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Rhodium(I) hydrogenation in water: Kinetic studies and the detection of an intermediate using $^{13}C\{^1H\}$ PHIP NMR spectroscopy

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Abstract

The mechanism for hydrogenation of dimethylmaleate in water using cationic rhodium complexes with water-soluble bi-dentate phosphines has been investigated using kinetics and a novel method for the indirect detection of intermediates in catalytic hydrogenation reactions, whereby a late intermediate was detected. A mechanism is proposed involving fast, irreversible substrate binding followed by a rate-determining reaction with dihydrogen.

Keywords: Hydrogenation; Rhodium; Water-soluble phosphines; Mechanism; *para*-Hydrogen; PHIP

1. Introduction

Asymmetric hydrogenation is an important way to obtain chiral molecules, and using cationic rhodium complexes has been one of the most successful approaches [1]. One variety of these catalysts is based on water-soluble phosphines, which allows for reactions to be performed in water or under bi-phasic conditions. They often show a high activity but in general the chiral induction is lower than in organic solvents [2]. Mechanistic investigations of aqueous systems are rare [3], but they point to a similar mechanism for aqueous hydrogenations as was earlier established in organic solvents [4]. Two of us have recently been involved in efforts towards inducing a polarisation enhancement in MRI contrast agents using rhodium catalysed hydrogenation reactions in water with *para*-hydrogen [5,6]. *para*-Hydrogen induced polarisation (PHIP) has also been used extensively for mechanistic work and Bargon and co-workers found some experimental evidence for the crucial dihydride intermediate proposed for these reactions [7]. Still, the general problem with detecting intermediates, also using *para*-hydrogen, is that there is no way to be sure that an observed intermediate is on the pathway to products. On the contrary, it has often been shown that the detection indicates high stability and a dead-end species. Here, we present a mechanistic investigation of the hydrogenation of dimethylmaleate with water-soluble cationic rhodium catalysts. It includes a novel, *para*-hydrogen-based technique for the detection of intermediates, that can provide evidence of catalytic competency.

2. Experimental

2.1. General procedures and materials

All experiments were carried out using standard Schlenk techniques or in a glove box under nitrogen. Water was degassed prior to use. All other solvents were dried and degassed prior to use. All other reagents were of the best quality available and used as received. $[Rh(nbd)_2]BF_4$ was prepared according to the literature methods [8]. Tetrasulf-

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onated bis(diphenylphosphino)butane (DPPBTS), and complexes **1** and **3** were prepared as described by Malmström et al. for the corresponding triflate complex [3]. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Varian Unity 300 or a Varian Unity Inova 500 spectrometer. Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H, ^{13}C NMR) or H_3PO_4 (^{31}P NMR δ 0) as external references. Assignments are based on NOESY, HSQC and HMBC experiments. Mass spectra were recorded on a Micromass Q-Tof Micro MS instrument, using ESI+ and ESI− ionisation and water/acetonitrile (50/50) with 0.1% formic acid as solvent.

2.2. Preparations

2.2.1. Tetrasulfonated bis(dianisylphosphino)butane (DAPBTS)

To a solution of dibutylphosphite (7.81 ml, 40 mmol) in THF, sodium metal (0.92 g, 40 mmol) was added and the mixture was stirred under reflux overnight. The solution of sodiumdibutylphosphite was added dropwise to an ice-cold grignard solution made from magnesium (2.19 g, 90 mmol) and 4-bromoanisole (10.7 ml, 85.5 mmol) in ether/THF. The mixture was refluxed for 3 h and then left stirring overnight. The reaction was quenched with 3 ml of water. After stirring for 1 h, the mixture was diluted with ethyl acetate and the organic phase was decanted into an Erlenmeyer flask and the solid grey residue was treated with 2 M HCl (aq) until it dissolved. The aqueous phase was poured into the organic phase and the mixture was stirred for 30 min. After phase separation the organic phase was washed twice with water, dried and after evaporation a white solid remained. This was recrystallised from ethyl actetate giving 8.27 g (79%) of the dianisylphosphine oxide. Fifty grams (0.19 mol) of this compound was dissolved in THF (ca. 500 ml) and 76 ml *n*-BuLi (2.5 M in hexanes) was added dropwise at RT. After 2 h, 1,4-dibromobutane (10.71 ml, 94.9 mmol) was added dropwise and after yet another 2 h, the reaction mixture was poured onto 500 ml of 1 M NaH_2PO_4 (aq). After extraction with dichloromethane (three times), the combined organic phases were dried, the solvent was evaporated and the product was purified by column chromatography on silica. Elution with dichloromethane:methanol (10:0.7) gave 39.5 g (72%) of the bis(dianisylphosphineoxide)butane. This was then reduced according to the literature [9] to give the corresponding phosphine, bis(dianisylphosphino)butane, which was pure according to ^{1}H NMR spectroscopy in $CDCl_3$: δ 1.54 (b, 4H) 2.02 (b, 4H) 3.79 (s, 12H) 6.85–6.90 (m, 8H) 7.30–7.40 (m, 8H).

A flask was charged with bis(dianisylphosphino)butane (277 mg), boric acid (200 mg) and 3 ml of conc. sulfuric acid. The mixture was stirred until everything dissolved and then was cooled on an ice-bath. Fuming H_2SO_4 (3.25 ml) was added dropwise and the mixture was stirred cold for 80 min. The mixture was quenched on 20 g degassed ice and a milky white suspension was obtained. Triisooctylamine (1 ml) and toluene (10 ml) were added. After stirring, another 10 ml of water was added and the toluene phase was separated off. The resulting suspension was centrifuged and the supernatant removed. The precipitate was dissolved in 15 ml of water and pH was adjusted to 8.6 with sodium hydroxide. A white solid precipitated and was collected. Based on carbon analysis and quantitative NMR it contains approximately 20% $Na_2SO_4 \cdot xH_2O$, which could not be removed. ^{1}H NMR (D_2O): δ 1.39 (b, 4H) 1.97 (b, 4H) 3.79 (s, 12H) 7.02 (bd, 4H) 7.40 (bt, 4H) 7.69 (bd, 4H). ^{31}P NMR: (D_2O) δ −18.0 (s). *Anal.* Calc. for $C_{32}H_{32}Na_4O_{16}P_2S_4$: C, 40.26; H, 3.38. Found: C, 31.61–32.64; H, 3.42–3.66% (different batches contain different amounts of sodium sulfate). *m/z* 977.0 $(M+Na)^+$, 930.7 $(M-Na)^-$, 886.9 $(MH_2-Na_3)^-$, 97.0 (HSO_4^-).

2.2.2. [RhDAPBTS(D_2O)$_2$]BF_4 (**2**-BF_4)

A solution of **4** in degassed D_2O was hydrogenated for 3 min followed by a nitrogen purge. The solution was used immediately. ^{1}H NMR (D_2O): δ 1.69 (bt, 4H) 2.12 (b, 4H) 3.82 (s, 12H) 7.1–7.9 (m, 12H). ^{31}P NMR (D_2O) δ 51.5 (d, $^{1}J_{Rh-P}$ 200 Hz).

2.2.3. [Rh(NBD)DAPBTS]BF_4 (**4**-BF_4)

In a typical procedure, a Schlenk flask was charged with $Rh(NBD)_2(BF_4)$ (2.1 mg, 5.7 μmol) and DAPBTS (6.4 mg, 5.3 μmol). One millilitre of D_2O was added giving a yellow solution that was used within two days. ^{1}H NMR (D_2O): δ 1.45 (s, 2H) 1.56 (bt, 4H) 2.42 (b, 4H) 3.78 (s, 2H) 3.88 (s, 12H) 4.46 (s, 4H) 7.1–7.9 (m, 12H). ^{31}P NMR (D_2O) δ 27.5 (d, $^{1}J_{Rh-P}$ 154 Hz).

2.2.4. [Rh(DMM)DPPBTS]BF_4 (**5**-BF_4)

A solution of **1** was prepared as described in Ref. [2] and an excess of dimethyl maleate (DMM) was added. ^{1}H NMR (D_2O): δ 3.56 (s, CH_3O) 6.75 (s, HC=CH). ^{31}P NMR (D_2O) δ 18.6 (bd, $^{1}J_{Rh-P}$ 129 Hz) 55.9 (bd, $^{1}J_{Rh-P}$ 155 Hz). ^{13}C NMR (D_2O) δ 133.5 (s, HC=CH) 177.0 (s, C=O).

2.2.5. Rh(DMM)DAPBTS]BF_4 (**6**-BF_4)

A solution of **2** was prepared as described above and approximately 1 equiv. of dimethyl maleate (DMM) was added. ^{1}H NMR (D_2O): δ 3.55 (s, CH_3OCO) 3.65 (s, CH_3O) 6.74 (s, HC=CH). ^{31}P NMR (D_2O): δ 17.3 (bd, $^{1}J_{Rh-P}$ 139 Hz) 53.5 (bd, $^{1}J_{Rh-P}$ 154 Hz) ^{13}C NMR (D_2O): δ 56.4 (s, CH_3O), 133.5 (s, HC=CH) 175.7 (s, C=O).

2.3. Hydrogenation of DMM

A solution of DMM (13.7 μl, 0.105 mmol) in 3.0 ml D_2O was prepared in a round bottomed flask equipped with a septum. The flask was flushed with N_2(g). A

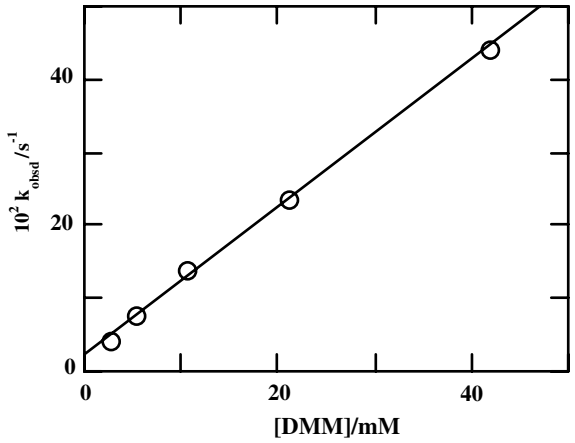


Fig. 1. Observed pseudo first-order rate constants for substrate binding to **1** as a function of DMM concentration. $T = 298.8$ K; [Rh] = 0.13 mM.

0.1 ml portion of the stock solution of **3** or **4** was added and H_2(g) was bubbled through for 5–15 min. The resulting solution contained only dimethylsuccinate as seen by ^{1}H NMR spectroscopy.

2.4. Kinetics

2.4.1. Substrate binding

The stopped-flow experiments were performed on an Applied Photophysics Bio Sequential SX-17 MX, stopped-flow spectrofluorimeter under anaerobic conditions. The substitution of water in **1** by DMM was studied in water by observing the decrease in absorbance at 330 nm. The complex solution (1.3×10^{-4} M) was mixed directly in the stopped-flow instrument with an equal volume of DMM solution, resulting in a large excess of the entering ligand ($1.3–21 \times 10^{-3}$ M), assuring pseudo first-order conditions. The kinetic traces were fitted to single exponentials using the software provided by Applied Photophysics,[1] resulting in observed rate constants at different concentrations of the incoming ligand. Rate constants are given as an average of at least five runs. Complete data are reported in Table S1 and in Fig. 1.

2.4.2. H_2-consumption in the catalytic reaction

As described above, a solution of **1** or **2** (or **4**) in H_2O was prepared and an appropriate amount of DMM was added to a 30 ml aliquot of the rhodium solution. Using a Büchi press-flow gascontroller 6002 apparatus, the H_2-consumption of these solutions was measured at constant H_2-pressure. In all experiments, the plots of H_2-consumption versus time were linear indicating a zero-order dependence in the limiting reagent, *i.e.* the olefin. Rates were evaluated as the slopes of these plots. Complete data are reported in Table S2 and S3.

2.5. para-Hydrogen experiments

2.5.1. Sample preparation

Samples were prepared in 10 mm NMR tubes with a drop-catching expansion volume by adding 5–10 μl of **7** and 1.5 ml degassed D_2O. The tube was equipped with a septum with a Teflon outlet and flushed with N_2(g). Through the septum, 0.25–0.50 ml of the catalyst stock solution was added *via* syringe and the tube was flushed with N_2(g) again. The tube was sealed with parafilm to keep oxygen out.

2.5.2. Experimental setup

Pure parahydrogen was produced at 3 MPa and 15 K in the presence of a hydrous ferric oxide catalyst purchased from C*chem, P.O. Box 640, Lafayette, CO, USA, and stored (<5 days) in an aluminium cylinder equipped with a regulator and teflon tubing. Before the experiment, the *p*-H_2 was flushed through the teflon tubing during ca. 10 min to saturate the material with *p*-H_2 and to remove all paramagnetic materials *e.g.* O_2. The tubing was led through the septum into the NMR-tube, until it reached the bottom, and, in addition, the septum was equipped with a teflon outlet. Some *para*-hydrogen was bubbled through carefully, to activate the catalyst and to remove other gases and the sample was placed inside the NMR spectrometer. Before collecting a spectrum full relaxation was allowed to take place.

For ordinary PASADENA spectra, *para*-hydrogen was bubbled through the sample inside the spectrometer, the sample was allowed to settle, and the spectrum was collected using a single 45° (^{1}H) or 90° (^{13}C) pulse.

Indirect detection experiments were performed in a similar way with a few additional elements. The decoupler offset frequency (dof) and decoupler power (dpwr) were set to an appropriate value. The decoupler was turned on and *p*-H_2 was bubbled through during 10 s. The decoupler was kept on for another 10 s (20 s in total), after which it was turned off to let the *J*-coupling evolve. This second delay was 30 ms, and the fid was collected using a single 90° pulse. The ^{13}C signal of the product was detected and integrated and after relaxation this procedure was repeated using a different dof. Thus, the indirectly detected spectra in Figs. 4, 5, S1 and S2 were constructed.

3. Results and discussion

The rhodium complex $[Rh(D_2O)_2DPPBTS]^+$ (**1**) (Chart 1) is a very active catalyst in the hydrogenation of α-acetamidoacrylic acid, especially at low pH and $[Rh(D_2O)_2$-DAPBTS$]^+$ (**2**) is expected to display similar behaviour [3].

They are readily formed via hydrogenation of the corresponding norbornadiene complexes **3** and **4** (Scheme 1); **1**

[1] Applied Photophysics Bio Sequential SX-17 MV Stopped Flow ASVD Spectrofluorimeter, software manual, Applied Photophysics Ltd. 203/205 Kingston Road, Leatherhead KT22 7PB, UK.

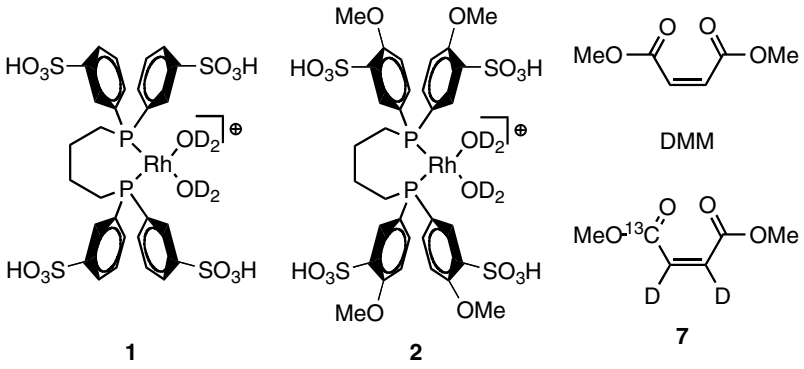
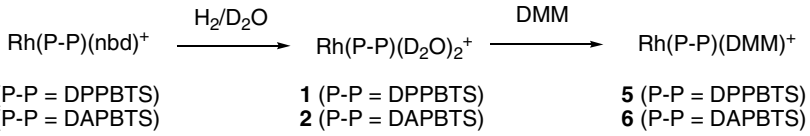


Chart 1.



Scheme 1.

has been characterised earlier [3] and **2** displays a similar ^{31}P NMR spectrum with a doublet at 51.5 ppm ($^{1}J_{Rh-P} = 200$ Hz). Addition of a slight excess of dimethylmaleate (DMM, Chart 1) to a D_2O solution of **1** rapidly yielded a ^{31}P NMR spectrum displaying a broadened doublet at 55.6 ppm ($^{1}J_{Rh-P} = 152$ Hz) and another broadened doublet at 18.2 ppm ($^{1}J_{Rh-P} = 128$ Hz) in accordance with the expected resonances for a $[Rh(DMM)DPPBTS]^{+}$ (**5**) complex. No resonances from **1** could be detected in solution. The coordination of DMM could be confirmed using ^{1}H NOESY spectroscopy, where the olefinic protons of DMM displayed cross-peaks with aliphatic and aromatic protons of the phosphine ligand, showing that they are close in space. The complex $[Rh(DMM)DAPBTS]^{+}$ (**6**) was obtained similarly and displayed similar spectral features. For both **5** and **6**, the coordination mode of DMM is probably bidentate with one phosphorus *trans* to an oxygen and one *trans* to the double bond. A monodentate binding fashion through the olefin moiety, with one water molecule also coordinated, cannot be ruled out. However, the coupling constants of the resonances at 55.6 and 53.5 for **5** and **6**, respectively, are substantially lower than those found in **1** and **2**, indicating a different *trans* influence of the coordinated ligand, and this speaks against water coordination. All reactions are depicted in Scheme 1.

Since the stability in solution of **1** is substantially higher than that of **2**, we chose the former to monitor the kinetics for the substrate binding reaction using UV–Vis stopped-flow spectroscopy. From the slope and intercept of a plot of observed pseudo first-order rate constants versus DMM concentrations, the forward and reverse rate constants were computed to be $20.0 \pm 0.6\ M^{-1}\ s^{-1}$ and $0.025 \pm 0.006\ s^{-1}$, *cf.* Fig. 1. From the ratio of these rate constants, a binding constant for DMM of $(8.0 \pm 1.8) \times 10^{2}\ M^{-1}$ was calculated.

Bubbling H_2 for 5–15 min through an aqueous solution of **1** or **2** and an excess of DMM, gave complete conversion of the substrate to dimethyl succinate, showing that the rhodium cations are effective catalysts.

The overall catalytic reaction with **4** as pre-catalyst (forming **2** in situ) was studied by measuring the hydrogen consumption at constant hydrogen pressure. The kinetic traces are zero-order, showing the reaction to be zero-order in olefin concentration. A plot of reaction rates at different hydrogen pressures (Fig. 2) shows that the reaction is first-order in $P(H_2)$. At constant hydrogen pressure the rhodium concentration was also varied giving the plot in Fig. 3. There seems to be some saturation but at low catalyst loadings a first-order dependence in catalyst concentration is observed. This behaviour has been reported earlier [3]. Overall this gives the following rate law,

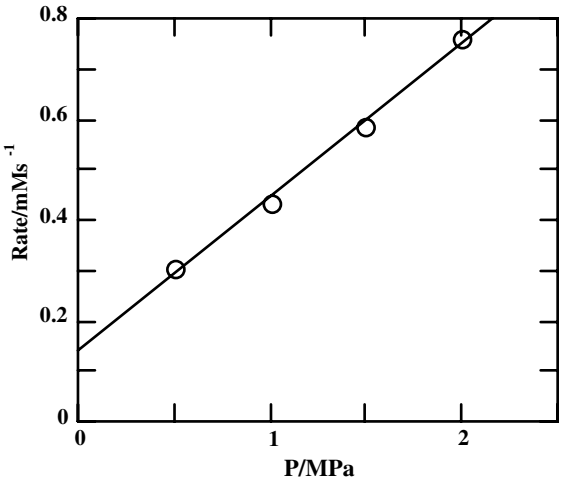


Fig. 2. Observed rate of hydrogenation of DMM as a function of dihydrogen pressure using **2** as a catalyst. $T = 298.8$ K; [Rh] = 0.24 mM.

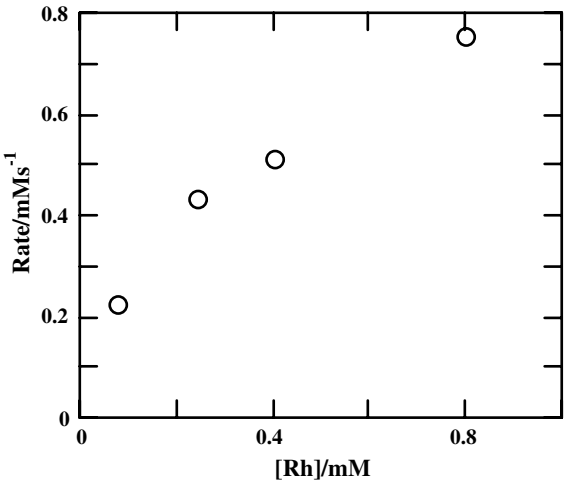


Fig. 3. Observed rate of hydrogenation of DMM as a function of rhodium concentration using **2** as a catalyst. $T = 298.8$ K; $p(H_2) = 1.0$ MPa.

$$\text{Rate} = kP(H_2)[\text{Rh}] \quad (1)$$

which is compatible with the mechanism proposed earlier for hydrogenation of dehydroamino acids involving fast, reversible (*vide infra*) substrate binding prior to the rate-determining reaction with H_2 [3,4]. The second-order rate constant, obtained from Fig. 2, was determined to be 1.2 ± 0.2 MPa^{-1} s^{-1}. The reaction using **3** as pre-catalyst was investigated less thoroughly, but gave essentially the same rate law, which is the same as reported for this catalyst with acetamido acrylic acid; see Supplementary material for all data. For **3**, the average second-order rate constant was 3.8 ± 0.5 MPa^{-1} s^{-1}. In this case, the zero-order dependence in olefin concentration is in agreement with the high binding constant found in the stopped-flow experiments, giving a fast formation of the DMM adduct. It is clear when comparing the first-order rate constants for DMM displacement by water (0.025 s^{-1}) and the forward reaction with dihydrogen (3.8 s^{-1} at 1 MPa) that the DMM binding is irreversible at practically all hydrogen pressures and that the DMM complex is the resting state of the catalyst.

Lately, a dihydride route (as opposed to an unsaturated route), *i.e.* where the dihydrogen activation precedes the substrate binding, has been shown to be a viable alternative also for some cationic rhodium systems [10]. However, the fact that substrate binding is faster than overall catalysis and essentially irreversible makes this unlikely in the current system.

Having established rate law and stoichiometric mechanism we conducted a number of PHIP experiments under PASADENA conditions [11]. Thus, a solution of **1** or **2**[2] and isotopically labelled dimethyl maleate (**7**, see Chart 1) were reacted with *para*-H_2, resulting in a ^{1}H NMR spectrum with a strong signal at 3.65 ppm originating from the methoxy-protons of the substrate, and one antiphase signal at 2.51 ppm with a complicated coupling pattern, originating from the polarised product. No signals from any hydridic (or other possible) intermediates were detected, implying that they are too short-lived under these conditions. ^{1}H spins usually relax faster than those of ^{13}C and indirect detection of a ^{1}H NMR-spectrum *via* ^{13}C could therefore circumvent these problems. The amount of PHIP observed in the product is dependent on how much of the effect is lost due to relaxation in the intermediates. By irradiating potential intermediates with a radio frequency corresponding to their ^{1}H NMR chemical shift during the hydrogenation, the singlet state of the protons, originating from the *para*-hydrogen, is prevented from evolving into the triplet manifold under the influence of chemical shifts and *J*-couplings. Little relaxation during catalysis should give a strong PHIP when observing the ^{13}C NMR signal of the product and thus we can get a correlation between the signal intensity from the product and the chemical shift of the intermediate. In this way the decoupler radio frequency was swept, in steps, over the whole region of possible ^{1}H NMR frequencies and the integral of the anti-phase ^{13}C signal of the product was measured. Hence, we could obtain a frequency-product signal response diagram similar to a classical continuous wave spectrum where absorption is measured as a function of frequency. Using a fairly high decoupler effect, the whole proton region from −20 to 10 ppm was swept giving spectra for both catalysts with one or two (depending on resolution) broad peaks centred around 1.6–2.0 ppm.

Lowering the decoupler power gave a lower peak width but the response always went through a null at around the same frequency. Since we have no phase information in the decoupling process we interpret this behaviour as a single anti-phase peak. At a decoupler bandwidth of approximately 40 Hz the experiment was performed with smaller

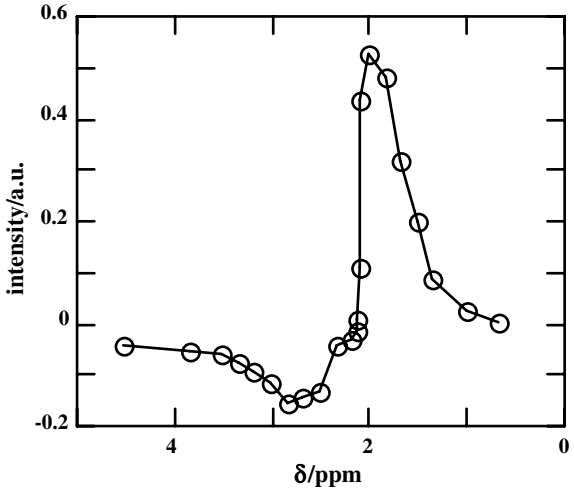


Fig. 4. Indirect ^{1}H NMR spectrum of the hydrogenation intermediate using **3** as catalyst. [Rh] = 1.32 mM; $[DMM]_0 =$ 40.0 mM; and $T = 298$ K.

[2] Complex **4** was mostly used to give **2** in situ. The reason for this is the relative instability of **2**.

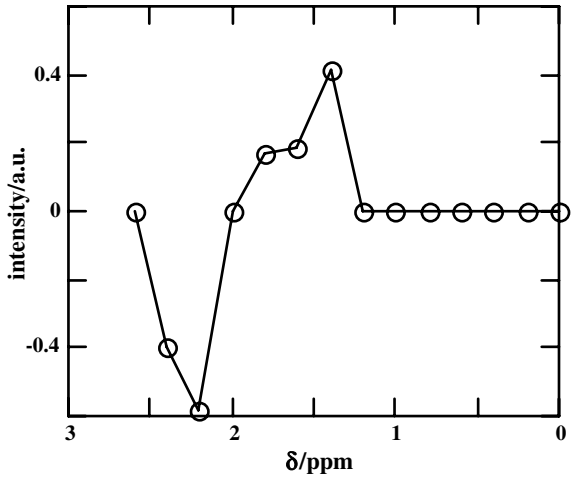
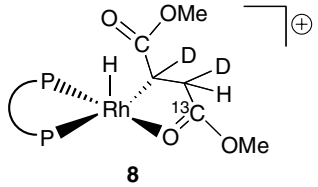


Fig. 5. Indirect ^{1}H NMR spectrum of the hydrogenation intermediate using **4** as catalyst. [Rh] = 1.06 mM; $[DMM]_0$ = 40.0 mM; and T = 298 K.

frequency increments, giving the ^{1}H NMR spectra shown in Figs. 4 and 5 for complexes **3** and **4**, respectively. No polarisation of the ^{13}C substrate signal was observed.

The fact that we see no polarisation of the substrate peak as observed in some other systems, indicates that there is no reversibility after the first C–H bond has been formed. Furthermore, a dihydride mechanism (as opposed to a mono-hydride mechanism) is operating also in water, *i.e.* the two hydrogens are transferred to the same product molecule and there is negligible proton exchange with the solvent. The spectra in Figs. 4 and 5 could in principle arise from *J*-coupling, but this would require a coupling constant of ca. 240 Hz [12]. It seems more likely that the spectrum is due to a single, broad, anti-phase signal centred at 1.9 and 2.0 ppm when using **3** and **4** as pre-catalysts, respectively; this cannot correspond to a dihydride intermediate. Instead we see a species where at least one hydrogen has been transferred and one C–H bond is fully formed. This leaves us with at least two possibilities: an alkyl hydride species (shown below (**8**)) or a catalyst-succinate complex.



8

A succinate complex is presumably very short-lived[3] and we therefore believe that what we see is the signal from the hydrogen atom sitting next to a ^{13}C carbonyl in an alkyl hydride species. The peaks are about 100–150 Hz wide, which corresponds to a rate for leaving the site of *ca.* 3–400 s^{-1} and hence a lifetime of the intermediate of approximately 3 ms. This means that the over-all rate is some two orders of magnitude slower than the decay of **8**. Thus, although this intermediate is long-lived enough to give a large contribution to the spin relaxation, its transformation into products cannot be the over-all rate-determining step [13]. This would fit well with an alkyl hydride, which according to the computational results by Landis et al. is formed in the rate-determining step. Obviously, any other intermediate after H_2 addition must contribute less to the relaxation. In the dihydrogen complex the symmetry has not been broken and so this gives no relaxation and presumably the dihydride also has a short life-time possibly due to a reversible character of the oxidative addition found in earlier computational results [13]. The lifetime of **8** corresponds to a reaction barrier of approximately 14 kcal/mol which is reasonable for a reductive elimination step. It must be noted that although we can link this intermediate directly to the catalytic cycle the lack of coupling and other features of its ^{1}H NMR spectrum makes any assignment far from definite.

In conclusion, we propose an unsaturated mechanism with fast substrate binding and a rate-determining step involving dihydrogen for the aqueous hydrogenation of dimethylmaleate using water-soluble rhodium cations. We also present a novel method for the indirect detection of intermediates in catalytic hydrogenation reactions.

Acknowledgements

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Appendix A. Supplementary material

Tables and figures giving all primary kinetic and NMR data. This material can be found, in the online version, at doi:10.1016/j.ica.2006.08.042.

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