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Immobilization of a Rhodium Carbene Complex to an Amphiphilic Block Copolymer for Hydroformylation of 1-Octene under Aqueous Two-Phase Conditions

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Summary: We present the first synthesis of an N-heterocyclic carbene (NHC) rhodium catalyst immobilized to an amphiphilic, water-soluble block copolymer support. The resulting macroligand was applied in the hydroformylation of 1-octene under aqueous two-phase conditions in four consecutive cycles and showed high activity up to 2360 h^{-1} (TOF).

The development of water-soluble catalysts compatible and stable in aqueous media for any given organic reaction is becoming an important research topic due to the advantages of environmentally benign process conditions and easy product/catalyst separation.[1]

In the past decade, metal complexes of *N-heterocyclic carbenes* (NHC) have been reported as a class of moisture- and air-stable catalysts with remarkable activity in C−C coupling reactions and have also been proposed to be valuable catalysts for hydroformylation reactions.[2] The stronger metal−carbon bond of these ligands compared to the bonding of the conventional phosphine ligands used reduces the dissociation from the metal center even at elevated temperatures, making NHC complexes ideal candidates for hydroformylation reactions. In addition, air stability would simplify catalyst handling drastically. This idea has been supported by a recent NMR study suggesting the stability of an NHC/rhodium catalyst under typical hydroformylation conditions.[3] Although in the past many rhodium carbene complexes have been described in the literature,[4] only a few reports have been presented so far on the application of such complexes as hydroformylation catalysts.[3,5,6] The results indicate low activities with TOF numbers of 3−8 h^{-1} and up to 30 h^{-1} in the case of homogeneous styrene transformation.[3,5] Biphasic hydroformylation has only been reported for 1-propene as substrate with moderate activities (TOF < 460 h^{-1}), whereas similar experiments with long-chain alkenes and recycling experiments have not been presented at all.[6]

In the present work, we wish to report our results on the first successful immobilization of an N-heterocyclic carbene (NHC)/rhodium catalyst to a water-soluble, amphiphilic block copolymer. The resulting polymeric macroligand was applied in four consecutive cycles in the aqueous two-phase hydroformylation of 1-octene, showing activities of up to 2360 h^{-1}.

We decided to synthesize the unsymmmetric, monohydroxy-functionalized rhodium NHC complex bromo-(η^4-1,5-cyclooctadiene)[1-(2′-hydroxyethyl)-3-methylimidazoline-2-ylidene]rhodium (**2**), featuring one hydroxy group for subsequent coupling to the block copolymer in order to avoid cross-linking during catalyst immobilization. The synthesis of the nonsymmetric catalyst involved a two-step approach. Refluxing *N*-methylimidazole with 2-bromoethanol in THF overnight afforded the precursor 1-(2′-hydroxyethyl)-3-methylimidazolium bromide (**1**) in 74% yield. The presence of the hydroxyethyl group was confirmed by the peaks at δ 3.70 and 4.21 ppm, corresponding to the methylene groups in ^{1}H NMR spectra. The imidazolium salt **1** was subsequently converted to the rhodium carbene complex **2** according to a general method described elsewhere (see Scheme 1).[7]

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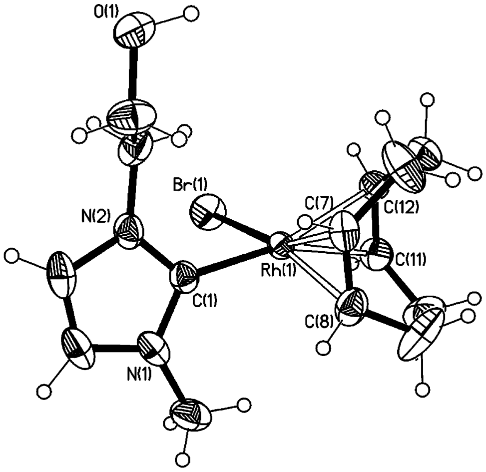
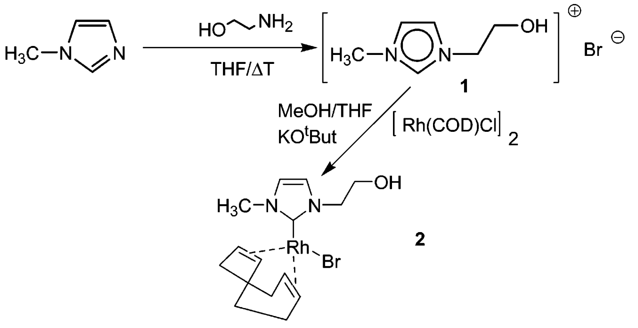


Figure 1. Crystal structure of **2**.

Scheme 1. Synthesis of the NHC Rhodium Complex 2



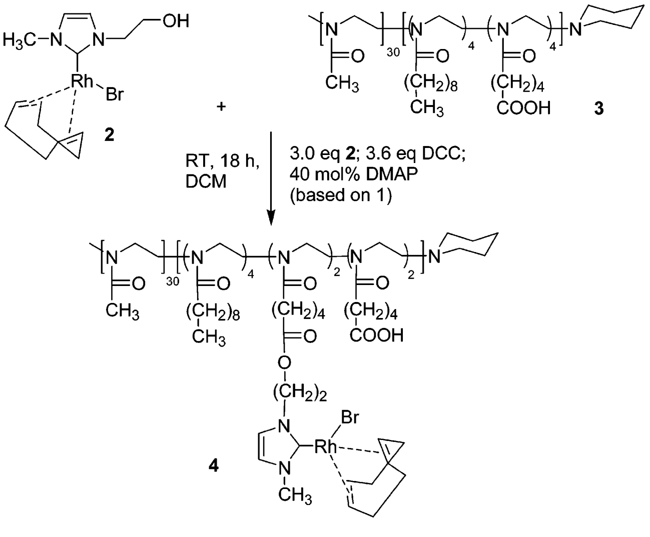
The crystal structure of **2** was established by X-ray crystallography (see Figure 1 and the Supporting Information), indicating also that there is no interaction of the free hydroxy group with the rhodium center.

Table 1. Analytical Results of the Hydroformylation of 1-Octene[a]

cycle	yield/%[b]	TOF/h^{-1} [c]	n:iso
1	22.0	1100	72:28
2	34.7	1790	66:34
3	43.7	2320	55:45
4	43.2	2360	57:43

[a] Reaction conditions: $T = 100$ °C, H_2:CO = 1:1 at 50 bar of gas pressure; TOF values determined after 2 h reaction time; 17.9 mg of **4** in 50 mL of distilled water; pH 6.0; 8.1 g of 1-octene (substrate:catalyst = 10 000:1). [b] *n*-Aldehyde + $\sum$(iso-aldehyde); isomerization also occurred. [c] Based on the amount of aldehydes formed and taking into account 2.7% rhodium loss on average per cycle on the basis of ^{1}H NMR data due to hydrolysis of the bound ester.

Scheme 2. Synthesis of the Water-Soluble, Amphiphilic Macroligand 4



Compound **2** was then examined in the homogeneous hydroformylation of 1-octene in benzene as solvent at 100 °C and 50 bar of pressure (CO:H_2 = 1:1) with a catalyst to substrate ratio of 1:10 000. After 2 h of reaction time, turnover frequencies (TOF) of 2400 h^{-1} were achieved with an n:iso selectivity of of 40:60 (0.67), indicating the highest activities for NHC/rhodium catalyst ever reported in hydroformylation reactions but with moderate selectivities. It should be noted here that the later results obtained with the polymer-bound catalyst **4** (see Table 1) show that even 2 h of reaction time is not sufficient to fully activate the catalyst; therefore, even higher activities can be expected for **2**. In view of these encouraging results, we were eager to use the catalyst in an aqueous two-phase system with the option of efficient and simple catalyst recycling. In the literature only one example of NHC catalyst immobilization to polymer supports is known, where the catalyst is immobilized to cross-linked polystyrene for the Heck reaction in organic solvents.[8] Due to the requirement of applying **2** under aqueous two-phase conditions, we decided to covalently link the catalyst to the amphiphilic polymer support **3** to gain access to a water-soluble polymer-catalyst system, which would at the same time accelerate the reaction rates for highly hydrophobic substrates due to the amphiphilic nature of the polymer. The choice of the poly(2-oxazolines) as the polymer support system was guided by several considerations. (i) The polymer is synthesized by a living cationic polymerization, thus allowing excellent control over polymer architecture, composition, and functionality. (ii) Amphiphilic polymers can be prepared by the use of water-soluble and hydrophobic monomers. (iii) More recently, the introduction of pendant carboxylic acid groups allowed versatile post-analogous modification of the resulting polymer.[9] (iv) Due to the polar amide backbone, these polymers remain quantitatively in the aqueous phase under aqueous two-phase conditions, since 1-octene behaves as a precipitant. By using the polymeric precursor **3** described in a recent publication,[9] the coupling reaction was performed in dichlororomethane by using 3 equiv of **2** for four −COOH groups in the polymer (see Scheme 2).

Successful catalyst immobilization to the polymer was monitored by ^{1}H NMR analysis of the purified product, showing typical signals between 4.4 and 4.9 ppm for the methylene groups linking catalyst **2** to the polymer (see Figure 2), and by GPC, indicating an increased molar mass from 3960 g/mol for **3** and to 4190 g/mol for **4** with polydispersities of 1.29 and 1.25, respectively.

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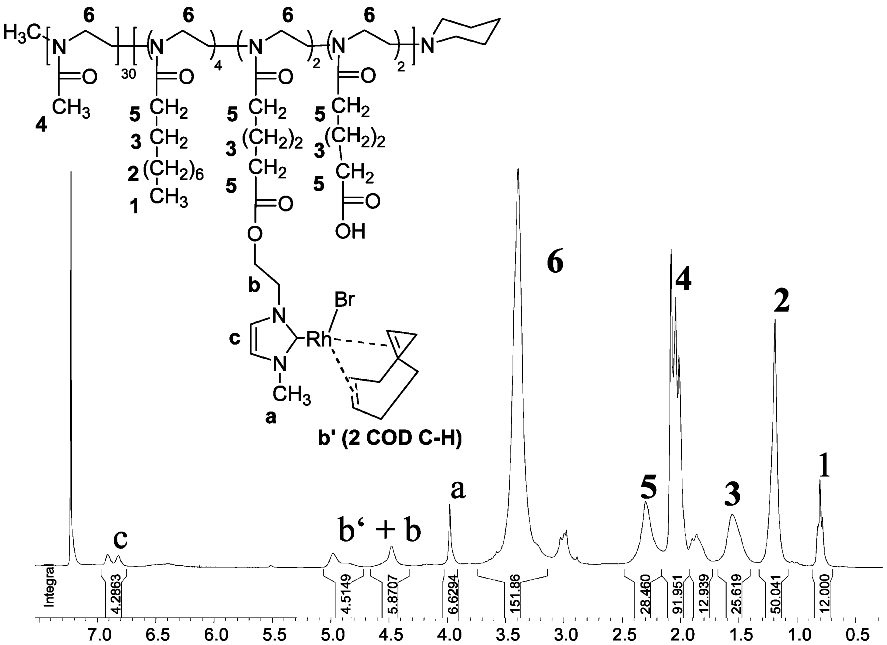

Figure 2. ^1H NMR of macroligand **4** in $CDCl_3$.

Quantitative analysis of the macroligand **4** by ^1H NMR and elemental analysis indicated that on average two rhodium/NHC complex molecules were bound to one polymer chain. On the basis of the work of Malmstroem and Andersson,[10] who described the successful application of poly(acrylic acid) as a water-soluble support for rhodium catalysts, we assumed that the free carboxylic acid groups would not interfere with the NHC/rhodium catalyst in polymer **4**.

The water-soluble polymer **4** was then used in the aqueous two-phase hydroformylation reaction of 1-octene at $T = 100$ °C and 50 bar of gas pressure ($CO{:}H_2 = 1{:}1$) without any additional solvent. A minimal amount of 17.9 mg of **4** was employed in 50 mL of degassed water and 8.1 g of 1-octene as the substrate phase (catalyst: substrate = 1:10 000). The reaction time for each cycle was 2 h. In the first cycle, TOF numbers of 1100 h^{-1} were found, which is roughly 50% below the value found for the homogeneous hydroformylation of **2** in benzene. After the reaction was finished, instantaneous phase separation occurred. The aqueous catalyst phase was red, whereas the organic phase composed of aldehydes and substrate was completely colorless, indicating excellent phase separation due to the low amount of polymeric macroligand used. This demonstrates also the beneficial effect of the amphiphilic macroligand **4** over traditional solutions to increase substrate solubility in water, such as the addition of surfactants[11] or the use of amphiphilic ligands[12] leading to high turnover numbers, but also difficulties in phase separation and catalyst recycling. Residual Rh content in the organic phase was determined by ICP-OES after the first cycle to be 0.4 ppm and fully supported the visual observation. Due to the insolubility of the polymer-bound catalyst **4** in 1-octene and the visual observation that **4** is solubilized only in the aqueous phase before and after the hydroformylation experiment, it can be concluded that the reaction only occurs in the aqueous phase and is not the result of any leaching.

Another interesting effect is the change in n:iso selectivity from 0.67 in benzene to 2.6 after the first cycle, indicating a pronounced change in the microenvironment of the catalytically active Rh center, when covalently bound to the amphiphilic block copolymer. The organic phase was separated by decantation, and fresh 1-octene was again added to the aqueous catalyst phase for the next cycle. By doing so, four cycles have been performed using the same catalyst solution until TOF numbers and selectivity remained constant. TOF numbers increased from the first cycle to the third one and remained around 2320−2360 h^{-1} in the third and fourth cycles. At the same time, n:iso selectivities changed from 2.6 in the first cycle to 1.22 in the third cycle and stayed almost constant at this value (see Table 1).

The somewhat higher activities observed in cycles 3 and 4 can be explained by the inhibiting effect of the halide, which is also a well-known phenomena for the Wilkinson catalyst $Rh(I)Cl(PPh_3)_3$.[13] In analogy to the Wilkinson catalyst, the active intermediate is presumably $(NHC)Rh(I)(CO)_2H$; thus, the halogen needs to be replaced by the hydride via oxidative addition of hydrogen and reductive elimination of hydrogen bromide (see Scheme 3). This mechanism of catalyst activation in the presence of CO and H_2 has also been proposed for other

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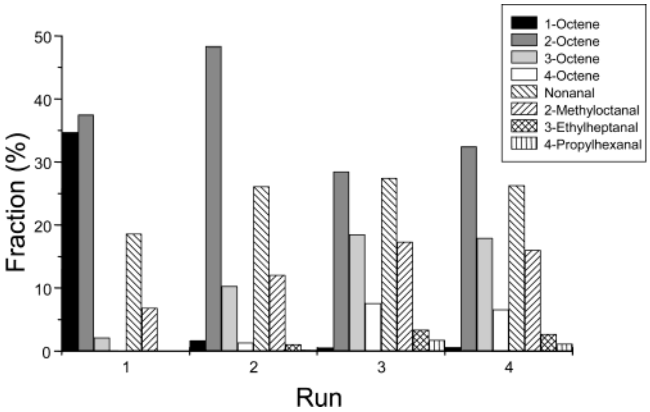
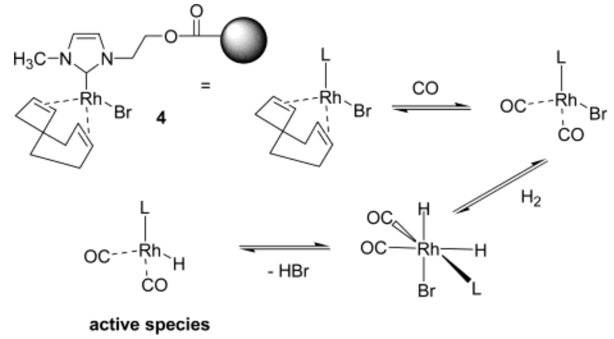


Figure 3. Fractions of each isomerization and hydroformylation product after runs 1−4, as determined by gas chromatography.

Scheme 3. Tentative Mechanism of Catalyst Activation



halogenated $Rh^{I}L(COD)Cl$ catalysts and is thus in excellent agreement with the literature.[14]

According to the results shown in Table 1, the polymer-bound catalyst needs roughly 4 h to be fully active and, in cycles 3 and 4, no difference is observed with respect to activity and selectivity. Important to note here is the minimal loss in activity on comparing the homogeneous catalysis reaction and the aqueous two-phase reaction in cycles 3 and 4, at 2400 and 2350 h^{-1}, respectively. Moreover, the microenvironment of the polymer-bound catalyst has a significant influence on selectivity and leads to an increase of n:iso from 0.66 to 1.22 (cycles 3 and 4) which corresponds to a doubling of the desired *n*-aldehyde in the presence of **4** with respect to the homogeneous catalyst **2**. A closer look at the product distribution after each cycle supports our assumption of catalyst activation during the first 3−4 h. As can be seen in Figure 3 after 2 h reaction time, part of the 1-octene has been isomerized to 2-octene, but a large amount of 1-octene remains unreacted after 2 h; accordingly, only 1-nonanal and 2-methyloctanal were formed as hydroformylation products. After the second run, 1-octene is almost completely converted to 2-octene and 3-octene, leading also to a higher amount of iso-aldehydes during cycle 2 and thus a decreasing n:iso ratio compared to the first cycle. In runs 3 and 4 significant changes can no longer be observed (see Figure 3).

The ester linkage of the catalyst to the polymer, however, remains a crucial parameter of macroligand **4**, especially for application of such polymer-bound catalysts in repetitive hydroformylation cycles, even if almost no rhodium loss has been detected after 2 h in the organic phase. With the aim to study long-term stability of the polymer-bound catalyst, we conducted a hydroformylation experiment for 18 h under the same reaction conditions used in cycle 1 and analyzed the polymer-bound catalyst **4** afterward by ^{1}H NMR (data not shown here). The spectrum revealed about 25% hydrolysis of the ester bond, which was surprisingly low compared to the harsh reaction conditions but confirmed our doubts. Assuming constant hydrolysis, this would correspond to 2.7% rhodium loss after each reaction cycle of 2 h in Table 1. To circumvent this problem in the future, catalyst attachment to the polymer backbone via amide linkages should be contemplated.

In summary, we have demonstrated the first successful application of a rhodium carbene complex bound to an amphiphilic polymer in the aqueous two-phase hydroformylation of 1-octene as substrate in four consecutive cycles. Activities with TOF numbers up to 2360 h^{-1} were observed, with the advantage that the polymer-bound catalyst can be handled in air and no ligand excess was needed. Most importantly, the organic phase could be easily removed by simple decantation after each cycle and fresh 1-octene could be added, allowing an approach for long-chain alkenes similar to that used in the Rhône-Poulenc Process for propene. In view of the promising results, it is expected that this approach of an amphiphilic macroligand can provide tremendous opportunities for aqueous two-phase catalysis reactions. Further studies will focus on the variation of the ligand sphere of the NHC/rhodium catalyst to get better insights in structure/activity and selectivity relationships and on the variation of different reaction parameters, such as pH value, pressure, and temperature, which are known to have an important influence on catalyst activity and selectivity.[15]

Supporting Information Available: Text giving experimental details and characterization data for the compounds prepared in this paper and a CIF file giving X-ray data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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