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Water-soluble carbene complexes as catalysts for the hydrogenation of acetophenone under hydrogen pressure

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ABSTRACT

The synthesis of water-soluble Rh(I), Ir(I), and Ru(II) N-heterocyclic carbene complexes is described. These complexes are applied as catalysts for aqueous phase hydrogenation reactions. Good hydrogenation activities under ca. 40 atm pressure H_2 at room temperature are observed.

1. Introduction

Development of catalysts applicable in aqueous systems is very important for a sustainable, environmentally friendly "green" chemistry. Water as a solvent bears a number of attractive physicochemical properties in comparison to traditional organic solvents, which are in many cases flammable, explosive, toxic or carcinogenic. Water in particular is one of the least expensive and most easily accessible solvents [1]. Accordingly, organometallic catalysis in aqueous media has attracted interest since the 1970s, with pioneering work being carried out for example by Joo, Sasson, and Sinou. A variety of catalytic reactions in aqueous phase have been documented since then [1–10]. Sometimes reaction rates even increase when water replaces organic solvents, e.g. in Diels–Alder and some coupling reactions [11,12]. However, a challenge often associated with catalysis in water is the need for water-soluble and water stable ligand/catalyst systems and the decrease in catalytic activity and/or stereoselectivity when going from organic solvents to water. Water-solubility of catalysts is often achieved by incorporating hydrophilic moieties in the ligands [13–17]. A wide variety of polar functional substituents e.g. SO_3Na, OSO_3Li, CO_2Na, OH, PMe_3^+, NMe_3^+, $P(O)(ONa)_2$, polyethers, etc. have been incorporated in order to render the respective ligands water-soluble [1,11,13]. Among these, the sulfonate moiety has been applied particularly successfully and is often used.

Since N-heterocyclic carbenes (NHCs) had been recognized as efficient ligands for catalytically applicable complexes in the mid 1990s [18], this group of ligands has experienced an almost unprecedented growth in importance [18,19]. A multitude of catalyst systems with NHC ligands, mostly as spectator ligands has been described, particularly during the last 15 years [20–37]. NHCs display bonding properties roughly comparable to phosphines when applied as ligands [20–40]. Furthermore, NHC ligands are two-electron σ-donors with little π-accepting ability [41–46]. They are considered to behave in several aspects similar to tertiary phosphines, but bind more strongly to the metal center and are additionally excellent electron donors. Therefore, NHCs display some advantages over phosphine ligands in the design of water-soluble catalysts. The advantages are: (i) NHCs may act as stabilizing ligands for transition metal complexes; thus they might improve the stability of catalysts in water; (ii) phosphines are easily oxidized, have to be applied in considerable excess in many cases and often generate undesirable byproducts or residues – most likely avoidable with carbene ligands; and (iii) NHCs are known to be less toxic than phosphines [47–51]. Based on the high interest in

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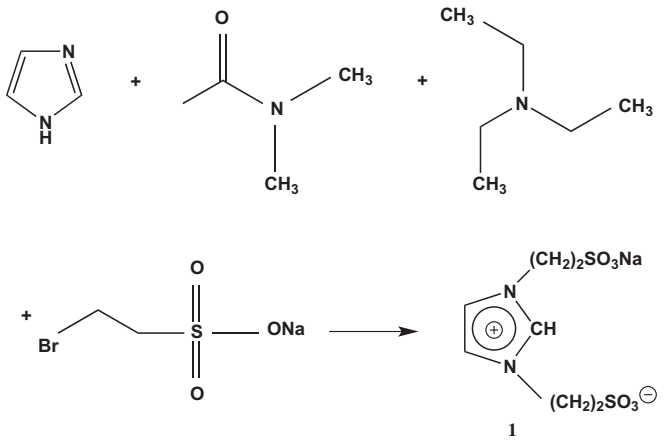


Scheme 1. Synthesis of ligand **1**.

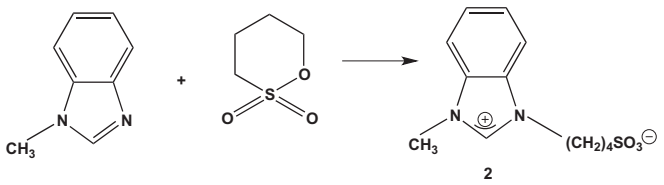
NHCs as ligands for homogeneous catalysts, the interest in the preparation of water-soluble derivatives is also increasing [49–58]. In this work, we report on the preparation and catalytic properties of sulfoalkyl-substituted azolium-derived NHC complexes in the hydrogenation of aromatic ketones in aqueous media.

2. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures and distilled under argon prior to use. Chemicals purchased from Alfa Aesar were used without further purification. NMR measurements were carried out using a Bruker Avance DPX 400 spectrometer and Bruker Avance DPX 300 spectrometer. Elemental analysis (C, H, N) was performed by the Microanalytical Laboratory of TUM. Mass spectra were performed with a Finnigan MAT 90 spectrometer using FAB technique. Catalytic runs were monitored by GC methods on a Hewlett-Packard instrument HP 5890 series II equipped with a FID and DB23 column.

*2.1. Synthesis of 1-methyl-3 (butyl-4-sulfonate) benzimidazolium betaine (**2**)*

Benzimidazole (1.32 g, 10 mmol) was stirred with 1,4-butanesultone (1.36 g, 10 mmol) at room temperature for 3 days under solvent-free condition. After solidification, the mass was washed 3 times with toluene and dried under high vacuum. The white solid was readily soluble in water.



Scheme 2. Synthesis of ligand **2**.

^{1}H NMR (400 MHz, D_2O, 25 °C), δ[ppm]: 1.81 (pq, 2H, CH_2), 2.14 (pq, 2H, CH_2), 2.94 (t, 2H, CH_2), 4.09 (s, 3H, CH_3), 4.53 (t, 2H, CH_2), 7.69 (d, 2H, C*H*CHarom), 7.83, 7.9 (d, 2H, C*H*CHarom), 9.28 (s, 1H, NC*H*N). ^{13}C NMR (100.5 MHz, D_2O, 25 °C), δ[ppm]: 21.13 (*C*H_2), 27.06 (*C*H_2), 32.78 (*C*H_2), 46.26 (N-*C*H_3), 49.98 (*C*H_2), 112.89, 126.62, 130.86 (*C*H*C*H*C*H*C*H), 132.02 (N*C*CN), 141.07 (N*C*HN). EA calcd. for ($C_{12}H_{16}N_2SO_3$) C: 53.71 H: 6.01 N: 10.44 S: 11.95, found: C: 53.14 H: 6.19 N: 10.15 S: 11.34. MS-FAB: *m*/*z* (%) = 268.7 (M^+).

*2.2. General synthesis procedure of the carbene complexes (**3**–**5**)*

1.6 ml of 1 M NaOEt/EtOH solution was dissolved in 10 ml ethanol and slowly added to a suspension of 0.6 mmol $(M(COD)Cl)_2$. After the mixture was stirred for 30 min at room temperature, the azolium precursor (1.2 mmol) was added. The suspension was stirred at room temperature for 72 h. Ethanol was removed in vacuo, and then the residue was washed with diethyl ether and dried under high vacuum. The rhodium/iridium precursors $(Ir(COD)OEt)_2$/$(Rh(COD)OEt)_2$ were prepared from $(Rh(COD)Cl)_2$/$(Ir(COD)Cl)_2$ by reaction with sodium ethanolate in ethanol at ambient temperature. Substitution of the chloro bridge of the dimeric precursor $(Rh(COD)Cl)_2$ by an ethoxy bridge allows the coordinated base to deprotonate the azolium in situ, leading to the desired carbene complexes.

*2.2.1. Complex **3** ($C_{20}H_{27}ClN_2NaO_3RhS$)*

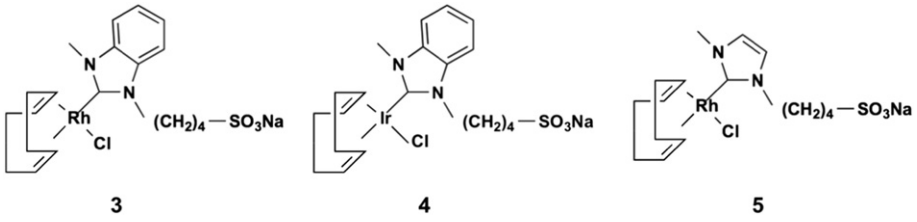
^{1}H NMR: (400 MHz, D_2O, 20 °C, ppm), δ[ppm]: 1.91 (m, COD allyl), 2,32 (pq, 2H, CH_2), 2.45 (pq, 2H, CH_2), 3.05 (t, 2H, CH_2), 3.23, 3.58 (COD vinyl), 4.11 (s, 3H, CH_3), 4.52 (t, 2H, CH_2), 7.26 (d, 2H, C*H*CHarom), 7.41 (d, 2H, C*H*arom). ^{13}C-MAS NMR (75.47 MHz, 25 °C), δ[ppm]: 24.3 (*C*H_2), 31.4 (COD allyl), 35.8 (*C*H_2), 51.1 (N*C*H_3), 51.2 (*C*H_2) 69.6 (COD allyl), 92.3, 99.5(COD vinyl), 115 (*C*HCHarom), 122.8 (*C*HCHarom), 135.5 (N*C*CNarom), 195.5 (NC_{carb}N). EA calcd. for ($C_{20}H_{27}ClN_2NaO_3RhS$): C: 44.74 H: 5.07 N: 5.22 S: 5.97, found: C: 42.96 H: 5.28 N: 5.60 S: 6.65. MS-FAB: *m*/*z* (%) = 512.1 (M^-).

*2.2.2. Complex **4** ($C_{20}H_{27}ClIrN_2NaO_3S$)*

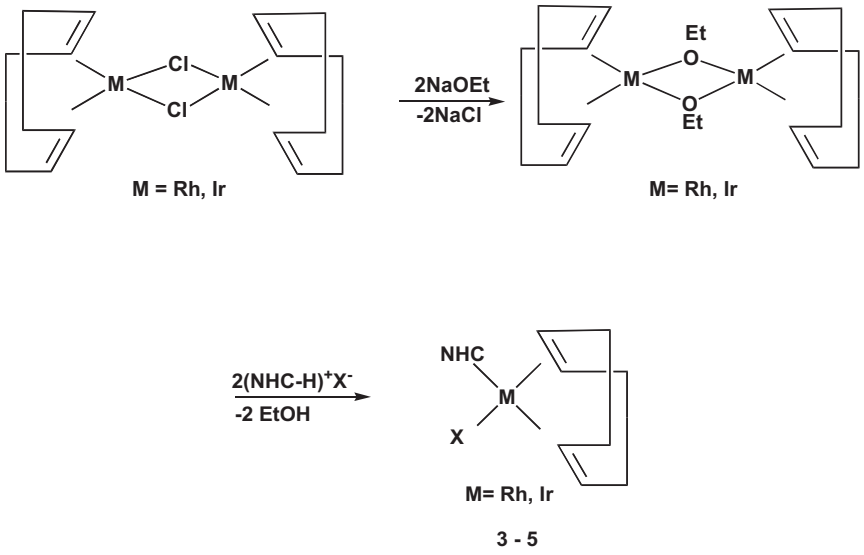
^{1}H NMR: (400 MHz, D_2O, 25 °C), δ[ppm]: 1.79 (m, COD allyl), 2.11 (pq, 4H, CH_2), 2.93 (t, 2H, CH_2), 3.85 (COD vinyl), 4.06 (s, 3H, CH_3), 4.34 (COD vinyl), 4.48 (t, 2H, CH_2), 7.62 (d, 2H, C*H*CHarom), 7.77, 7.83 (d, 2H, C*H*arom). ^{13}C-MAS NMR (75.47 MHz, 25 °C), δ[ppm]: 23.8 (*C*H_2),26.3(*C*H_2), 30.7 (COD allyl), 34.1 (*C*H_2), 48.3 (N*C*H_3), 50.8 (*C*H_2), 85.7 (CODvinyl), 111.4 (*C*HCHarom), 124.7 (*C*HCHarom), 135.5 (N*C*CNarom), 191.7 (NC_{carb}N). EA calcd. for ($C_{20}H_{27}ClIrN_2NaO_3S$): C: 38.36 H: 4.35 N: 4.47 S: 5.12, found: C: 37.89 H: 4.68 N: 4.97 S: 6.02. MS-FAB: *m*/*z* (%) = 602 (M^-).

*2.2.3. Complex **5** ($C_{16}H_{25}N_2RhClNaO_3S$)*

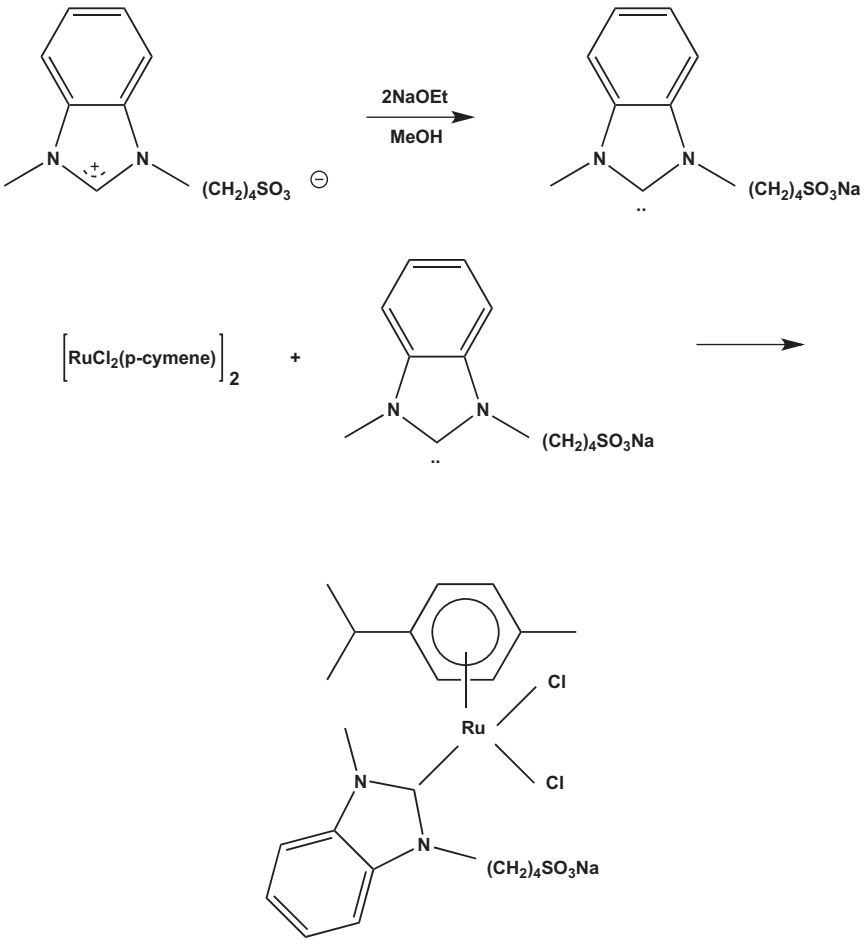
^{1}H NMR (400 MHz, D_2O, 25 °C), δ[ppm]: 1.71 (m, COD allyl), 2.42 (pq, 2H, CH_2), 2.87 (pq, 2H, CH_2), 3.55, 3.67 (COD vinyl), 3.98 (t, 2H,



Scheme 3. Rhodium – and iridium – NHC complexes **3**–**5**.

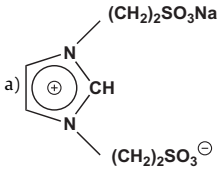
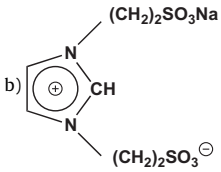
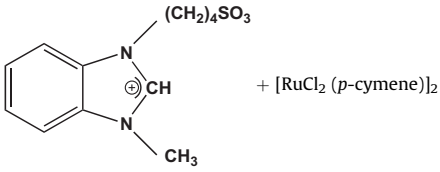
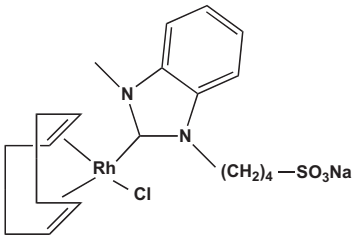
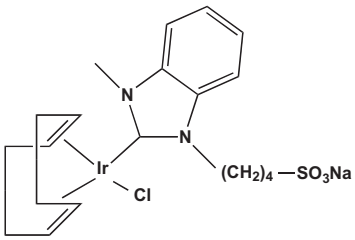
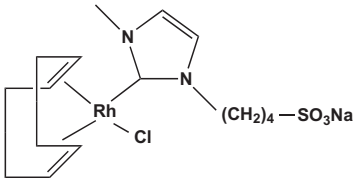
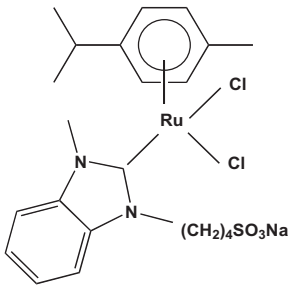


Scheme 4. Synthesis of rhodium – and iridium – NHC complexes **3**–**5**.



Scheme 5. Synthesis of the ruthenium – NHC complex **6**.

Table 1
Aqueous hydrogenation of acetophenone, catalyzed by water-soluble carbene complexes.

No	Catalyst	Catalyst loading (mol%)	Conversion[a] (%)	Yield[b] (%)	Selectivity[c] (%)
1	a)  + Rh (III) Acetate	2.5	92	74	81
	b)  + $[RuCl_2\ (p\text{-cymene})]_2$	2.5	75	58	78
2	 + $[RuCl_2\ (p\text{-cymene})]_2$	2.5	68	65	95
3		2.5	95	89	94
4		2.5	51	37	71
5		2.5	98	46	47
6		2.5	90	87	96

[a] Conversion = (moles acetophenone reacted)/(moles acetophenone fed).
[b] Yield = (moles 1-phenylethanol formed)/(moles acetophenone fed).
[c] Selectivity = (moles 1-phenylethanol formed)/(moles acetophenone reacted).

CH_2), 4.15 (s, 3H, CH_3), 4.50 (t, 2H, CH_2), 7.12 (1H, NC*H*N), 7.16, (1H, NC*H*N). ^{13}C-MAS NMR (75.47 MHz, 25 °C), δ[ppm]: 23.9 (CH_2), 30.7 (CH_2),31.6 (COD allyl), 39.0 (CH_2), 51.9 (NCH_3), 57.7 (CH_2), 67.3, 89.6, 96.6 (COD vinyl), 124.0 (NCHCHN), 180.6 ($NC_{carb}N$). EA calcd. for ($C_{16}H_{25}N_2RhClNaO_3S$): C: 39.48 H: 5.18 N: 5.75 S: 6.59, found: C: 38.04 H: 5.36 N: 6.18 S: 7.97. MS-FAB: *m*/*z* (%) = 462.9 (M^-).

2.3. Synthesis procedure for of the carbene complexes (**6**)

1 ml of 1 M NaOEt/MeOH solution was slowly added to a suspension of 1 mmol azolium precursor in 10 ml methanol. After the mixture was stirred for 24 h at room temperature and free carbene was formed, 0.5 mmol ruthenium precursor [$RuCl_2$(*p*-cymene)]$_2$ in 5 ml methanol was added. The suspension was stirred at room temperature for another 24 h. Methanol was removed under vacuum. The residue was then washed with diethyl ether and dried under high vacuum.

2.3.1. Complex **6** ($C_{22}H_{29}Cl_2RuN_2NaO_3S$)

^{1}H NMR (400 MHz, CD_3OD, 25 °C), δ[ppm]: 1.31 (m, 6H, CH(CH_3)), 1.85 (pq, 2H, CH_2), 2.17(s, 3H, C(CH_3)), 2.19(m, 2H, CH_2), 2.76 (sept, 1H, $CHCH_3$), 2.87 (t, 2H, CH_2), 4.14 (s, 3H, N-CH_3), 4.57(m, NCH_2), 5.29(m, 2H, C_6H_4), 5.54 (m, 2H, C_6H_4), 7.70(d, 2H, C*H*C*H*arom), 7.92 (d, 2H, C*H*C*H*arom). ^{13}C NMR (100.5 MHz, CD_3OD, 25 °C), δ[ppm]: 17.35 (CH(CH_3)), 20.90 (C(CH_3)), 21.35 (CH_2), 27.44 (CH_2), 31.16 (*C*H(CH_3)), 31.32 (CH_2), 46.47 (NCH_3), 49.84 (NCH_2), 76.26 (2C, C_6H_4), 78.27 (2C, C_6H_4), 93.54 (1C, *C*Me, *p*-cymene), 97.28 (1C, *Ci*Pr, *p*-cymene), 112.87 (*CH*CHarom), 126.89 (*CH*CHarom), 131.53, 132. 15 (NCCNarom), 180.09 ($NC_{carb}N$). EA calcd. for ($C_{22}H_{29}Cl_2RuN_2NaO_3S$): C: 44.30 H: 4.90 N: 4.70 S: 5.38 Cl: 11.89 Na: 3.85, found: C: 44.07 H: 5.30 N: 5.03 S: 5.42 Cl: 12.13 Na: 3.5. MS-FAB: *m*/*z* (%) = 573 (M^-).

2.4. General procedure for hydrogenation [59]

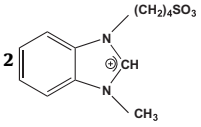
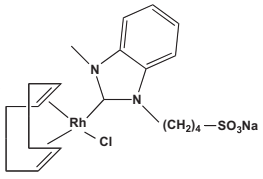
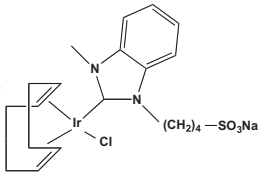
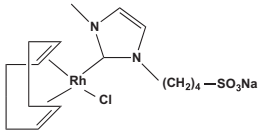
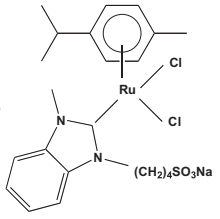
In a Schlenk tube 0.06 mmol of ligand (**1**, **2**) and 0.96 ml of 1 M aqueous sodium hydroxide solution was added to 10 ml of water under argon and the mixture was degassed. After complete dissolution of the ligand, 0.03 mmol of metal precursor (Rh (III) acetate, [$RuCl_2$(*p*-cymene)]$_2$) was added. After stirring for 24 h at room temperature, the solution was transferred to a 50 ml stainless steel glass coated autoclave and 1.2 mmol of substrate was added. The autoclave was purged with hydrogen and final pressure was adjusted to 40 atm. The mixture was stirred at room temperature for 21 h and then analyzed by gas chromatography to determine the conversions and reaction yields using diethylene glycol dibutyl ether as an internal standard.

For comparison, the same reaction condition were applied for the isolated NHC complex catalysts (**3**–**6**)

3. Results and discussion

For the synthesis of water-soluble NHC complexes, sulfonated N-alkylazolium salts were applied to prepare the ligands. Ligand **1**

Table 2
NMR results.

	^{1}H	^{13}C
Ligand **2** 	1.81 (pq, 2H, CH_2), 2.14 (pq, 2H, CH_2), 2.94 (t, 2H, CH_2), 4.09 (s, 3H, CH_3), 4.53 (t, 2H, CH_2), 7.69 (d, 2H, C*H*C*H*arom), 7.83, 7.9 (d, 2H, C*H*C*H*arom), 9.28 (s, 1H, NC*H*N).	21.13 (*C*H$_2$), 27.06 (CH_2), 32.78 (CH_2), 46.26 (N-*C*H$_3$), 49.98 (CH_2), 112.89, 126.62, 130.86 (CHCHCHCHarom), 132.02 (NCCNarom), 141.07 (NCHN).
Complex **3** 	1.91 (m, COD allyl), 2,32 (pq, 2H, CH_2), 2.45 (pq, 2H, CH_2), 3.05 (t, 2H, CH_2), 3.23, 3.58 (COD vinyl), 4.11 (3H, CH_3), 4.52 (t, 2H, CH_2), 7.26 (d, 2H, C*H*C*H*arom), 7.41 (d, 2H, C*H*C*H*arom).	24.3 (CH_2), 31.4 (COD allyl), 35.8 (CH_2), 51.1 (N-*C*H$_3$), 51.2 (CH_2) 69.6 (COD allyl), 92.3, 99.5(COD vinyl), 115 (*C*HCHarom), 122.8 (CHCHarom), 135.5 (NCCNarom), 195.5 ($NC_{carb}N$).
Complex **4** 	1.79, (m, COD allyl), 2.11 (pq, 4H, CH_2), 2.93 (t, 2H, CH_2), 3.85 (COD vinyl), 4.06 (3H, CH_3), 4.34 (COD vinyl), 4.48 (t, 2H, CH_2), 7.62 (d, 2H, C*H*C*H*arom), 7.77 (d, 1H, C*H*arom), 7.83(d, 1H, C*H*arom).	23.8(CH_2), 26.3(CH_2), 30.7 (COD allyl), 34.1 (CH_2), 48.3 (NCH_3), 50.8 (CH_2), 85.7 (CODvinyl), 111.4 (*C*HCHarom), 124.7 (*C*HCHarom), 135.5 (NCCNarom), 191.7 ($NC_{carb}N$).
Complex **5** 	1.71 (m, COD allyl), 2.42 (pq, 2H, CH_2), 2.87 (pq, 2H, CH_2), 3.55, 3.67 (COD vinyl), 3.98 (t, 2H, CH_2), 4.15 (3H, CH_3), 4.50 (t, 2H, CH_2), 7.12 (d, 1H, NC*H*N), 7.16 (d, 1H, NC*H*N).	23.9 (CH_2), 30.7 (CH_2), 31.6 (COD allyl), 39.0 (CH_2), 51.9 (NCH_3), 57.7 (CH_2), 67.3, 89.6, 96.6 (COD vinyl), 124.0 (NCHCHN), 180.6 ($NC_{carb}N$).
Complex **6** 	1.31 (d, 6H, CH (CH_3)), 1.85 (pq, 2H, CH_2), 2.17 (s, 3H, C (CH_3)), 2.19 (pq, 2H, CH_2), 2.76 (sept, 1H, $CHCH_3$), 2.87 (t, 2H, CH_2), 4.14 (s, 3H, NCH_3), 4.57 (t, NCH_2), 5.29 (m, 2H, C_6H_4), 5.54 (m, 2H, C_6H_4), 7.70 (d, 2H, C*H*C*H*arom), 7.92 (d, 2H, C*H*C*H*arom).	17.35 (CH(CH_3)), 20.90 (C(CH_3)), 21.35 (CH_2), 27.44 (CH_2), 31.16 (*C*H(CH_3), 31.32(CH_2), 46.47 (NCH_3), 49.84 (NCH_2), 76.26 (2C, C_6H_4), 78.27 (2C, C_6H_4), 93.54 (1C, *C*Me, *p*-cymene), 97.28 (1C, *Ci*Pr, *p*-cymene), 112.87 (*CH*CHarom), 126.89 (*CH*CHarom), 131.53, 132.15 (NCCNarom), 180.09 ($NC_{carb}N$).

(see Scheme 1) was synthesized by reaction of imidazole with dimethylacetamide, triethylamine, and the sodium salt of 2-bromoethanesulfonic acid similar to a previously published work [60]. Ligand **2** (see Scheme 2) was synthesized via the reaction of methyl benzimidazole and 1,4-butanesultone at room temperature, similar to a previously published procedure, using a different azolium salt, however (see experimental part and ref. [60])

The new complexes **3**–**5** (see Scheme 3) were prepared by in situ deprotonation of azolium salts and subsequent reaction of rhodium/iridium precursors $(Rh(COD)Cl)_2$/$(Ir(COD)Cl)_2$ with the sulfonated ligands **2** at ambient temperature (see Scheme 4). Complexes **3**–**5** are readily soluble and stable in H_2O.

In situ deprotonation of azolium salt to form free carbene and subsequent reaction of ruthenium precursor $[RuCl_2(p\text{-cymene})]_2$ were used to prepare the new complex **6** (see Scheme 5).

In the ^1H NMR spectrum of complex **3**, pseudo-quintets are observed at $\delta(^1H) = 2.32$ and 2.45 ppm and triplets at $\delta(^1H) = 3.05$ and 4.52 ppm. They are assigned to the non-equivalent CH_2 protons. The signals at $\delta(^1H) = 1.91$, 3.23 and 3.58 ppm are indicative for the COD protons. The signal at 4.11 ppm stems from the CH_3 methyl substituent. The CH signals of the benzimidazole ring are observed at 7.26 and 7.41 ppm, respectively. In the ^{13}C NMR spectrum of complex **3**, the signal at $\delta(^{13}C) = 195.5$ ppm originates from the Rh-C carbene carbon atom, whereas the signals at $\delta(^{13}C) = 31.4$, 69.6, 92.3, and 99.5 ppm are caused by the COD carbons. The NCH_3 signal is observed at 51.1 ppm and the CH_2 signals of the ligand are found at 24.3, 35.8, and 51.2 ppm.

For the ^1H NMR spectrum of complex **4**, the non-equivalent CH_2 protons are observed at $\delta(^1H) = 2.11$, 2.93, and 4.48 ppm, showed pseudo-quintets and triplets, while the signals at $\delta(^1H) = 1.79$, 3.85, and 4.34 ppm are assigned to the COD protons. The signal at 4.06 ppm comes from the CH_3 methyl substituent. The CH signals of the benzimidazole ring are found at 7.62, 7.77, and 7.83 ppm, respectively. In the ^{13}C NMR spectrum of complex **4**, the signal at $\delta(^{13}C) = 191.7$ ppm stems from the Rh-C carbene carbon atom, whereas the signals at $\delta(^{13}C) = 30.7$ and 85.7 ppm are due to the COD carbons. The NCH_3 signal is observed at 48.3 ppm and the CH_2 signals of the ligand can be seen at 23.8, 26.3, 34.1 and 50.8 ppm.

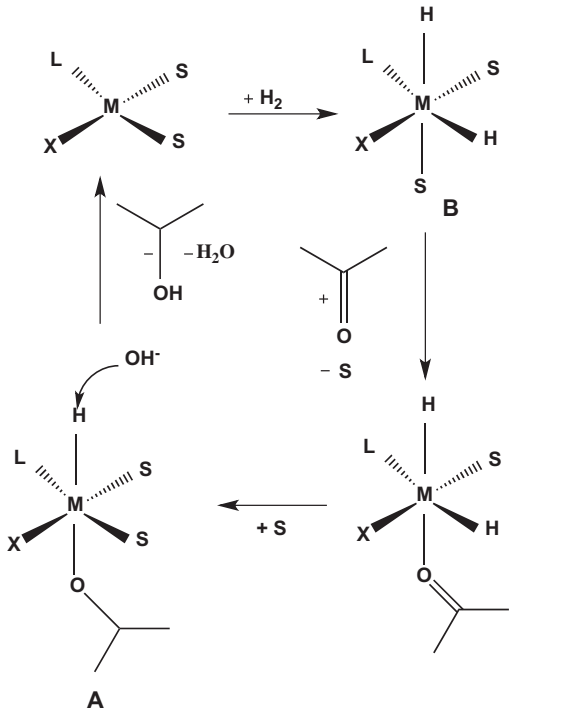
The ^1H NMR spectrum of complex **5** shows pseudo-quintets at $\delta(^1H) = 2.42$ and 2.87 ppm and triplets at 3.98 and 4.50 ppm, which are assigned to the non-equivalent CH_2 protons. The signals at $\delta(^1H) = 1.71$, 3.55 and 3.67 ppm are indicative for the COD protons. The signal at $\delta(^1H) = 4.15$ ppm stems from the CH_3 methyl substituent. The CH signals of the benzimidazole ring are observed at 7.12 and 7.16 ppm. For the ^{13}C NMR spectrum of complex **5**, the signal at $\delta(^{13}C) = 180.6$ ppm originates from the Rh-C carbene carbon atom, while the signals at $\delta(^{13}C) = 31.6$, 67.3, 89.6, and 96.6 ppm come from the COD carbons. The NCH_3 signal is seen at 51.9 ppm and the CH_2 signals of the ligand are observed at 23.9, 30.7 and 39 and 57.7 ppm.

Derived from a different metal precursor, complex **6** has NMR signals differing from complexes **3**–**5**. The non-equivalent CH_2 protons for complex **6** are found at $\delta(^1H) = 1.85$, 2.19, 2.87 and 4.57 ppm. The signals at 1.85 and 2.19 ppm are seen as pseudo-quintets, whereas the signals at 2.87 and 4.57 ppm are triplets. The CH_3 signals of the isopropyl group, being attached to the *p*-cymene ring are seen at 1.31 ppm. The signal at $\delta(^1H) = 2.17$ ppm is referred to the CH_3 methyl substituent of *p*-cymene ring. The signal at $\delta(^1H) = 4.14$ ppm stems from the CH_3 methyl substituent of benzimidazole. The CH signals of the benzimidazole ring are observed at 7.70 and 7.92 ppm, respectively. For the ^{13}C NMR spectrum of complex **6**, the signal at $\delta(^{13}C) = 180.09$ ppm stems from the Ru–C carbene carbon atom. The signals at $\delta(^{13}C) = 17.35$ come from the isopropyl carbons. The CH_3 methyl substituent of *p*-cymene ring occurs at 20.90 ppm. The CH substituent of *p*-cymene ring is seen at 31.16 ppm. Substituted C atoms of *p*-cymene ring result in the signal at 76.26 and 78.27 ppm. The NCH_3 signal is seen at 46.47 ppm and the CH_2 signals of the ligand are observed at 21.35, 27.44, 31.32 and 49.84 ppm respectively. For the better understanding of NMR, Table 2 gives an overview of the signals of the ligands and the complexes.

The catalytic activities of complexes **3**–**5** were examined in the hydrogenation of acetophenone in water under a pressure of 40 atm H_2 at room temperature. In order to be able to compare the activity of the catalysts, a fixed reaction time of 21 h was applied. Complexes **3**–**5** show good activities in basic media in the aqueous hydrogenation of acetophenone under hydrogen pressure without any phase-transfer agent. In situ formed complexes of Ru and Rh with ligands **1**–**2** also show quite good activities for aqueous hydrogenation of acetophenone. The catalytic reaction results are summarized in Table 1.

The mechanism of these hydrogenations catalyzed by those complexes is not well examined at present. Based on the commonly accepted mechanism together with observations made in the literature by Bujoli et al. [59] and Zhang et al. [61] (see Scheme 6), the main role of the added base appears to be deprotonation of the intermediate **A**, while water can protonate the alkoxide ligand. **A** is obtained from the insertion of a ketone into one of the M-H bonds. A push-pull process would favor the reductive elimination of **A**, allowing the oxidative addition of hydrogen to generate **B**. More research is currently under way to gain better insight into the reaction mechanism.

With the same carbene ligand, the Rh complex **3** produces a higher yield, conversion, and selectivity than compound **4** with the larger Ir as central atom. Furthermore, **3**, as benzimidazole derived complex, leads to higher yield and selectivity, but almost the same conversion, when compared to the imidazole derived



Scheme 6. Mechanism for the aqueous hydrogenation of acetophenone.

complex **5**. An explanation might be the influence of the steric bulk of the carbene ligand on directing the reaction. Particularly in octahedral intermediates the steric bulk of the carbene ligand could be decisive for the selectivity of the catalyst. Using the same catalytic reaction condition, the isolated complex **6** described in this work shows generally higher activities compared to the in situ formed compound **2** (see Table 1). A possible reason for this might be the higher purity of the isolated (and purified) complex prior to catalytic application. However, the sampling size (with respect to the number of compounds examined) and the non-uniformity of the catalyst compounds (i. e. different set of ligands) prohibits a more detailed interpretation of the obtained data.

With respect to byproducts, beside 1-phenylethanol as the main product, the hydrogenation of acetophenone also produces cyclohexylethanol. The formation of the latter compound has been reported in the literature [62–66]. Cheng et al. mention that product formation follows the route: acetophenone → 1-phenyethanol → cyclohexylethanol, with the reaction selectivity towards 1-phenylethanol being increased with decreasing formation of cyclohexylethanol as its follow-up product [67].

4. Conclusions

Four new water-soluble complexes containing Ir, Rh, Ru as central atoms and an NHC ligand have been synthesized. For the hydrogenation of acetophenone in water under 40 bar hydrogen pressure, acceptable to good catalytic activities in basic media and in absence of phase-transfer agent are observed. The NHC-based catalysts contain a hydrophilic functionality allowing a homogeneously catalyzed hydrogenation reaction in water.

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