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High-Pressure NMR Study of Imine Hydrogenation Catalyzed by Rhodium(I)/Phosphine Complexes. Characterization of Species Present under Catalytic Conditions

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A high-pressure NMR cell based upon the use of a sapphire NMR tube and simple valve design was constructed. The use of the cell to study the hydrogenation of imines under 1000–2000 psi of hydrogen mediated by [tertiary bis(phosphine)]rhodium(I) catalysts is described. Complexes of the type $[\{Rh(diphos)\}_2(\mu\text{-}H)(\mu\text{-}X)]$ (X = Cl, I, OMe), which are formed at these elevated hydrogen pressures, were characterized *in situ*, and the possible significance of these complexes in the catalysis is discussed. The dihydride *cis*-$[RhH_2(diphos)_2]Cl$, produced in a side reaction, was spectroscopically characterized at low temperature under 1200 psi of H_2.

Introduction

Previous work from these laboratories has been aimed at using enantiopure [tertiary bis(phosphine)]rhodium(I) complexes to catalyze the asymmetric hydrogenation of imines.[1] Optical yields of up to 71% have been achieved by using $[Rh(NBD)Cl]_2$ and (*R*)-cycphos[2] as catalyst precursors. Addition of iodide to the catalyst can lead to increased optical yields, up to 91%. The optimum solvent mixture was 1:1 C_6H_6/MeOH, the turnover rate being much reduced in the absence of MeOH. Most importantly for the work described herein, however, was the observation that reduction of imines is extremely slow at ambient pressures of H_2 and that 1000 psi or more of H_2 is required to drive the reaction at a useful rate. Application of NMR spectroscopy to the study of this system at elevated pressures with the possibility of detecting possible catalytic intermediates or obtaining mechanistic information via kinetic studies was clearly desirable. The use of sapphire NMR tubes opened up this possibility since they have been found to have a bursting pressure of 11 000 psi and so can be used at the relevant pressures with a reasonable safety margin.[3,4] Indeed, the combination of sapphire NMR tubes and elevated hydrogen pressures has been used successfully to study several areas of transition metal chemistry,[5] including the characterization of hydrides and dihydrogen complexes such as $[FeH_2(CO)_4]$[6] and $[Cr(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2]$,[7] which are unstable at ambient pressures, and the stoichiometric hydrogenation of bound diimine ligands.[8]

This paper describes the use of a sapphire NMR tube based system to investigate the nature of complexes present under true catalytic conditions and attempts to extract mechanistic information via kinetic studies. A brief description of the design and operation of the high-pressure NMR cell is included since this differs somewhat from other variants described in the literature. Also, although an enantiopure phosphine (*e.g.* cycphos etc.) is obviously required to induce maximum asymmetric induction,[1] the present study focused solely on the optically inactive analogue diphos to simplify the results by eliminating the possibility of observing diastereoisomers.

Design and Operation of the HP-NMR cell

A schematic of the HP-NMR cell is shown in Figure 1. The valve design differs from those previously described in that it features a sapphire ball pressed against an HPLC seat as the pressure retaining mechanism.

The valve is in three parts, A, B, and C, the lower part A being glued to the tube. The alloy and glue used were those recommended in the original design.[3] Parts B and C are removed to allow filling via a syringe, and then B is attached using four brass bolts. The base of B is fitted with a Rulon gasket to ensure a gastight seal. For the preparation of air-sensitive samples, the sapphire tube and parts B and C are flushed with nitrogen in a modified Schlenk apparatus. The sample (0.3–0.4 mL) is then injected, and the upper valve assembly parts B and C are bolted on against a flow of nitrogen. The system is pressurized by means of the detachable housing C which fits and seals flush on top of part B. Part C is in turn connected to a standard gas tank regulator (from which the pressure is controlled) using standard high-pressure fittings. Rapid removal of the tank gas pressure causes the sapphire ball to be forced against the HPLC seat by the excess pressure in the tube. Because of the manner in which the tube is sealed, it is possible that some gas escapes in the process, but this is likely to be a very small amount. While there is no way of directly monitoring the pressure inside the tube, pressure was apparently still retained after 2 weeks. The pressure is released by means of a bolt which is threaded through the detachable housing and screwed down against the sapphire ball.

After pressurization, the detachable housing C is removed and a copper wire bridge bolted to the top of the valve in its place. This is used in conjunction with a hook attached to a string to lower and raise the tube into and out of the magnet/probe. This was deemed safer than lowering the pressurized tube by using the pneumatic lift, where there is probably a greater possibility of the tube striking the top of the probe with potentially dire consequences! The total weight of 58 g allows spinning at 15–20 Hz. For safety reasons, the NMR spinner is attached before pressurization. As recommended by other authors,[3,5] direct operator exposure to the pressurized assembly is always avoided by placing the tube portion of the cell in a protective Perspex cylinder. Pressures up to 2000 psi have been routinely used without incident.

Experimental Section

General Procedures. All solutions were handled under an atmosphere of nitrogen by using standard Schlenk and syringe techniques. Deuterated solvents were used as supplied and vacuum-degassed before use. Reagent grade toluene was distilled from sodium/benzophenone and hexane was distilled from calcium hydride prior to use. Hydrogen (prepurified grade, Matheson) was used as supplied.

[●] Abstract published in *Advance ACS Abstracts,* February 15, 1994.

(1) (a) Becalski, A. G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G.-J.; Rettig, S. J. *Inorg. Chem.* **1991**, *30*, 5002. (b) Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P.; Kang, G.-J.; Herb, G.; Thorburn, I. S.; Spogliarich, R. *J. Mol.Catal.* **1990**, *62*, 243.

(2) Abbreviations used: NBD = norbornadiene; COD = 1,5-cyclooctadiene; cycphos = $Ph_2PCH(C_6H_{11})CH_2PPh_2$; diphos = $Ph_2PCH_2CH_2PPh_2$; dippe = ${}^iPr_2PCH_2CH_2P{}^iPr_2$; Proton Sponge = 1,8-bis(dimethylamino)naphthalene.

(3) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388.

(4) Horváth, I. T.; Ponce, E. C. *Rev. Sci. Instrum.* **1991**, *62*, 1104.

(5) Horváth, I. T.; Millar, J. M. *Chem. Rev.* **1991**, *91*, 1339.

(6) Krusic, J. P.; Jones, D. J.; Roe, D. C. *Organometallics* **1986**, *5*, 456.

(7) Millar, J. M.; Kastrup, R. J.; Melchior, M. T.; Horváth, I. T.; Hoff, C. D.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 9643.

(8) Zoet, R.; Elsevier, C. J.; van Koten, G.; Versloot, P.; Vrieze, K.; van Wijnkoop, M.; Duineveld, C. A.; Goubitz, K.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1989**, *8*, 23.

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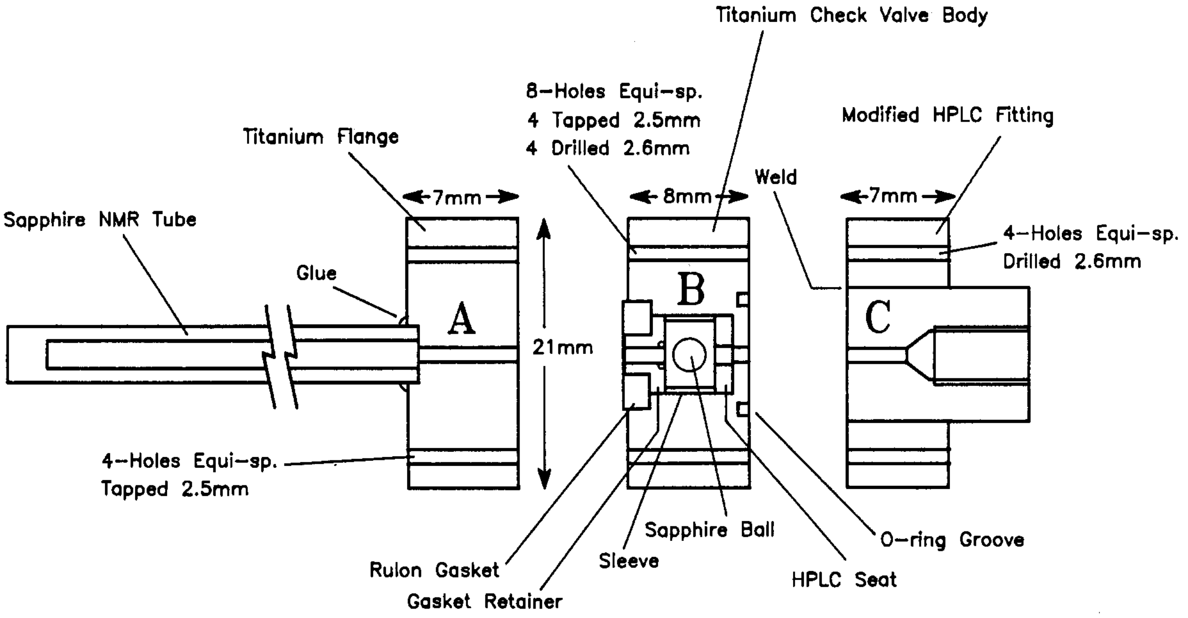

Figure 1. High-pressure NMR assembly. The valve is essentially constructed from a Waters HPLC check valve kit; Equi-sp = equispaced.

NMR spectra in the high-pressure cell were recorded on either a Varian XL-300 (both ^1H and ^{31}P spectra) or Bruker WH-400 (^1H spectra only) spectrometer. Spectra of samples in standard tubes (including the ^{31}P–^{31}P COSY, ^1H–^{31}P HMQC, and $^1H\{^{31}P\}$ experiments) were recorded on a Bruker AMX-500 spectrometer fitted with an inverse probe. (HMQC = heteronuclear multiple quantum coherence, which is NMR jargon for a proton-detected proton–phosphorus correlation). ^{31}P chemical shifts are relative to external phosphoric acid, with increasing frequency positive. ^1H NMR chemical shifts were measured relative to residual protons in deuterated solvents (benzene 7.15, methanol 3.30, and toluene methyl 2.09 ppm). $[Rh(NBD)Cl]_2$,[9] $[Rh(diphos)X]_2$ (X: Cl, 4; I)[1a,10] and $[Rh(COD)(OMe)]_2$[11] were prepared according to published procedures. Imine 1 was prepared from the appropriate ketone precursor and benzylamine by refluxing in a Dean Stark water separator.[1,12]

Preparation of NMR Samples for Reduction under High H_2 Pressure. Typically, $[Rh(NBD)Cl]_2$ (10.0 mg, 0.022 mmol), 2 equiv of diphos (17.3 mg, 0.043 mmol), and excess imine (1) (103.5 mg, 0.43 mmol) were dissolved in 1:1 C_6D_6/CD_3OD (0.4 mL) with stirring. An aliquot (0.3–0.4 mL) was then transferred to the HP-NMR tube, and ^1H and ^{31}P NMR spectra were recorded. The solution was then pressurized at room temperature to the required pressure (1000–2000 psi), and the tube was repeatedly inverted and reoriented to ensure efficient mixing of phases before further spectra were taken. Observed turnover rates were between 14 and 66 h^{-1} at pressures between 1000 and 1200 psi of H_2, the exact rate being dependent primarily on the amount of mixing of liquid and gas phases. Measured rates were not reproducible because they were diffusion controlled, and attempted kinetic studies were abandoned.

Reactions involving $[Rh(COD)(OMe)]_2$ in place of $[Rh(NBD)Cl]_2$ were performed analogously. Occasionally higher C_6D_6-to-CD_3OD ratios were used to increase the solubility of complexes. $C_6D_5CD_3$ was used in place of C_6D_6 for low-temperature experiments. CD_3OD was replaced with normal CH_3OH for studies of hydride-containing species.

Solutions containing $[Rh(diphos)Cl]_2$ (4) or $[Rh(diphos)I]_2$, in place of $[Rh(NBD)Cl]_2$ and diphos, were studied. A higher C_6D_6-to-CD_3OD ratio solvent mixture (typically 3:1) was employed to increase the solubility of the complexes. Typically, saturated solutions of the complexes were necessary to obtain usable spectra.

Hydrogenation of Deuterated Imine 1. Imine 1 was deuterated at the α-CH_3 position by dissolving a sample in CH_3OD and then removing the solvent *in vacuo* after 4 h. This was performed three times. Imine-d_3 (*ca.* 41 mg, 0.17 mmol), $[Rh(NBD)Cl]_2$ (10.0 mg, 0.022 mmol), and diphos (17.3 mg, 0.043 mmol) were then dissolved in 1:1 C_6D_6/CD_3OD. The ^1H NMR spectrum showed the presence of 0.15 proton per α-methyl group on average (95% D incorporation) immediately before hydrogenation. After complete reduction in the HP-NMR tube under 1200 psi of H_2, 0.28 proton per α-methyl group (91% D incorporation) was observed.

Fast Hydrogenation of Imine 1 in the Presence of CD_3OD. Imine 1 (*ca.* 45 mg, 0.17 mmol), $[Rh(NBD)Cl]_2$ (10.0 mg, 0.022 mmol), and diphos (17.3 mg, 0.043 mmol) were dissolved in C_6D_6 (0.3 mL). A portion (0.2 mL) of the solution was placed in the HP-NMR cell. CD_3OD (0.2 mL) was then layered on top of this solution to avoid mixing. The mixture was pressurized to 1500 psi of H_2 and then vigorously mixed to ensure rapid hydrogenation (complete in less than 5 min). The ^1H NMR spectrum of the product amine showed predominantly a doublet pattern for the methyl group, indicative of no D incorporation. Relative integration showed *ca.* 94% protonation of the α-methyl group (average 0.18 deuteron per methyl group).

Characterization of $[\{Rh(diphos)\}_2(\mu\text{-}H)(\mu\text{-}X)]$ (7). Typically, $[Rh(diphos)Cl]_2$ (4) (5–10 mg) and excess imine 1 (20–50 mg) were dissolved in 3:1 C_6D_6/CD_3OH (0.4 mL). ^1H, ^{31}P, and ^{31}P-^{31}P COSY NMR experiments were performed on the sample. The sample was then pressurized in the HP-NMR cell to 1500 psi of H_2, and the ^1H and ^{31}P spectra were recorded once more. The major product 7 accounted for *ca.* 80% of the intensity in the ^{31}P NMR spectrum. After complete imine reduction (^1H NMR monitoring), the pressure was released and the sample transferred to a normal NMR tube under an atmosphere of H_2. The ^{31}P NMR spectrum indicated that 7 accounted for *ca.* 30% of the intensity. Resonance assignments were confirmed by a ^1H–^{31}P HMQC experiment and selective and broad-band decoupling of the phosphorus nuclei: $^{31}P\{^1H\}$ NMR (3:1 C_6D_6/CD_3OH) δ 65.8 (m, $^1J(Rh–P)$ = 167.4 Hz, 2P, P *trans* to hydride), 78.7 (m, $^1J(Rh–P)$ = 196.3 Hz, 2P, P *cis* to hydride); ^1H NMR (3:1 C_6D_6/CD_3OH) δ −8.38 (ttt, $^2J(P_{trans}–H)$ = 56.5 Hz, $^2J(P_{cis}–H)$ = 13.4 Hz, $^1J(Rh–H)$ = 23.5 Hz, 1H, hydride), 1.85 (br m, 4H, $P_{trans}–CH_2$), 1.90 (br m, 4H, $P_{cis}–CH_2$), 6.83 (m, 24H, *meta* and *para* phenyl protons), 7.63 (m, 8H, *ortho* phenyl protons of P_{trans}), 7.83 (m, 8H, *ortho* phenyl protons of P_{cis}).

Complex 7 slowly decayed at room temperature under 1 atm of H_2 ($t_{1/2} \sim 8$ h) in 3:1 C_6D_6/CD_3OH. The experiment was repeated, but this time the hydrogen pressure was released before hydrogenation of the imine was complete. Hydrogenation effectively ceased after depressurization, and there was no obvious difference in the rate of decomposition of 7 (^1H and ^{31}P NMR monitoring).

Reaction of $[Rh(diphos)Cl]_2$ (4) with Proton Sponge and H_2. In a procedure analogous to that used for the characterization of 7, the dimer 4 (*ca.* 5 mg) and excess Proton Sponge (10 mg) were dissolved in 3:1 $C_6D_5CD_3/CD_3OD$ (0.5 mL). The $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded and showed 4 to be unchanged. The sample was then pressurized to 2000 psi of H_2; NMR spectra indicated 7 to be the major product. When the sample was progressively cooled to −90 °C (at which temperature some precipitation was evident leading to low signal-to-noise ratios in the NMR spectra), no new peaks were observed in the $^{31}P\{^1H\}$ NMR spectrum at this or intermediate temperatures.

Characterization of $[RhH_2(diphos)_2]Cl$ (9). $[Rh(NBD)Cl]_2$ (10.0 mg,

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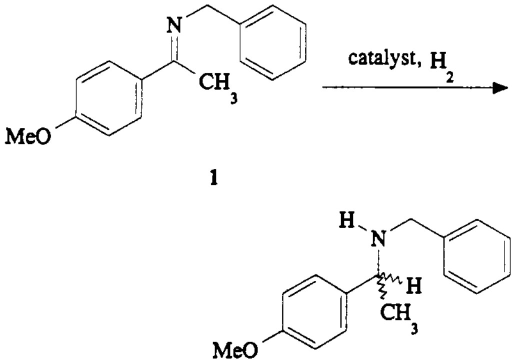
(9) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178.
(10) Fairlie, D. P.; Bosnich, B. *Organometallics* **1988**, *7*, 936.
(11) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.
(12) *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970.

0.022 mmol), diphos (17.3 mg, 0.043 mmol), and excess imine **1** were dissolved in 1:1 $C_6D_5CD_3/CD_3OD$ (0.4 mL) with stirring. The resulting solution was transferred to the HP-NMR cell and pressurized with H_2 to 1200 psi. The ^{31}P NMR spectrum was recorded at room temperature, and it included a resonance at δ 57.9 (^1J(Rh–P) = 133 Hz) due to [Rh(diphos)$_2$]Cl (as well as resonances due to **7** and **4**). On cooling of the sample below 0 °C, this resonance was progressively replaced by new signals (in slow exchange) due to the formation of [RhH$_2$(diphos)$_2$]Cl, and at −90 °C only a trace of [Rh(diphos)$_2$]Cl remained.

cis-[RhH$_2$(diphos)$_2$]Cl: ^1H NMR (1:1 $C_6D_5CD_3/CD_3OD$, −90 °C) δ −8.9 (br d, 2H, $^2J(P_{trans}$–H) ~ 139 Hz, hydride); $^{31}P\{^1H\}$ NMR: δ 45.1 (dt, 2P, ^1J(Rh–P) = 90 Hz, ^2J(P–P) = 15 Hz, P *trans* to hydride), 62.1 (dt, 2P, ^1J(Rh–P) = 100 Hz, P *cis* to hydride).

Results and Discussion

Monitoring Imine Hydrogenation by HP-NMR. In a previous study of asymmetric imine hydrogenation,[1] of the imines surveyed, 4-methoxyacetophenonebenzylimine (**1**) was found to be a convenient substrate in terms of both rate and optical yields and thus was used throughout the present study (eq 1).



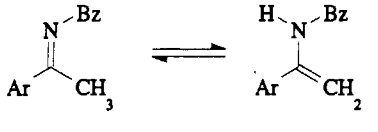
1

2

(1)

When a solution of imine **1** dissolved in 1:1 C_6D_6/CD_3OD along with the appropriate catalyst precursor, typically 0.025–0.05 equiv of [Rh(NBD)Cl]$_2$ and 0.05–0.1 equiv of diphos, is then pressurized to ≥1000 psi of H_2 in the HP-NMR tube, the reaction can be monitored by observing the disappearance of resonances due to the imine **1** and concomitant appearance of resonances due to the amine, **2**. The major geometric isomer of **1** was shown by 1D NOE difference and 2D NOESY spectra to be the *E*-isomer (as drawn above); the *E*:*Z* ratio of 14:1, determined by integration, remained approximately the same throughout the catalytic hydrogenation. In the NOE difference and NOESY spectra, peaks due to exchange between the *E*- and *Z*-isomers were also apparent, and integration of the exchange cross peaks and diagonal peaks in the latter (mixing time 1.8 s) gave estimates of the interconversion rates of the isomers as ~155 h^{-1} (for $Z \rightarrow E$) and ~11 h^{-1} (for $E \rightarrow Z$) at 25 °C.[13] As these rates are comparable to those observed for hydrogenation (14–66 h^{-1}, depending upon conditions), no conclusions regarding hydrogenation selectivity can be drawn. The rate of reduction was found to be entirely dependent upon the rate at which the liquid and gaseous phases were mixed, implying that diffusion of H_2 into the solution was rate determining under the conditions used. Keeping the tube vertical in the spectrometer resulted in a rate that was apparently zero because the "NMR-active" region of the sample is typically 3–3.5 cm below the surface of the solution. The internal diameter of the sapphire tube is small (*ca.* 3 mm), resulting in a very low surface area-to-volume ratio, which mitigates against rapid diffusion. Although reaction rates could probably have been reduced to the point where H_2 diffusion was no longer rate limiting by lowering reactant concentrations, this line was not pursued, as it was clear that the HP-NMR tube was far from an ideal environment for kinetic studies. This is in contrast with other studies where 5-mm sapphire tubes were used apparently successfully for kinetic measurements on a two-phase hydrogenation system.[8] In these studies, conditions were significantly different and most notably reaction rates (≤ *ca.* 1.0 h^{-1}) were 1–2 orders of magnitude slower than we encountered. The diffusion problem could be alleviated to some extent by using 10 mm o.d. sapphire tubes, which are also commercially available.[5]

Mechanistic Studies. Rhodium(I) tertiary phosphine complexes have long been known to be excellent catalysts for the hydrogenation of alkene functionalities, at rates often orders of magnitude greater than the ones observed for imine hydrogenation in the current study.[14] One factor possibly contributing to the lower rates is the presence of a low equilibrium concentration of the enamine tautomer that is actually being hydrogenated (eq 2).

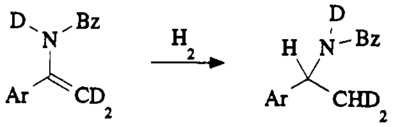


imine **1** enamine **3**

(2)

The incorporation of deuterium into the α-methyl site of imine **1** is clearly observed in the ^1H NMR spectrum in all the experiments performed in the presence of CD_3OD and presumably occurs because of the presence of the enamine tautomer (or corresponding deprotonated anion), where exchange of the nitrogen-bound proton with CD_3OD would be rapid.

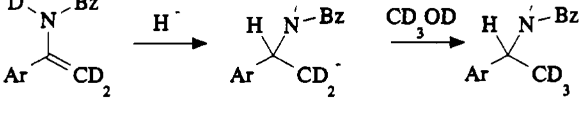
The possibility that the enamine tautomer is the species being hydrogenated is ruled out on the basis of two isotopic labeling experiments. In the first, the methyl group of imine **1** was deuterated and subsequent hydrogenation showed no significant incorporation of protons in the methyl site. Hydrogenation of the enamine would have resulted in a CHD_2 group in the amine **2** (eq 3).



D_3-**3**

(3)

A similar labeling experiment has been studied involving an iridium(III)–tertiary bis(phosphine)–hydride-based catalytic hydrogenation system and a different α-methyl imine with the same result.[15] Because reaction 1 is performed in the presence of CD_3OD, one further possibility not ruled out by the above results is that the enamine tautomer is still hydrogenated and that deuterium from the CD_3OD is incorporated, for example via transfer of anionic hydride (eq 4). This can be rejected because relatively rapid hydrogenation of the fully protio imine in the presence of CD_3OD results in essentially fully protio amine **2**.



(4)

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(13) The intensities of the diagonal and exchange cross peaks represent the amount of *Z*-isomer remaining and that converted to the *E*-isomer in 1.8 s, respectively; the intensity of the latter was 7.8% of the total intensity of the two peaks, this indicating a rate of 4.3% s^{-1} or 0.043 s^{-1} (155 h^{-1}). Details of the method may be found in *Chem. Rev.* **1990**, *90*, 939; accuracy is increased when the mixing time is short compared with the T_1 values of the species involved, a condition not maintained in our studies, but nevertheless we consider the estimated rates to be of the same order of magnitude as the hydrogenation rates.

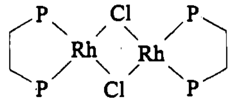
(14) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.

(15) Ng Cheong Chan, Y.; Osborn, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9400.

Some deuterium incorporation into **2** is evident in this experiment, but this is likely to result from exchange of protons for deuterium in imine **1** prior to hydrogenation.

The relative slowness of imine hydrogenation may result in part from the presence of only low concentrations of intermediate η^2-imine-bonded species.[1a]

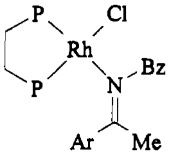
Characterization of Rhodium Complexes Present under Catalytic Conditions. In previous work, the active catalyst has usually been generated *in situ* from $[Rh(NBD)Cl]_2$ and the appropriate tertiary bis(phosphine). Addition of H_2 generates the $[Rh(P\text{-}P)Cl]_2$ species, for example $[Rh(diphos)Cl]_2$ (**4**) when P-P = diphos, which is the active catalyst precursor and is readily isolated.[10]



4

The $^{31}P\{^1H\}$ NMR spectrum of **4** (C_6D_6 solution) prepared by the literature method invariably shows two doublets, the major species (δ 73.5, $^1J(Rh\text{–}P)$ = 198.5 Hz) being assignable to **4** and an unassigned minor species (δ 77.5, $^1J(Rh\text{–}P)$ = 200.3 Hz). One possibility is that the minor component is the monomer [Rh(diphos)Cl] based on the larger $^1J(Rh\text{–}P)$ value. Similar monomer–dimer equilibria in complexes such as $[Rh(PCy_3)_2Cl]$ have been previously proposed with similar trends in coupling constants, *i.e.* $^1J(Rh\text{–}P)$ monomer > $^1J(Rh\text{–}P)$ dimer.[16,17]

When **4** is dissolved in 3:1 C_6D_6/CD_3OD, in the presence of 5–10 equiv of imine **1**, five species are observed in the $^{31}P\{^1H\}$ NMR spectrum. These include unchanged **4**, but the minor species noted above is absent. Two new ABX patterns are also observed consistent with the formation of monomeric species **5** and **6** with bound imine **1** (δ 70.0, $^1J(Rh\text{–}P)$ = 166.9 Hz, and δ 73.1, $^1J(Rh\text{–}P)$ = 203.5 Hz, $^2J(P\text{–}P)$ = 42.9 Hz; δ 71.7, $^1J(Rh\text{–}P)$ ~171 Hz, and δ 76.8, $^1J(Rh\text{–}P)$ = 199.4 Hz, $^2J(P\text{–}P)$ = 43.5 Hz). Coupling partners were confirmed by using a $^{31}P\text{–}^{31}P$ COSY experiment. Related observations have been previously reported.[1a] Two new unidentified doublet resonances (δ 71.9, $^1J(Rh\text{–}P)$ = 191.3 Hz and δ 71.9, $^1J(Rh\text{–}P)$ = 181.9 Hz) are also seen; one possibility is that these arise from *syn*- and *anti*-isomers of a $Rh(P\text{-}P)(imine)_2^+$ species.[1a]



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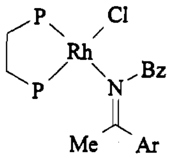


6

When the solution is pressurized with H_2 to greater than 1500 psi, the color changes from orange to red-brown and a radical change is observed in the $^{31}P\{^1H\}$ NMR spectrum. The major product (*ca.* 80% of the phosphorus intensity) has an AA′MM′XX′ spin system (A, M = ^{31}P; X = ^{103}Rh):[18] a corresponding hydride signal at δ −8.38 is also observed. These observations are consistent with the presence of a bridged hydride species of formulation $[\{Rh(diphos)\}_2(\mu\text{-}H)(\mu\text{-}X)]$ (**7**). Although this species is stable only under high pressure of hydrogen, the rate at which the complex decomposes under 1 atm of H_2 is sufficiently slow to allow further elucidation of the structure. Thus after a solution is transferred from the HP-NMR cell to a regular NMR tube under 1 atm of H_2, about 30% of the phosphorus intensity in the $^{31}P\{^1H\}$ NMR spectrum, shown in Figure 2, is due to **7**. Further decomposition, resulting primarily in the re-formation of **4**, is slow with half of the material decomposing in about 8 h. A $^1H\text{-}^{31}P$ HMQC experiment showed the hydride at δ −8.38 and the two ^{31}P resonances at δ 65.8 and 78.7 to be coupled and hence part of the same complex. The hydride resonance, shown in Figure 3, is a 17-line multiplet caused by an overlapping triplet of triplet of triplets ($^1J(Rh\text{–}H)$ = 23.5 Hz, $^2J(P_{trans}\text{–}H)$ = 56.5 Hz, $^2J(P_{cis}\text{–}H)$ = 13.4 Hz). Selective ^{31}P decoupling of the high-frequency phosphorus resonance collapses the hydride proton resonance to a triplet of triplets, with two small *cis* PH couplings being removed. Likewise, selective ^{31}P decoupling of the low-frequency phosphorus resonance collapses the hydride proton resonance to a triplet of triplets, with two large *trans* PH couplings being removed. Broadband ^{31}P decoupling reduces the hydride resonance to a triplet due to coupling to two equivalent ^{103}Rh nuclei (Figure 3). The nature of the other bridging ligand X is not revealed by NMR methods, but chloride is the most likely on the basis of the results of other experiments discussed below.

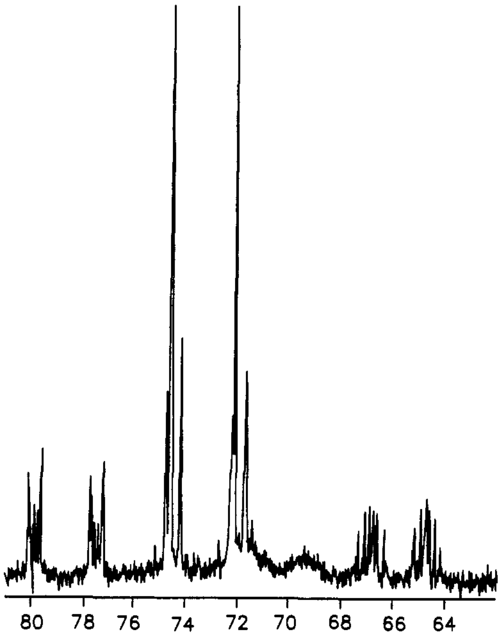
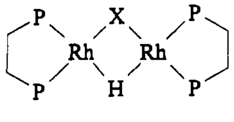


Figure 2. $^{31}P\{^1H\}$ NMR spectrum (3:1 C_6D_6/CD_3OD) of the reaction solution at 1 atm of H_2, after hydrogenation of imine **1** at 1500 psi of H_2 by using **4** as the catalyst. Peaks due to **7** are centered at about δ 80, 77.5, 67, and 65; major doublet is due to **4**.



7

In order to generate **7**, all of the components of the "catalytic mixture" must usually be present. Pressurizing a solution of **4** and excess imine **1** in C_6D_6 does not form **7**, implying that methanol is necessary for its formation. Pressurizing a solution of **4** in C_6D_6/CD_3OH in the absence of imine again does not generate **7**. However, **7** is generated when a mixture containing Proton Sponge in place of the imine is similarly pressurized. Thus the imine (or the amine hydrogenation product) probably functions as a base in generating **7** (eq 5). The fact that **7** can be generated in the absence of imine **1** precludes the possibility that the bridging ligand X is derived from the imine (or an amine).

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(16) van Gaal, H. L. M.; van den Bekerom, F. L. A. *J. Organomet. Chem.* **1977**, *134*, 237.

(17) Attempts to quantify the possible monomer–dimer equilibrium for **4** by measuring $^{31}P\{^1H\}$ spectra from 20 to 60 °C were thwarted by the poor solubility of **4** in C_6D_6; indeed, the minor species was detected only when some undissolved **4** was visible, while the ratio of major:minor species increased gradually from 15 to 25 over the temperature range 20–60 °C (six values).

(18) McKenna, S. T.; Andersen, R. A.; Muetterties, E. L. *Organometallics* **1986**, *5*, 2233.

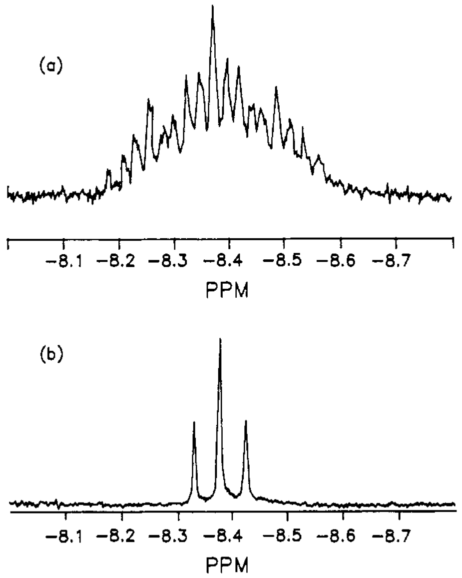
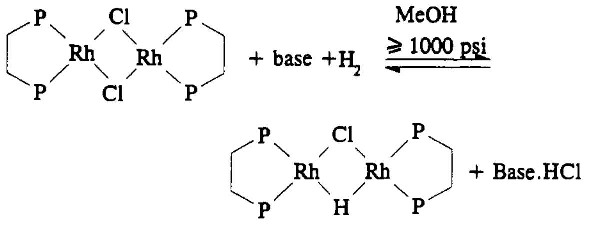


Figure 3. (a) The hydride resonance of **7** (spectrum measured in 3:1 C_6D_6/CD_3OD under 1 atm of H_2). (b) Broad-band ^{31}P-decoupled spectrum.



(5)

The rate of decomposition of **7** in the presence of unreduced imine **1**, under 1 atm of H_2, is much the same as in the presence of only the amine reaction product **2**, and this rate is much slower (by ~2 orders of magnitude) than that of imine reduction under high pressure. This implies that a stable insertion product is not formed from **7** and the imine, and indeed no such species is detected by NMR. Such insertions into the bridged hydride species [{Rh(dippe)}$_2$(μ-H)$_2$] have been demonstrated with the formation of amido–hydride complexes of the general type [{Rh(dippe)}$_2$(μ-H)(μ-NRR′)].[19] The findings are consistent with (i) a rate-determining reversible formation of a low concentration of an insertion product that is hydrogenated relatively rapidly at high H_2 pressure and/or (ii) the possibility that **7** is a catalyst precursor to an active species formed by oxidative addition of H_2 (*e.g.* to give a trihydride) or a net heterolytic cleavage of H_2 (*e.g.* to give a doubly hydride-bridged species). However, even at H_2 pressures of 2000 psi, solutions containing **7** and no imine (after complete reduction to amine) showed no detectable NMR resonances that could be attributed to other hydrides. A related tetrahydride species [{Rh(dippe)}$_2$H$_4$] has been found to be a marginal catalyst or catalyst precursor for imine reduction, but in this case catalysis is slow and eventually ceases due to the formation of a catalytically inert insertion product of the type [{Rh(dippe)}$_2$(μ-H)(μ-NRR′)].[19] The apparent lack of reactivity of **7** with imine **1** observed in the present study accounts for its relative longevity as a catalyst precursor.

Nearly identical results are found when the catalyst is generated *in situ* from [Rh(NBD)Cl]$_2$ and 2 equiv of diphos. Thus **7** is formed, as from **4**, as the major species although extra peaks are observed in the NMR spectra. For example, when a solution of [Rh(NBD)Cl]$_2$, 2 equiv of diphos, and excess imine **1** in 1:1 toluene-d_8/CD_3OD is pressurized to 1200 psi of H_2 at room temperature, the major product seen in the ^{31}P{^{1}H} NMR spectrum is **7** along with a small amount of **4**; however, there is an extra doublet at δ 57.9, ^1J(Rh–P) = 133 Hz (also present before the addition of hydrogen), due to the formation of [Rh(diphos)$_2$]Cl.[20] When the temperature of the pressurized solution is lowered, a new species appears and grows at the expense of [Rh(diphos)$_2$]Cl: by −90 °C, only a trace of [Rh(diphos)$_2$]Cl remains. The ^{31}P{^{1}H} NMR spectrum of the new species consists of two doublet of triplet resonances (^1J(Rh–P) = 100, 90 Hz; ^2J(P–P) = 15 Hz); a hydride resonance consistent with the formation of an AA′MM′NN′X (M, N = ^{31}P; X = ^{103}Rh; $^2J(P_{trans}$–H) ~ 139 Hz) spin system grows in concurrently, similar to that observed for *cis*-[RhH$_2$(dppp)$_2$]Cl.[21] These data suggest the formation of the *cis*-dihydride [RhH$_2$(diphos)$_2$]Cl. Earlier studies have noted that this species is not obtained from the reaction of [Rh(diphos)$_2$]Cl with 1 atm of H_2 at room temperature.[20,22]

Apart from chloride, another possibility for the bridging ligand X in **7** is methoxide, which could account for the importance of methanol in the catalytic process. In the event that X is methoxide, it seems likely that such a complex would be formed under catalytic conditions when [Rh(COD)(OMe)]$_2$ is used in place of [Rh(NBD)Cl]$_2$ as catalyst precursor. However, pressurizing a solution of [Rh(COD)(OMe)]$_2$ with diphos and excess imine in 3:1 C_6D_6/CH_3OH to 2000 psi does not result in the formation of **7** although relatively efficient imine hydrogenation is observed. The ^{31}P NMR spectrum of this mixture is dominated by two extremely broad ($\Delta\nu_{1/2}$ *ca.* 400–500 Hz) resonances and numerous other smaller peaks. Two broad featureless resonances (δ −8.7, $\Delta\nu_{1/2}$ *ca.* 240 Hz; δ −12.1, $\Delta\nu_{1/2}$ *ca.* 280 Hz) are also seen in the ^{1}H NMR spectrum. An AA′MM′XX′ spin system (A, M = ^{31}P; X = ^{103}Rh) of low intensity which is clearly different from that of **7** is observed in the ^{31}P{^{1}H} NMR spectrum (with δ = 80.0 and 62.8) and may be due to [{Rh(diphos)}$_2$(μ-H)(μ-OMe)]: a hydride signal at δ −7.70 (ttt, ^2J(P–P) = *ca.* 61 and 12 Hz, ^1J(Rh–H) = 23 Hz) is also observed, again consistent with this formulation. Of interest, and in contrast with the formation of **7** from **4**, these resonances tentatively associated with a bridged methoxide species are present even before the addition of H_2, implying some other source of hydride, presumably coordinated methoxide.

Preliminary data obtained when [Rh(diphos)I]$_2$ is likewise dissolved in 3:1 C_6D_6/CD_3OH in the presence of excess imine **1** and then pressurized to 1500 psi of H_2 suggest incomplete conversion to [{Rh(diphos)}$_2$(μ-H)(μ-I)] (^{31}P{^{1}H} NMR: δ 75.3, ^1J(Rh–P) ~ 196 Hz; 71.0, ^1J(Rh–P) ~ 167 Hz. ^{1}H NMR: δ −7.5 (br m). Low solubility and rapid decomposition of this product under only 1 atm of H_2 back to the starting material have hampered more complete characterization of this product.

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