50; N, 6.76; Cl, 15.57.

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Supporting Information Available: NMR and ESI-TOF-MS characterization data for the complexes obtained, pH−potentiometric titration of **1**, details of the hydrogenation of various substrates, and an ORTEP view of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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