Synthesis, spectroscopic and catalytic properties of cationic Rh(I) complexes bound to phosphine functionalized water-soluble polymers

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Abstract

Coupling of phosphine moieties to water-soluble polymers yields macromolecular ligands, L = PAA-PNH (phosphinated polyacrylic acid) and PEI-PNH (phosphinated polyethyleneimine) which are water-soluble at basic and acidic pH values, respectively. Preparation of and spectroscopic characterization (^{31}P-NMR) of [(NBD)RhL$_2$]$^+$ complexes 1 (L = PAA-PNH) and 2 (L = PEI-PNH) demonstrate the complex forming properties of the ligands. Reaction of 1 and 2 with H$_2$ results in the formation of a solvato complex [RhL$_2$S$_2$]$^+$ (S = H$_2$O) for 1, whereas 2 gives a mixture of [RhL$_2$S$_2$]$^+$ and [RhL$_2$(H)$_2$]$^+$, and this difference is an effect of pH. Hydrogenations using water-miscible (acrylic acid, 4-propenoic acid, and 1-buten-4-ol) and water-insoluble (1-hexen) olefins as substrate using 1 and 2 as catalyst precursors demonstrate inhibiting interaction of the acrylate anion while 1-buten-4-ol give normal first order kinetics in olefin. 1-hexene requires addition of surfactants (anionic as SDS in the case of 1 and cationic as DTA or non-charged as Tween 80 in the case of 2) because of slow diffusion of into the water-phase.

Keywords: Water-soluble; Phosphine; Polymers; Rhodium complexes; Hydrogenation; Amphiphile

1. Introduction

Research and applications in the field of catalysis in water or in biphasic media have recently undergone a rapid development [1]. The main motive for carrying out catalysis in bi-phasic media is related to separational and recycling advantages [2] although cost and environmental benefits of water as a solvent is also worth considering [3]. The first generation [4] of

water-soluble transition metal phosphine complexes were prepared using monosulphonated triphenylphosphine (TPPMS) as the ligand [5]. The syntheses of trisulfonated triphenyl phosphine [2,6], which has become the prototype ligand in the field, have contributed substancially in the development [7] and both the number and the degree of sophistication of newly synthesised water-soluble phosphine ligands are constantly increasing. The most straight-forward method to achieve water-solubility is by introducing charged or polar substituents on parent phosphine ligands [8]; however, other methods

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have also been published [9]. By coupling of phosphine moieties to water-soluble polymers yet another entry into the field was recently demonstrated [10]. This methodology has certain advantages: Solubility can be attained over a very broad pH range by a proper selection of the polymers. The coupling procedure is relatively easy, thus enabling the conversion of a broad spectrum of aldehyde or amine functionalised parent phosphine ligands to their water-soluble counterparts. Depending on the particular application in mind, there is the possibility to bring beneficial polymer properties other than water-solubility into the concept, which is the ability of polymers to form ordered structures like micelles. The high mass to phosphine ratio is a drawback however, which might necessitate large reactor volumes in technical applications.

The questions we address in the present study are related to the chemical consequences of the polymer backbone in such systems. What are the complex forming properties of macromolecules viz. phosphinated polyacrylic acid (PAA-PNH) and phosphinated polyethyleneimine (PEI-PNH)? How will the difference in pH (PAA-PNH is basic in its soluble sodium salt form, whereas PEI-PNH is acidic in its soluble ammonium form) affect the complex formation and the catalytic performance complexes based on these polymers? Cationic Rh(I) complexes, for which both complex formation and catalysis are well-documented [8,11], were selected as model substances in this study with the aim of comparing the water-soluble PAA-PNH and PEI-PNH based ligands with their organo-soluble triphenylphosphine counterpart.

2. Results and discussion

2.1. Syntheses, characterization and reactivity of the complexes

Substitution of one of the norbornadiene ligands in the precursor complex $[Rh(NBD)_2]^+$ $[CH_3SO_3]^-$ with the phosphine groups of PAA-

PNH or PEI-PNH in a bi-phasic solvent system (H_2O/CH_2Cl_2) proceeds smoothly. Immediately after mixing the water-phase turns orange, indicating fast phase-transfer and substitution. The complexes are straightforwardly isolated by phase-separation and evaporation of the aqueous phase. In principle the choice of non-coordinating anion in the precursor is arbitrary, but methane sulphonate was selected in order not to involve yet another type of anion beside the one already present in the PEI-PNH ligand. When isolated and dry, the ligands contain varying amounts of water (in the order of 15–20%), thus neither the ligands as such nor the complexes give an elemental analysis which can be used to deduce their exact composition. A stoichiometric ratio $Rh/P = 1:2$ was applied in the syntheses and this ratio is also the exact ratio found by an elemental analysis of 1, while for 2 a ratio of 1:2.7 was found despite the fact that no free phosphine is observed by NMR. The phosphine groups on both polymers are relatively separate (average one phosphine per five acrylate units in PAA-PNH; one phosphine per seven ethylenimine units in PEI-PNH) and at low ionic strength the polymers are of a rod-like elongated shape [12]. Thus, the 1:2 stoichiometry of the complexes, which is indicated by the elemental analysis and ^{31}P-NMR (vide infra), implies that the complex formation induces chain-coiling or inter-chain binding.

The ^{1}H-NMR of the complexes recorded in D_2O are of low diagnostic value, peaks originating from the water which is present in the complexes after isolation and drying as well as those due to the polymer-back-bone make these spectra hard to rationalize. Despite a substantial line broadening (vide infra) the ^{31}P spectra are however easier to interpret. For both complexes a doublet is observed at 29.5 ppm, $J_{Rh-P} = 155$ Hz and at 29.5, $J_{Rh-P} = 156$ Hz for 1 and 2, respectively, which are in exellent agreement with that earlier observed for the triphenylphosphine [8]a and the TPPTS [13] analogues. The good agreement in the observed shifts of complex 1 and the TPPTS complex on the one hand

and complex **2** on the other is worth nothing; the pH of the solution in these cases differs widely yet the shift remains constant. A slight tendency for formation of phosphine oxide (less than 5%) is also evident from the ^{31}P spectra. No oxide peaks are present in the pure ligands so this oxidation occurs during the syntheses and work up of the complexes, despite working under inert conditions. The observed formation of phosphine oxide points to another drawback of the systems; once the phosphineoxide is formed this is an integrated part of the polymer which can not be separated.

The similarity in chemical reactivity between triphenyl phosphine and the water-soluble ligands of the present study is also demonstrated by bridge splitting of the dimer [(NBD)RhCl]$_2$. Using triphenylphosphine in dichloromethane solution or the PEI-PNH ligand in water/dichloromethane to initiate the splitting leads to analogous products viz. (NBD)RhClL (L = PPh$_3$; ^{31}P = 31.6 ppm (d), J_{Rh-P} = 171 Hz and L = PEI-PNH; ^{31}P = 31.6 ppm (d), J_{Rh-P} = 168 Hz, respectively).

2.1.1. Reactions with dihydrogen

The reaction of cationic [(NBD)RhL$_2$]$^+$ complexes with dihydrogen to form hydrido complexes is well-documented for a large number of different phosphines [14,11]. For some phosphines the resulting hydrido-complex is stable enough to be isolated, others can only be identified by spectroscopic methods. To disclose any differences or similarities implied by the solvent, the pH or by the polymeric nature

of our ligands both complexes **1** and **2** were reacted with dihydrogen using the triphenylphosphine and the TPPTS analogues as reference compounds. Attempts to isolate hydrido complexes were discouraging; the complexes are very difficult to precipitate from the water-solution by addition of non-aqueous solvents and evaporation leads to loss of dihydrogen. Identification of the complexes formed are therefore based on comparison of observed ^{31}P-NMR shifts and couplings with that of the reference compounds (Table 1).

Generally, the peaks in the ^{31}P spectra of complexes based on the polymeric ligands are very broad, substantially more so for the PAA-PNH ligand. This line broadening hampers the extraction of coupling constants from the spectra and the small P-H coupling is lost for both polymeric ligands. In the PAA-PNH case not even the larger Rh-P coupling constants can be obtained. The assignments in Table 1 are therefore mainly based on a comparison of chemical shifts with the reference compounds. The outcome of such a comparison is clearcut for those species having analogues in the case of the ligands triphenylphosphine or TPPTS. In the case of the polymeric ligands, an additional specie giving a resonance at around 50 ppm is present. This has a number of uniqe features; it is only observed for the polymeric ligands and the corresponding line is considerably broader than any other lines observed. Moreover, since it is observed for both polymers its presence is neither pH nor cation/anion dependent. The lack of any analogue in the non-polymer cases

Table 1
^{31}P-NMR data for the products formed by reacting [(NBD)RhL$_2$]$^+$ with H$_2$

| | | Assignement | | | | |
| | | RhL$_2$S$_2$ | | RhL$_2$H$_2$ | | Unknown |
L =	S =	shift (ppm)	J_{Rh-P}(Hz)	shift (ppm)	J_{Rh-P}(Hz)	shift (ppm)
PPh$_3$ [#]	MeOH	57.2 (d)	207	41.8 (d)	121	–
TPPTS	D$_2$O	59.1 (d)	196	44.7 (d)	122	–
PAA-PNH	D$_2$O	60.0 (br)	–	–	–	52.0
PEI-PNH	D$_2$O	56.6 (d)	201	41.7 (d)	106	49.2

[#] Ref. [8]a.

and any distiguishable coupling pattern has led us to refrain from speculation as to its constitution.

The stability of the dihydride complex is pH dependent. In the basic PAA-PNH ligand system no dihydride is observed but for the less basic TPPTS ligand as well as for the acidic PEI-PNH ligand system the dihydride is stable. Besides pH, the distribution between the solvato and the dihydride complex is goverened by the concentration of dihydrogen in the liquid phase and/or by competing complex formation. This is evident since attempts to isolate the dihydride by solvent evaporation lead to conversion to the solvato complex. It is also easily demonstrated in simple NMR-tube experiments for the PEI-PNH ligand system which gives sharper ^{31}P spectra. Lowering of the H_2 concentration by bubbling of CO to a solution containing an equilibrium mixture of $[L_2RhS_2]^+$ and $[L_2RhH_2]^+$ leads to formation of the dicarbonyl complex $[(CO)_2 RhL_2]^+$ (^{31}P-NMR: (d), 30.6 ppm, $J_{Rh-P} = 115$ Hz) which by subsequent bubbling of N_2 transforms to the monocarbonyl $[(CO)RhL_2S]^+$ (^{31}P-NMR: (d), 30.4 ppm, $J_{Rh-P} = 121$ Hz). The monocarbonyl can be isolated by evaporation of the solvent and the yellow powder so obtained shows a CO stretching vibration at 1978 cm^{-1} in accord with published data for the triphenylphosphine analogue [15]. Similarly, addition of excess PEI-PNH to an equilibrium mixture $[L_2RhS_2]^+$ and $[L_2RhH_2]^+$ leads to the formation of a trisphosphine complex $[L_3RhS]^+$ showing two peaks in a 2:1 ratio (^{31}P-NMR: (d), 34.0 ppm, $J_{Rh-P} = 84$ Hz and 52.0 ppm broad). The formation of this trisphosphine complex is a noteworthy indicator of a high degree of conformational flexibility of the PEI-polymer.

2.1.2. NMR features

The ^{31}P-NMR line-broadening observed for both polymer-based systems indicate some kind of dynamic process. Generally, it is most pronounced for the PAA-PNH ligand but not at all observed for the non-polymer systems thus its

origin is worth considering: The carboxylate groups incorporated in the PAA-PNH ligand were previously found [13] to be non-innocent with respect to complex binding to another Rh(I) centre. An exchange between free and bound carboxylates might therefore contribute to the line broadening also in the present case. This possibility can, however, be ruled out, since addition of acetate (up to 0.5 M) does not change the line-width of the ^{31}P-NMR spectra of the $(TPPTS)_2Rh(NBD)$ complex. There is also no reason to believe that the polymer based ligands should alter the chemistry of the rhodium to phosphorus bond making this more labile. The observed increase in the ^{31}P-NMR linewidths are therefore probably best ascribed to chemical shift anisotropy (CAS) caused by slow motions of the entire polymer chain. In such case, the difference in linewidths between the PAA-PNH and the PEI-PNH ligand systems should reflect a difference in size and coiling of the two polymers. NMR experiments currently underway at a lower field strength will hopefully solve this issue.

Attempts to observe the hydride resonance of the hydrido complexes by ^{1}H-NMR were discouraging. This failure can in part be caused by the presence of water (although the NMR was run in D_2O a small amount of H_2O always accompanies the polymer based complexes). More importantly though, the CSA discussed above will, however, also affect the proton spectrum since both ^{31}P and ^{103}Rh are CSA-sensitive nuclei which are coupled to the proton.

2.2. Catalysis

The polymer based ligands PAA-PNH and PEI-PNH are neither markedly different from the reference ligands with respect to formation of cationic Rh(I) bisphosphine complexes nor do these complexes react differently with H_2 and CO. However, the catalytic testing of the complexes is the most interesting object of this study. This evaluation of catalytic performance was carried out by hydrogenation of water soluble as well as water insoluble olefins.

2.2.1. Stability of the catalysts

Generally, under an atmosphere of dihydrogen, the RhL_2^+ (L = phosphine) class of complexes show a slight tendency to be reduced to the metallic state if the rhodium to phosphine ratio in the system exceeds 0.5. This is the main cause for the stability problems encountered in attempts to immobilise such complexes on solid supports [16]. The observed tendency for formation of phosphine oxide on the PAA-PNH and PEI-PNH polymers will decrease the phosphine concentration, hence Rh/phosphine becomes > 0.5, which in its turn will make the catalysts susceptible to reduction to Rh(s). This reaction sequence is also verified for complex 1 and 2; when the hydrogenations were carried out with strict exclusion of oxygen from the system, neither phosphine oxide nor Rh(s) were formed in detectable amounts. On the other hand, the unintentional presence of trace amounts of oxygen led to the formation of phosphine oxide (^{31}P-NMR) concomitant with clear signs of Rh(s) at the end of the reaction, i.e., when the concentration of olefin becomes low. Thus, being a π-acceptor the olefin can partly fulfill the stabilizing role of the phosphine ligand which is lost by oxidation. The main problem relating to formation of small amounts of Rh(s) in the system concerns detection. Rh(s) in the form of colloidal particles is a very active hydrogenation catalyst; moreover, the color of such particles can vary considerably to reach that of bulk metal when the particles become big. For all hydrogenation experiments carried out, careful visual color examinations were done. In those cases were the color deviated from the normal orange-yellow color, the influence of the selective poison cyclooctatetraene on the catalytic reaction was also studied. All those experiments accounted for in the following are therefore considered truly homogeneous catalysis.

2.2.2. Water-soluble olefins

For catalyst 2 the hydrogenation of acrylic acid proceeds smoothly (Fig. 1). The course of the reaction deviates from the normally ob-
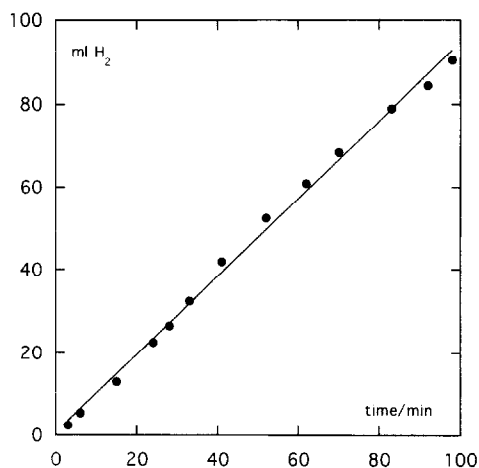

Fig. 1. Hydrogenation of acrylic acid at $T = 25°C$ and $P = 1$ atm. using 2 as a catalyst. Conditions: 0.0235 mmol Rh, 2.35 mmol olefin, [Rh] = 4.7 mM.

served first-order dependence in olefin, i.e., the kinetic trace is linear up to 100% conversion. Such behaviour indicates strong complex-binding between the olefin and the catalyst, thereby moving the rate-determining step from coordination of the olefin to some other later step in the catalytic cycle (hydrogen activation/transfer or reductive elimination). For catalyst 1 the situation is quite different in that addition of acrylic acid precipitates the catalysts leading to a completely inactive system. Catalyst 1 is only soluble below pH ≈ 7 and the precipitation is caused by the change in pH which the acid brings about. The observed difference in behaviour of catalysts 1 and 2 underlines the advantage of being able to cover a wide pH range. Using the anion of the acid should in priciple solve the pH-related solubility problem encountered with acrylic acid. Attempts to apply this methodology were, however, unsuccessful, giving no measurable catalytic activity. Strong bonding of the substrate as π-olefin, $\sigma-O^-$ chelate can inhibit further reactions at the metal-center. This is one possible explanation for the lack of activity which can be tested rather easily using a substrate in which the olefinic bond and the carboxylate oxygens are moved further apart. The kinetic traces (Fig. 2)

of such experiments using 4-propenoic acid or its sodium salt as substrates are clear-cut evidence for the importance of strong substrate metal interaction in the case of acrylic acid. Both catalysts are active, using 4-pentenoic acid as the substrate, catalyst **2** being the superior one. The zero-order dependence in olefin observed in the case of catalyst **2** and acrylic acid is no longer valid, the rate decreases as the olefin is consumed. Moreover, after reacting a water solution of **2** with H_2 and acrylic acid, the ^{31}P-NMR spectrum shows two doublets at 52.8 ppm, $J_{Rh-P} = 178$ Hz and at 22.2ppm, $J_{Rh-P} = 158$ Hz which can be assigned to the acrylic acid complex [17]. The kinetic traces for 1-buten-4-ol, which was selected as a substrate to allow a comparision of substituent effects, are shown in Fig. 3. Compared to pentenoic acid/pentenoate (Fig. 2) there is a substancial increase in rate for catalyst **1**, while the activity of catalyst **2** is not much influenced by the change in substrate. This can be taken as an indication that even in the case of 4-propenoate there is inhibitory interaction between the carboxylate group and the metal center. Because of the rather low water-solubility of 1-buten-4-ol, the kinetics might also be partly governed by the rate by which the substrates diffuses into the
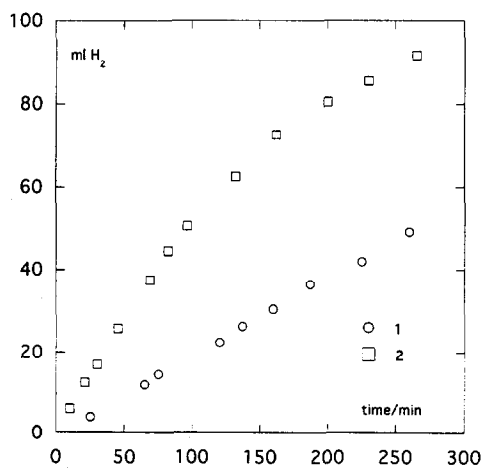

Fig. 3. Hydrogenation of 1-buten-4-ol at $T = 25°C$, $P = 1$ atm. using **1** and **2** as catalysts. Conditions: Catalyst **1**: 0.031 mmol Rh, 4.5 mmol olefin, [Rh]= 10.3 mM. Catalyst **2**: 0.0165 mmol Rh, 3.40 mmol olefin, [Rh]= 6.86 mM,

aqueous phase therefore no definite conclusions can be drawn.

2.2.3. Water-insoluble olefins

Biphasic catalysis is an interesting objective from the separational point of view. For a water-soluble catalyst this methodology implics that both the substate and the product have a low solubility in the aqueous phase. Using 1-hexene as a water-insoluble substrate, the activity of both catalysts **1** and **2** is very low indeed with no measurable consumption of hydrogen over a period of 2 h. Since similar results have been observed previously [18], using other non-polymer based catalysts in biphasic hydroformy-lations and the low rate is merely an reflection of diffusion limitations. On the other hand, in cases where the catalysts decompose to give Rh(s), high rates of reaction have been observed in biphasic hydrogenations of water-insoluble substrates [19] The reason in this case being that the active catalysts, Rh(s), is not confined to the aqueous phase but instead distributed over the phase boundary. The negligible reaction rate observed in the present study is thus further evidence for the stability of catalysts **1** and **2**.

Previous studies [20] have shown that surface active phosphines giving aggregates or micelles

Fig. 2. Hydrogenation of 4-propenoic acid at $T = 25°C$, $P = 1$ atm. using complex **1** and **2** as catalysts. Conditions: Catalyst **1**: 0.0258 mmol Rh, 2.60 mmol olefin, [Rh]= 4.30 mM. Catalyst **2**: 0.0225 mmol Rh, 2.25 mmol olefin, [Rh]= 5.64 mM.

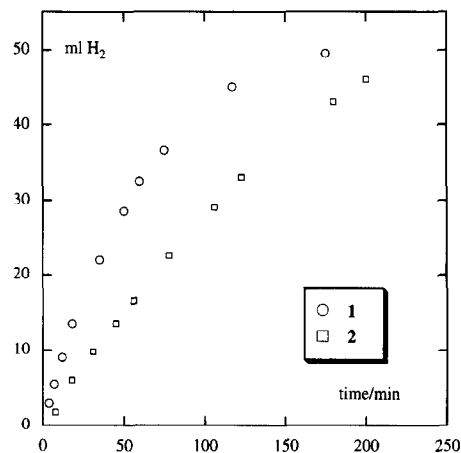lead to a rate-enhancement. Since no activity whatsoever is found for **1** and **2** it can be concluded that these systems do not facilitate phase transfer, despite their amphiphilic character. Brief attempts in the present study to monitor the surface active properties of the phophinated polymers using Orange OT as an indicator show that the concentration of polymers necessary for dissolution of the indicator in the water-phase is far beyond the catalyst concentration applicable in the experimental setup used in the hydrogenations.

Further experiments in 1-hexen hydrogenations were therefore carried out using external surfactants, the results of which are displayed in Fig. 4 Fig. 5. The importance of substrate-solubility is clearly demonstrated in these experiments; the activity of catalysts **1** at the critical micelle forming concentration (CMC = 8 mM) of SDS is very high and further addition of SDS does not improve the activity. The addition of SDS to the reaction mixture causes difficulties in judging the color of the solution and hence to certify that no Rh(s) is formed. However, additional experiments with added cyclooctatetraene (Fig. 4) show that the activity of the catalyst is almost completly lost in that case, hence that
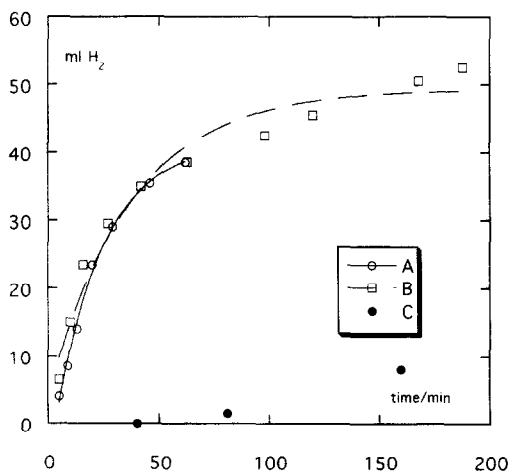

Fig. 5. Hydrogenation of 1-hexen at $T = 25°C$, $P = 1$ atm. using **2** as catalyst. Conditions: 0.019 mmol Rh, 2.39 mmol olefin, [Rh] = 4.7 mM (A) DTA (dodecyltrimethyl-ammoniumchloride) = 38 mM. (B) DTA = 60 mM. (C) Tween 80 (poly-oxyethylenesorbitan monooleate) 440 mg.

the active specie is a rhodium complex and not Rh(s).

SDS, a anionic surfactant, can not be used together with catalysts **2** because of electrostatic neutralisation. A number of different cationic surfactants were therefore tested with this catalyst but it has not been possible to match the activity of the catalyst **1** SDS couple with any combination of catalyst **2** and surfactants (DTA, Tween-80 or Brij-50). As evident from Fig. 5, there is an activity dependence with respect to the surfactant applied but probably not large enough to fully account for the difference in rate between **1** and **2**. Thus, inherent differences between catalysts **1** and **2** or effects related to pH differences are probably operating.

3. Experimental

All reactions were carried out under argon using degassed solvents. Solvents were of p.a. quality and used as received. $[Rh(NBD)_2]^+[CH_3SO_3]^-$ was prepared according to the literature [21]. NMR spectra were recorded on a Varian Unity 300 spectrometer.

Fig. 4. Hydrogenation of 1-hexen at $T = 25°C$, $P = 1$ atm. using **1** as catalyst. Conditions: (A) 0.0214 mmol Rh, 3.20 mmol olefin, [Rh] = 5.35 mM, SDS = 10 mM. (B) As in A but 30 mM SDS. (C) As in A but 0.34 mmol cyclooctatetraen added
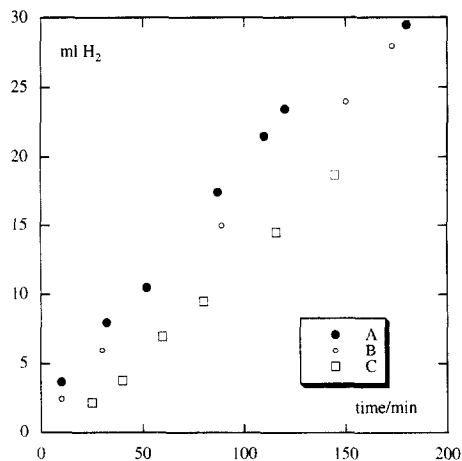
^{31}P resonances are given relative H$_3$PO$_4$ as external standard with positive values downfield at an observation frequency of 121,426 MHz. Elemental analyses were performed by AB Mikro Kemi, Uppsala Sweden.

3.1. Preparation of [(NBD)RhL$_2$]$^+$[CH$_3$SO$_3$]$^-$, L = PAA-PNH (1)

A Schlenk tube with 8 ml degassed water was charged with 0.99 g PAA-PNH (1.02 mmol P) and stirred for 5 min. 0.21 g [Rh(NBD)$_2$]$^+$[CH$_3$SO$_3$]$^-$ (0.55 mmol) in 5 ml of CH$_2$Cl$_2$ was added and the solution was vigorously stirred for 1 h at room temperature.

The phases were separated and the aqueous phase washed twice with 5 ml portions of CH$_2$Cl$_2$. Evaporation of the water to dryness afforded 1.15 g of the product as an orange powder.

NMR: ^{31}P (D$_2$O); $\delta = 29.5$ (d). $J_{Rh-P} = 155$ Hz.

Elemental analysis. Found: N = 1.13%. P = 2.7%. Rh = 4.2%.

3.2. Preparation of [(NBD)RhL$_2$]$^+$[CH$_3$SO$_3$]$^-$, L = PEI-PNH (2)

Following the same procedure as for complex (1) using 1.0 g PEI-PNH (0.84 mmol P) and 0.16 g [Rh(NBD)$_2$]$^+$[CH$_3$SO$_3$]$^-$ (0.43 mmol) afforded 1.1 g of the product as an orange powder.

NMR: ^{31}P (D$_2$O); $\delta = 29.5$ (d). $J_{Rh-P} = 156$ Hz.

Elemental analysis: Found: P = 2.1%, Rh = 2.4%.

3.3. Preparation of [(NBD)RhClL], L = PEI-PNH

1.81 g PEI-PNH (1.52 mmol) and 0.347 g ((NBD)RhCl)$_2$ were dissolved in 8.0 ml of water and 4.0 ml of CH$_2$Cl$_2$, respectively. Stirring, phase separation, washing and evaporation as in

the case of catalyst 1 gave 2.1 g of the title compound as an orange powder.

NMR: ^{31}P (D$_2$O); $\delta = 31.9$ (d). $J_{Rh-P} = 168$ Hz.

3.4. In situ generation of [Rh(H)$_2$L$_2$)]$^+$ and [(Rh(OH$_2$)$_2$L$_2$)]$^+$, L = PAA-PNH or PEI-PNH

The parent [(NBD)RhL$_2$]$^+$ complex was dissolved in degassed water in a Schlenk tube. The tube was evacuated and refilled with H$_2$. The solution was stirred for 10 min after which it was transferred to an NMR tube and the spectra recorded.

4. Hydrogenations

A round bottomed flask equipped with a septa, magnetic stirring bar and a side arm containing the solvent (H$_2$O) was connected to a gas-burette and a Hg-leveling manometer via a vacuum-manifold. A weighed amount of the catalyst was added to the flask. The water in the side arm frozen out with liquid nitrogen and the apparatus purged with nitrogen in three separate freeze-thaw cycles. Finally, hydrogen was admitted, and after having reached room temperature the water was added by rotation of the side arm. After dissolution of the catalyst the appropiate volume of olefin was injected via the septa and the pressure adjusted to 1 atm. The gas consumption was monitored at 1 atm by the gas-burette. In cases where an amphiphile was used it was dissolved in the water prior to purging. In experiments using cyclooctatetraene as a catalysts poison, a 15-fold excess relative the amount of Rh was added together with the reacting olefin at the start of the reaction.

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