DALTON
FULL PAPER

pH Effects on reaction rates in rhodium catalysed hydrogenation in water

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Received 23rd March 1999, Accepted 17th June 1999

The compound [Rh(DPPBTS)(NBD)][O_3SCF_3] **1** (DPPBTS = tetrasulfonated 1,4-bis(diphenylphosphino)butane, NBD = norbornadiene) has been prepared. On reaction of **1** with H_2 different complexes [Rh(DPPBTS)$(H_2O)_3$(H)]$^{2+}$, [Rh(DPPBTS)$(H_2O)_2$]$^+$ or [Rh(DPPBTS)(OH)]$_2$ are formed depending on the pH of the aqueous solution. Addition of α-acetamidoacrylic acid (AAA) to an aqueous solution of [Rh(DPPBTS)$(H_2O)_2$]$^+$ affords a substrate complex in which the co-ordination mode of AAA is pH dependent, *i.e.* it co-ordinates *via* the double bond and the amide carbonyl at a pH below the pK_a of AAA, or *via* the double bond and the carboxylate group at a pH higher than the pK_a. The co-ordination mode has a dramatic effect on the rate of hydrogenation of AAA catalysed by **1**, being extremely fast at a pH below the pK_a of the substrate (270 000 mol h^{-1}), but approximately 2000 times slower at a pH higher than the pK_a. The hydrogenation rate is zero order in olefin concentration at pH 4.7 and a k_H/k_D isotope effect of 1.25 has been observed at pH 4.5. These observations indicate that the oxidative addition of H_2 is the rate determining step in the hydrogenation using **1** as a catalyst, and that the mechanism is the same in water as in organic solvents.

Introduction

Catalysis in water or under biphasic conditions are areas of homogeneous catalysis that have captured considerable attention during the last decade.[1] The synthesis of trisulfonated triphenylphosphine (TPPTS, triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt) and the subsequent development of the biphasic industrial process for hydroformylation of propene by Rhone-Poulenc/Ruhr-Chemie has triggered the synthesis of various water-soluble phosphines[2] and their complexes have been used in biphasic hydrogenations and hydroformylations.[3]

Rhodium catalysed enantioselective hydrogenations of enamide precursors using water-soluble chiral phosphines as ligands have been performed,[4] but the chiral induction in water is generally lower than that in neat organic solvents. Water has also been shown to give dramatic effects on the hydrogenation rate of maleic and fumaric acid using [RhCl(TPPMS)$_3$] (monosulfonated triphenylphosphine) as the catalyst.[5] In organic solvents, maleic acid (*cis* isomer) is hydrogenated faster but under specific conditions in water fumaric acid is hydrogenated faster. Rather little research has been focused on the underlying reasons for the differences in catalytic performance that are observed in changing from organic solvents to water. One of the few mechanistic studies, on the catalytic features of such systems in water, reports that the oxidative addition of H_2 to [Ir(CO)Cl(TPPMS)$_2$] (TPPMS = triphenylphosphine-3-sulfonic acid trisodium salt) proceeds much faster in water than in organic solvents.[6]

We have previously studied the enantioselective hydrogenation of prochiral olefins under biphasic conditions using (2*S*,4*S*)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine (PPM) bound to polyacrylic acid as ligand and noticed that the rate of hydrogenation was pH-dependent.[7] To gain further insight into the mechanism of these reactions we have used tetrasulfonated bis(diphenylphosphino)butane (DPPBTS) as a model ligand. In a similar manner to the PPM ligand, it forms a seven-membered chelate ring with rhodium. The present paper describes the hydrogenation of α-acetamidoacrylic acid, using cationic rhodium(I) complexes of the DPPBTS ligand at different pH values in water and proposes a mechanism that can account for the extremely high rates observed at low pH.

Experimental

General procedures and chemicals

All reactions were performed under an inert atmosphere using degassed solvents. Water was doubly distilled from quartz prior to use. 1,4-Bis(diphenylphosphino)butane, DPPB (Lancaster), and α-acetamidoacrylic acid (Acros) were used as received. Hydrogen (5.7 quality) and deuterium gas were purchased from AGA AB, Sweden; [Rh(NBD)$_2$][O_3SCF_3] was prepared according to the literature.[8] The NMR spectra were recorded on a Varian UNITY 300 spectrometer at observation frequencies of 299.79 (^{1}H) or 121.36 (^{31}P) MHz. Chemical shifts are given in ppm downfield from TMS (^{1}H) or H_3PO_4 (^{31}P) using residual solvent peaks and 85% H_3PO_4 as internal and external reference, respectively. The UV/Vis spectra were recorded on a Milton Roy 3000 Diode Array spectrophotometer. pH Measurements were performed using a glass electrode connected to a Metrohm 632 pH-meter. Using potentiometric titration with 0.100 M NaOH (Merck Titrisol) as titrator the pK_a value of α-acetamidoacrylic acid was determined to be 3.26.

Preparations

DPPBTS. Fuming H_2SO_4 (45 ml) was cooled to 0 °C under an inert atmosphere. The compound DPPB (3.5 g) was added slowly while the temperature was kept at 0 °C. The reaction mixture was stirred at this temperature for 54 h after which time the acid was neutralised with 25% NaOH to pH 10 while the temperature was kept below 5 °C. The solvent was evaporated, degassed MeOH (200 ml) was added and the so formed slurry was refluxed for 2 h under N_2. The Na_2SO_4 formed was filtered off and the filtrate evaporated. The evaporate was recrystallised from water–MeOH (1 : 10 v/v) giving 5.9 g (80%) of DPPBTS. NMR (D_2O): ^{31}P, δ −14.24 (s); ^{1}H, δ 1.44 (m, 4 H), 2.08 (m, 4 H), 7.40 (m, 8 H) and 7.72 (m, 8 H). Found: C, 36.2; H, 3.35; P,

6.7; S, 13.7. Calc. for $C_{28}H_{24}Na_4O_{12}P_2S_4 \cdot 4H_2O$: C, 37.1; H, 3.46; P, 6.80; S, 14.1% (S/P = 2.05).

[Rh(DPPBTS)(NBD)][O_3SCF_3] 1. A Schlenk tube containing water (3 ml) was charged with DPPBTS (100 mg, 0.11 mmol) and [$Rh(NBD)_2$][O_3SCF_3] (48 mg, 0.11 mmol). The solution was stirred for 1 h after which time the aqueous phase was washed once with CH_2Cl_2 (3 ml). The water solution was evaporated to dryness giving an orange powder (134 mg, 97%). NMR (D_2O): ^{31}P, δ 29.48 (d, J_{Rh-P} 149 Hz); ^1H, δ 1.46 (br, 2 H), 1.60 (m, 4 H), 2.55 (m, 4 H), 3.83 (br, 2 H), 4.51 (br, 4 H), 7.60 (m, 8 H) and 7.91 (m, 8 H).

[Rh(DPPB)(NBD)][O_3SCF_3] 2. The compound DPPB (100 mg, 0.234 mmol) was dissolved in CH_2Cl_2 (2.5 ml) and [$Rh(NBD)_2$][O_3SCF_3] (100 mg, 0.230 mmol) added. The solution was stirred for 30 min at room temperature and diethyl ether added. The precipitate which formed was filtered off and washed twice with diethyl ether. NMR ($CDCl_3$): ^{31}P, δ 27.90 (d, J_{Rh-P} 153 Hz); ^1H, δ 1.54 (br, 2 H), 1.68 (br, 4 H), 2.52 (br, 4 H), 3.95 (br, 2 H), 4.49 (br, 4 H) and 7.58 (m, 20 H).

Treatment of [Rh(DPPBTS)(NBD)][O_3SCF_3] 1 with H_2

An aqueous solution of compound **1** in carefully degassed D_2O was charged in a Schlenk tube under N_2 and the pH adjusted to the selected value with either Na_2CO_3 or CH_3SO_3H. An atmosphere of H_2 was introduced, the solution was stirred for 5 min whereafter it was transferred to an NMR tube *via* a syringe and a septum. ^{31}P NMR data are given in Table 1.

Hydrogenation of α-acetamidoacrylic acid (AAA)

In a typical experiment 27 mg (0.21 mmol) of the olefin were dissolved in 7.0 ml of degassed water. The calculated volume of a 4.36 mM stock solution of **1** was added. The pH was adjusted to the selected value and the hydrogenation started by bubbling H_2 through the solution for 5 min. After the hydrogenation N_2 was bubbled through for approximately 1 min. The solution was then evaporated to dryness and the yield of *N*-acetylalanine determined by ^1H NMR. ^1H NMR (D_2O): δ 1.28 (d, CH_3-CH), 1.89 (s, $CH_3C(O)N$) and 4.2 (q, CH_3CH). After D_2 reduction in water: δ (D_2O). δ 1.35 (br, DCH_2CD), 1.89 (s, $CH_3C(O)N$). After incorporation of H from water. δ 1.36 (d, DCH_2CH) and 4.13 (t, DCH_2CH).

Results

Synthesis

Reaction of DPPB with fuming sulfuric acid for 54 h at low temperature (<5 °C) gives tetrasulfonated DPPB (DPPBTS) in 80% yield. The crude product is easily recrystallised from MeOH–water (10 : 1 v/v) giving a product displaying only one resonance in its ^{31}P NMR spectrum at δ −14.2, and importantly no resonance of a phosphine oxide.

Reaction of DPPBTS with [$Rh(NBD)_2$][O_3SCF_3] in a 1 : 1 stoichiometry results in the substitution of one of the norbornadiene ligands and formation of the complex [Rh(DPPBTS)(NBD)][O_3SCF_3] **1**. Its ^{31}P NMR spectrum displays a doublet at δ 29.5 with a Rh–P coupling constant of 149 Hz. The identity of the complex is confirmed by its shift and coupling constant which are in good agreement with those of the corresponding $[Rh(DPPB)(L–L)]^+$ complex (L–L = cycloocta-1,5-diene or NBD).[9]

Reaction of complex 1 with H_2

Hydrogenation of $[Rh(L–L)(NBD)]^+$ complexes, where L–L is a bidentate phosphine, is expected to give norbornane and the bis(solvato) complex, $[Rh(L–L)(solv)_2]^+$; the bis(hydrido) complex formed upon reaction of $[Rh(L)_2(NBD)]^+$ with hydrogen can not be observed for bidentate phosphines.[10]

Table 1 ^{31}P NMR Data observed on treating compound **1** with H_2 at different pH value

pH	$\delta/(^1J_{Rh-P}/Hz)$	Assignment
1.5	45.9 (133)	**3** $[Rh(DPPBTS)(H_2O)_3(H)]^{2+}$
2.9	54.2 (195)	**4** $[Rh(DPPBTS)(H_2O)_2]^+$
4.2	54.2 (195)	**4** $[Rh(DPPBTS)(H_2O)_2]^+$
9.5	52.2 (185)	**5** $[Rh(DPPBTS)(OH)]_2$

The speciation as a function of pH in the solution can be followed by conducting the H_2 treatment at different pH values. At pH 2.9 and 4.2 the ^{31}P NMR spectra display doublets at δ 54.2 with coupling constants of 195 Hz. This is in good agreement with data for the DPPB analogue in methanol solution; the bis(methanol) complex $[Rh(DPPB)(MeOH)_2]^+$ gives a doublet at δ 53.6 with a J_{Rh-P} of 199 Hz.[9] The observed ^{31}P NMR resonance is consequently assigned to the bis(aqua) complex **4**, and the observation that no spectral change occurs in the pH range 2.9 to 4.2 implies that protolysis and formation of the hydroxo complex [Rh(DPPBTS)(H_2O)(OH)] does not occur to any observable extent below pH 4.2.

Increasing the pH further to 9.5 gives a slight change in the ^{31}P NMR spectrum revealing a doublet at δ 52.2 with a coupling constant of 185 Hz. We assign this resonance to the hydroxo bridged dimer $[Rh(DPPBTS)(OH)]_2$ **5**. This suggestion is in no way unprecedented; protolysis and formation of such dimers is a common feature in aqueous organometallic chemistry of the late transition metals.[11]

The ^{31}P NMR spectrum is dramatically different at pH 1.5, displaying a doublet at δ 45.9 with a coupling constant of 133 Hz. Hydrides of the late transition elements are generally acidic, and protonation of the solvato complex $[Rh(L–L)(MeOH)_2]^+$ (L–L = 1,2-bis(diphenylphosphino)ethane) giving $[Rh(L–L)(MeOH)_3(H)]^{2+}$ has previously been shown to occur at low pH.[10] The appearance of a single doublet in the ^{31}P NMR spectrum implies that the two phosphines are equivalent. Accordingly, we suggest that the complex [Rh(DPPBTS)-$(H_2O)_3(H)]^{2+}$ **3**, with an axial hydride, is formed at pH 1.5. All attempts to detect a hydride resonance by ^1H NMR however failed, probably due to a fast exchange with the solvent water. Consequently, no attempts to isolate the complex were made.

Reaction of $[Rh(L–L)(H_2O)_2]^+$ with enamides

Addition of α-acetamidoacrylic acid (AAA) to a solution of $[Rh(DPPBTS)(H_2O)_2]^+$ at pH 3 gives a doublet at δ 44.8 with a J_{Rh-P} of 166 Hz together with a broad resonance at δ 38.2 ppm (20%) in the ^{31}P NMR spectrum. The ^1H NMR spectrum exhibits, besides the resonances from the DPPBTS ligand, broad resonances at δ 5.45 (d) and 2.43 (s) indicative of an exchange process between free and co-ordinated olefin. The corresponding ^{31}P NMR spectrum at pH 9 reveals two doublet of doublets, one centred at δ 20.4 (J_{Rh-P} = 162 and J_{P-P} = 67 Hz) and one at δ 57.0 (J_{Rh-P} = 164 and J_{P-P} = 67 Hz). We suggest that the peak at δ 44.8 exhibited at pH 3 can be assigned to an AAA substrate complex, *i.e.* a chelate complex involving the double bond and the amide carbonyl group, which because of a fast exchange process only reveals the averaged resonance. We refrain from speculating on the origin of the broad resonance at δ 38.2. The substrate which has a pK_a of 3.26 is deprotonated at pH 9 and a chelate complex involving the double bond and the carboxylate anion is therefore formed at this pH. Since this complex has a lower olefin exchange rate both phosphines appear as separate resonances at pH 9.

The UV/Vis spectrum of compound **1** exhibits two absorptions at 330 and 470 nm. Following the ^{31}P NMR assignments, hydrogenation of **1** at pH 3 or 9 gives the bis(aqua) complex **4**

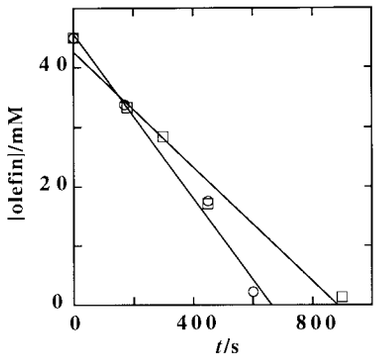


Fig. 1 Olefin concentration as a function of time for hydrogenation of AAA at pH 4.7 (○) and 9.4 (□).

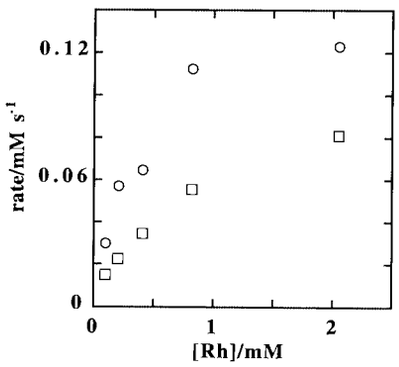


Fig. 2 Rate of hydrogenation of AAA as a function of rhodium concentration at pH 4.7 (○) and 9.4 (□).

or the hydroxo bridged dimer **5** which do not show any distinct absorptions below 315 nm, besides the strong bands from the ligand phenyl rings. Addition of 1 equivalent of AAA to **4** and **5** at pH 3 and 9, respectively, results in a slight but significant decrease in absorption between 340 and 450 nm. Addition of more olefin does not change the spectrum further. Surprisingly the increase of the absorption previously described for the chelate complexes of ethylacetamidocinnamic acid (EAC) with cationic rhodium(I) complexes of chiraphos [(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane] in methanol could not be observed.[12]

Addition of α-acetamidocinnamic acid (ACA) to a solution of compound **4** at pH 3 changes the UV/Vis spectrum giving a new very strong absorption below 320 nm and a similar decrease in absorption between 340 and 450 nm as noted upon addition of AAA.

The methanol complex $[Rh(DPPB)(MeOH)_2]^+$ can be used to test if the olefin co-ordination mode is changed with a change of solvent from methanol to water. Addition of methylacetamidocinnamic acid (MAC), which co-ordinates *via* the double bond and the amide carbonyl oxygen, to a solution of $[Rh(DPPB)(MeOH)_2]^+$ reveals a very strong absorption below 325 nm concomitant with a decrease in absorption above 340 nm. Additions of AAA and ACA give spectral changes which are almost identical to those observed before for complex **4** in water.

Although the UV/Vis study does not provide a clear-cut proof of the formation of an olefin complex, the similarities in spectral changes observed upon addition of olefins (AAA, ACA or MAC) to either $[Rh(DPPB)(MeOH)_2]^+$ or $[Rh(DPPBTS)(H_2O)_2]^+$ **4** implies that the bis(aqua) complex **4** undergoes solvent–olefin exchange in the same way as the bis(methanol) complex.

Catalysis

The hydrogenations of AAA were performed at different pH values in a homogeneous aqueous phase, continuously bubbling a stream of H_2 through the solution to ensure H_2 saturation of the solution throughout the reaction. Thus, measured rates of conversion are true rates unaffected by phase-transfer and gas-diffusion limitations.

The yield of *N*-acetylalanine at constant rhodium concentration was determined at 25 °C for different reaction times. The plots of [olefin] *vs.* time are given at pH 4.7 and 9.4 in Fig. 1, and show a zero-order dependence on olefin concentration. At those pH values the rate of olefin consumption was also determined at different [Rh], *cf.* Fig. 2. The plots show a first-order dependence at low [Rh], which levels off towards a zero-order dependence at high [Rh]. The experimental rate law at low [Rh] and constant pH is of the form (1). At a pH below 3.2 the rate

$$\text{Rate} = k_{obs}[\text{Rh}] \quad (1)$$

increases dramatically and even with a very low [Rh] the reaction goes to 100% conversion, thus making any rate law determination impossible with the experimental set-up applied. However, using a large excess of substrate over metal and assuming the same rate law as at higher pH it was possible to determine approximate rate constants at pH 2.4 and 3.2. The low metal concentrations employed in these experiments made the reproducibility low. All rate constants are given in Table 2. It should be noted that the highest rate, at pH 2.4, corresponds to a TOF of at least 270 000 mol h^{-1}.

Table 2 Observed rate constants for the hydrogenation of AAA at different pH values, $T = 25$ °C

	k_{obs}/s^{-1}		
pH	*a*,*b*	*a*,*c*	k_{obs} [a,c]$(D_2)/s^{-1}$
2.4		125	
3.2		60	
4.5		0.21	0.17
4.7	0.083	0.11	
9.4	0.058	0.055	

[a] As defined in eqn. (1). [b] Determined from Fig. 1. [c] Determined from Fig. 2 at low [RH] or as initial rate.

Table 3 Incorporation of deuterium at the α-carbon in experiments employing D_2 and D_2O

pH	D_2/H_2O (%)	H_2/D_2O (%)
2.4	79	<3
4.5	87	<3
9.2	>97	<3

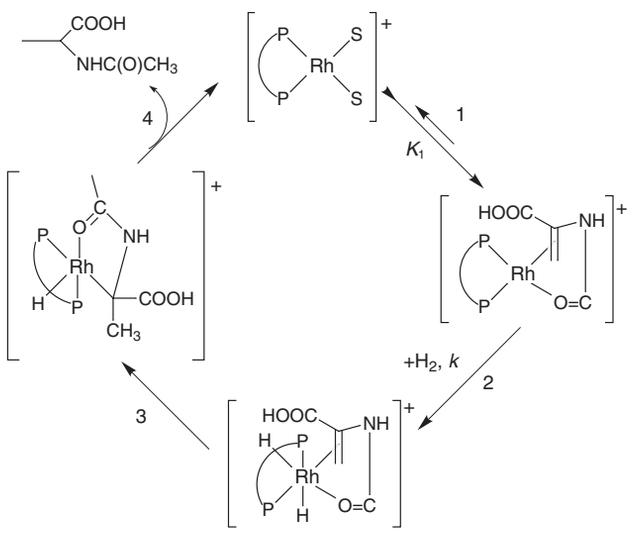
To determine the deuterium effect on the hydrogenation reaction D_2 was used alternatively to H_2 in a set of experiments. The rate constant for hydrogenation with D_2 in water at pH 4.5 is given in Table 2. The incorporation of deuterium in the product using D_2 in water or H_2 in D_2O at different pH values is given in Table 3. The incorporation degree was determined by comparing the areas of the CH and CH_2 resonances in the ^1H NMR spectra using the acetamido group as internal reference.

Discussion

Rate law and mechanism

Owing to their central role in enantioselective hydrogenation, reactions between dehydroamino acids and H_2, catalysed by rhodium complexes with chelating bidentate phosphines, have been thoroughly studied.[13] Addition of enamide precursors to a bis(solvato) complex displaces the solvent molecules forming a chelate complex co-ordinated *via* the amide carbonyl group and the olefin moiety. This mode has been verified by crystal structure determinations and by NMR studies of complexes ligated by different bidentate chiral phosphines and enamide precursors.[14]

Our findings also support olefin co-ordination prior to oxidative addition of dihydrogen. Sinou and co-workers **4a** have shown that the addition of α-acetamidocinnamic acid (ACA) to $[Rh(L–L)(H_2O)_2]^+$ (L–L = tetra sulfonated BDPP) gives an olefin chelate complex in water. The ^{31}P NMR spectrum of this complex exhibits a doublet of doublets at δ 56.2 ($J_{Rh–P}$ = 169, $J_{P–P}$ = 43 Hz) and a doublet of doublets at δ 43.6 ($J_{Rh–P}$ = 157, $J_{P–P}$ = 43 Hz) and we observe an approximate weighted average of these features in the spectrum of the AAA complex. There is no indication that the bis(aqua) complex undergoes oxidative addition of H_2 and the postulated catalytic cycle is thus the same as that found for the bis(methanol) complex (Scheme 1).



Scheme 1 Proposed catalytic cycle for the hydrogenation of AAA with complex **4**.

Assuming reaction (2) (Scheme 1) to be rate determining gives a rate law of the form (2) which if K_1[olefin] ≫ 1 reduces to

$$v = kK_1[\text{olefin}][H_2][\text{Rh}](1 + K_1[\text{olefin}]) \quad (2)$$

eqn. (3) which if $k_{obs} = k[H_2]$ is consistent with the experimental

$$v = k[H_2][\text{Rh}] \quad (3)$$

rate law in (1). The assumption regarding the equilibrium is validated by the UV/Vis experiments which show that addition of one equivalent of the olefin shifts the olefin co-ordination reaction to completion. The decrease in the reaction order in metal at higher metal concentration is explained by the formation of a non-reactive hydroxo bridged dimer.

The deuterium isotope effect (k_H/k_D) of 1.25 found in the hydrogenation experiments indicates an early transition state involving little breaking of the hydrogen–hydrogen bond. Still it indicates that oxidative addition is the rate-determining step. The degree of hydrogen incorporation from water, at the α position of the *N*-acetylalanine product, is comparable with previous results while the deuterium incorporation originating from D_2O is much lower.[15] The different degrees of incorporation observed, by changing the solvent from water to D_2O, must be a reflection of the different abilities for water and D_2O to undergo H–O and D–O bond breaking, respectively, and the higher ionic dissociation constant for water compared to D_2O is a reflection of the difference in bond strengths.[16] Thus, it can be suggested that the exchange process must proceed *via* a mechanism involving a H–O or a D-O bond breaking step, that is the incorporation must proceed *via* an isotopic exchange process. The unexpectedly low deuterium incorporation indicates that reaction 3 (Scheme 1) is very fast.

So far everything in the present bis(aqua) system agrees with the corresponding bis(methanol) system. However, in water there is also a dramatic effect of pH on the rate of hydrogenation. First it should be noted that the very high rates at low pH made a detailed kinetic investigation impossible, but yet it seems reasonable to assume that the basic mechanistic pattern, rapid olefin co-ordination followed by rate determining oxidative addition of hydrogen, is the same at low pH. This implies that oxidative addition of H_2 is faster at low pH and has also been found for $[Ir(CO)Cl(TPPMS)_2]$.[6] However, the rate enhancements brought about by pH changes for this latter complex are relatively small. In our system we see large effects and a leap in reactivity between pH 3.2 and 4.5, indicative of the involvement of a protolysis step. It can probably not be ascribed to protolysis at the metal centre, since the ^{31}P NMR experiments point to a pK_a of the water ligands higher than 4.2, and furthermore the leaving ligand (whether water or hydroxide) is not present in the transition state. The key feature instead seems to be the protolysis of the olefin and the implications this will have on its co-ordination. Between pH 3.2 and 4.5 the AAA goes from being almost completely protonated to being completely deprotonated. As shown by ^{31}P NMR this changes the mode of co-ordination and the carbonyl complex obviously undergoes oxidative addition much faster than the carboxylate complex. Thus, both the earlier found pH effect on oxidative addition and the fact that the reactant in reaction 1 changes (Scheme 1) account for the observed pH dependence. The complex [Rh(DPPB)Cl(solv)] has previously been used as a catalyst for the hydrogenation of ACA in organic solvents.[17] The hydrogenation rate is comparable to those rates observed for the $[Rh(DPPBTS)(NBD)]^+$ catalysed hydrogenations of AAA at a pH higher than the pK_a for the substrate. The reason for the extremely high rates observed at low pH is, however, hard to rationalise and must thus be further investigated.

Acknowledgements

We gratefully acknowledge TFR (Swedish Research Council for Engineering Sciences) for financial support.

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Paper 9/02288K