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Parahydrogen derived illumination of pyridine based coordination products obtained from reactions involving rhodium phosphine complexes

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The reactions of $RhCl(PBz_3)_3$ with H_2 and pyridine or 4-methylpyridine yield $RhCl(H)_2(PBz_3)_2(py)$ and $RhCl(H)_2(PBz_3)_2(4\text{-Me-py})$, respectively. These species undergo hydride site exchange *via* the loss of the pyridyl donor and formation of $RhCl(H)_2(PBz_3)_2$ which contains equivalent hydride ligands; for the py system the activation free energy, $\Delta G^{\ddagger}_{300}$, is 57.4 ± 0.1 kJ mol^{-1} while for 4-Me-py the value is 59.6 ± 0.3 kJ mol^{-1}. These products only showed parahydrogen enhancement in the corresponding hydride resonances when a sacrificial substrate was added to promote hydrogen cycling. When $RhCl(PPh_3)_3$ was used as the precursor similar observations were made, while when $RhCl(PCy_3)_2(C_2H_4)$ was examined, H_2 addition led to the formation of the binuclear complex $(H)_2Rh(PCy_3)_2(\mu\text{-}Cl)_2Rh(H)_2(PCy_3)_2$ which was differentiated from $RhCl(H)_2(PCy_3)_2$ on the basis of the similarity in diffusion coefficient (5.5×10^{-9} m^2 s^{-1}) to that of $(H)_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ (5.3×10^{-9} m^2 s^{-1}). The detection of $RhCl(H)_2(PCy_3)_2(py)$ was facilitated when pyridine was added to a solution of $RhCl(PCy_3)_2(C_2H_4)$ before the introduction of H_2. During these reactions trace amounts of the double substitution products, $RhCl(H)_2(phosphine)(py)_2$, were also detected.

Introduction

Hydrogen exists in two forms, parahydrogen (*p*-H_2) and orthohydrogen (*o*-H_2).[1] The para form of H_2 exists as a nuclear singlet state where both hydrogen atoms have opposite spin. It can be prepared by cooling H_2 to 20 K in the presence of a suitable paramagnetic catalyst. When this form of hydrogen is involved in a chemical reaction where the two nuclei become distinct and maintain their original nuclear spin alignment, enhanced NMR signals can be observed. It has been recently shown for the situation where pure parahydrogen is employed as the reactant that $Ru(dpae)(CO)_2(H)_2$ (dpae = bisdiphenylarsinoethane) can be formed in a spin-selective reaction with $Ru(dpae)(CO)_2$ and that the two hydride ligands yield NMR signals that show a 31 000 fold increase in size over normal level.[2] The formation of a product in a pure spin state has therefore been achieved.

The parahydrogen (*p*-H_2) effect has also been called PHIP (parahydrogen induced polarisation)[3] and PASADENA (parahydrogen and synthesis allow dramatically enhanced nuclear alignment).[1] It has been extensively reviewed.[4] The PHIP approach has enabled the observation of several reaction intermediates which range from classical dihydrides[5] to species that contain agostic hydrides.[6] More recently, PHIP has been employed in the sensitisation of a hydroformylation product containing a single *p*-H_2 atom[7] and the transfer of polarisation *via* a ^{13}C nucleus to deuterium after the hydrogenation of a perdeuterated substrate.[8] This technique has also been used to enhance organic components that lie within a metal's ligand sphere during catalysis.[9]

One reason that metal hydride complexes are normally visible through this approach stems from the fact that hydride chemical shifts often fall in the normally clear region of the ^1H NMR spectrum between δ −5 and −25. Opportunities therefore exist to utilise the ability of metal complexes to bind stable ligands and then employ the associated hydride chemical shifts as information that is diagnostic of the ligand. If parahydrogen is employed in this approach, these signals should be visible even when the ligand is present in very low concentration. Wilkinson's catalyst, $RhCl(PPh_3)_3$, provides an ideal starting point for such a study since it is known to access $RhCl(H_2)(PPh_3)_3$, a species which contains a labile phosphine.[10] This system has been studied with parahydrogen and yields very broad hydride signals even at 295 K in the absence of any substrate.[11] Heaton *et al.*[12] have described how $RhCl(PPh_3)_3$ reacts with pyridine (py) and H_2, characterising $RhCl(H)_2(PPh_3)_2(py)$ and the double substitution products $Rh(H)_2(PPh_3)_2(py)_2{}^+Cl^-$ and $RhCl(H)_2(PPh_3)(py)_2$. Dragon *et al.*[13] have also reported on a similar series of reactions with the corresponding *para*-tolylphosphine ($P(p\text{-tol})_3$) containing system.

Here we report a study where the interactions of $Rh(H)_2(PBz_3)_2Cl$, $Rh(H)_2(PPh_3)_2Cl$ and $Rh(H)_2(PCy_3)_2Cl$ with pyridine (and 4-methyl pyridine) are followed. We employ $Rh(PBz_3)_3Cl$ (where PBz_3 = tribenzylphosphine), $Rh(PPh_3)_3Cl$ and $Rh(C_2H_4)(PCy_3)_2Cl$] (where PCy_3 = tricyclohexylphosphine) as the precursors. NMR measurements that include ^1H–^{15}N HMQC, ^1H–^{103}Rh HMQC, EXSY, DOSY and nOe techniques have been used to characterise the products and study their reactivity. In addition it is shown that the addition of the sacrificial hydrogen acceptor, 1-phenyl-1-propyne, dramatically increases the size of hydride signals that are detected for the key pyridine containing complexes.

Experimental

General methods and chemicals

All reactions and purifications were carried out under N_2 using glove box or Schlenk line techniques. Tetrahydrofuran (THF), toluene and hexane were distilled over sodium benzophenone ketyl under nitrogen prior to use. Ethanol was distilled over molecular sieves. Benzophenone (Aldrich), sodium (Lancaster), hydrogen (99.99%, BOC), tri(methyl)phosphine (PMe_3) (Aldrich) and $RhCl(PPh_3)_3$ (Aldrich) were used as received. Tri(benzyl)phosphine (PBz_3) (Aldrich) and

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tri(cyclohexyl)phosphine (PCy_3) (Aldrich) were purified by crystallisation from hot ethanol. 1-Phenyl-1-propyne (Aldrich) was degassed and stored under nitrogen and used without further purification. $Rh_2Cl_2(C_2H_4)_4$ was synthesised according to established methods[14] and then used for the synthesis of tris(tribenzylphosphine)rodium(I) chloride $RhCl(PBz_3)_3$ and $RhCl(C_2H_4)(PCy_3)_2$ which were stored in a glove box.[15]

Parahydrogen were prepared by cooling H_2 to 18 K using a helium refrigeration system in the presence of a paramagnetic material using the system described previously.[4e]

Synthesis of $RhCl(PBz_3)_3$

0.195 g (0.5 mmol) of $[RhCl(C_2H_4)_2]_2$ were reacted with 0.918 g (3 mmol) of PBz_3 in 10 ml toluene. After stirring for 30 min the solution was filtered and 20 ml of dry hexane added to precipitate the product. The orange–yellow product was collected, washed with dry hexane, and dried under vacuum. Yield 0.890 g (80%). FAB mass (*m*/*z*): 746 $[RhCl(P(CH_2Ph)_3)_2]^+$; 711 $[Rh(P(CH_2Ph)_3)_2]^+$; 406 $[RhP(CH_2Ph)_3]^+$; 315 $[RhP(CH_2Ph)_2]^+$; 223 $[RhP{=}CH{-}Ph]^+$.

NMR methods

The deuterated toluene and benzene (Aldrich) were dried over potassium and degassed prior to use. Pyridine-d_5 was dried over molecular sieve, while ^{15}N-labelled pyridine (Aldrich) was used as received. In a typical experiment 1 mg of the specified rhodium complex was transferred into an NMR tube fitted with a Young's valve in a nitrogen-filled glove-box. Pyridine and phenyl propyne were then added by micro-syringe in the glove box when necessary. Samples were then transferred to a high vacuum line where the NMR solvent was introduced by vacuum transfer. The resealable NMR tubes were then filled with 3 atm *p*-H_2, shaken and introduced into the NMR spectrometer which was pre-set to a specific temperature. In some cases, the solvent and *p*-H_2 were added before the ligand or substrate.

NMR spectra were recorded on Bruker DRX-400 spectrometers with ^{1}H at 400.13 MHz, ^{31}P at 161.9 MHz, ^{15}N at 40.6 MHz and ^{103}Rh at 15.737 MHz, respectively. ^{1}H NMR chemical shifts are reported in ppm relative to residual ^{1}H signals in the deuterated solvents (benzene-d_5, 7.13 and toluene-d_7, 2.13), ^{31}P{^{1}H} NMR in ppm downfield of an external 85% solution of phosphoric acid, and ^{103}Rh chemical shift are reported in ppm from the absolute frequency standard of 3.16 MHz. ^{15}N spectra are relative to pyridine at δ −60.6.[16] Modified ^{1}H–^{31}P, ^{1}H–^{103}Rh, ^{1}H–^{15}N HMQC (heteronuclear multiple quantum correlation) and 1D ^{1}H{^{31}P}, and nOe pulse sequences were used as previously described.[17] NOe spectra were analysed according to standard methods.[18]

A series of diffusion ordered spectra (DOSY) were collected on samples using the LEDbp pulse sequence.[19] Pulse-field gradients were incremented in 20 steps from 2% up to 95% of the maximum gradient strength in a linear ramp. Between 2400 and 3200 transients were recorded per experiment. Gradient lengths were selected between 2.8 and 3.0 ms, with a diffusion time of 75 ms, and an eddy current delay of 5 ms. After Fourier transformation and baseline correction, the diffusion dimension was processed using the Bruker Xwinnmr package (version 3.5) and the diffusion values were read directly from the spectra (referenced relative to 1.9×10^{-9} m^2 s^{-1} for D_2O at 298 K).

Results and discussion

Studies involving $RhCl(PBz_3)_3$

When $[RhCl(C_2H_4)_2]_2$ was reacted with 6 equivalents of tribenzylphosphine, PBz_3, only one species was produced according to ^{31}P NMR spectroscopy. This product yielded two ^{31}P resonances, one appearing as a doublet of triplets at δ 22.2 (J_{PP} = 38 Hz, J_{PRh} = 196 Hz) and the second as a doublet of doublets at δ 16.2 (J_{PP} = 38 Hz, J_{PRh} = 139 Hz). These features match those found for the analogous complex $RhCl(PPh_3)_3$[5f] and confirm that $RhCl(PBz_3)_3$ was prepared.

When a 1 mM solution of $RhCl(PBz_3)_3$ in toluene-d_8 was mixed with *ca.* 3 atm *p*-H_2 and the resultant reaction monitored by ^{1}H NMR spectroscopy at 295 K, two sets of hydride resonances were detected at δ −10.6 and −19.2. These resonances, illustrated in Fig. 1, are assigned to the hydride ligands, H_a and H_b, respectively of $RhCl(H)_2(PBz_3)_3$. The hydride resonance of $RhCl(H)_2(PBz_3)_3$, for the ligand *trans* to PBz_3, H_a, resonates at δ −10.6 and possesses a large coupling to a single ^{31}P centre of 163 Hz, while the hydride ligand *trans* to chloride, H_b, appears at δ −19.2 and couples to three *cis* phosphine ligands, with essentially identical J_{PH} values of 14 Hz (Table 1). This reaction is similar to the known reaction of H_2 with $RhCl(PPh_3)_3$, and related systems, that forms analogous Rh(III) product such as $RhCl(H)_2(PPh_3)_3$.[9] The corresponding ^{1}H{^{31}P} NMR spectrum (Fig. 1(b)) simplifies the original hydride resonances into doublets of antiphase doublets where J_{RhH_a} = 12 Hz, J_{HH} = 8 Hz, and J_{RhH_b} = 20 Hz. A gradient assisted ^{1}H–^{31}P HMQC experiment was used to probe the ^{31}P nuclei in this product. Two phosphorus signals were observed due to P_a and P_b at δ 32.3 (a doublet of doublets) and at δ −1.95 (a doublet of triplets) with $J_{P_aP_b}$ = 22, J_{P_aRh} = 113, and J_{P_bRh} = 93 Hz, respectively. A 2D ^{1}H–^{103}Rh HMQC spectrum located the ^{103}Rh centres resonance at δ −393, and confirmed that the molecule contained three ^{31}P centres.

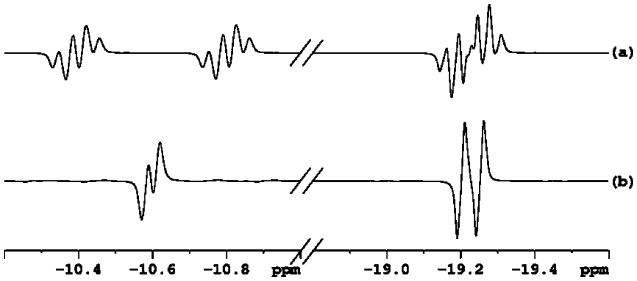


Fig. 1 Selected hydride regions of ^{1}H NMR spectra showing hydride resonances for $RhCl(H)_2(PBz_3)_3$ that were obtained with *p*-H_2 at 295 K in toluene-d_8. The antiphase components arise in transitions involving protons that originate from *p*-H_2. (a) ^{1}H NMR spectrum and (b) ^{1}H{^{31}P} NMR spectrum.

The dynamic behaviour of this complex was then monitored by EXSY spectroscopy. The data from these experiments revealed that no exchange processes involving the hydride ligands of $RhCl(H)_2(PBz_3)_3$ occurred at 273 K. However, when the measurements were repeated at 295 K (Fig. 2), mutual hydride site interchange and hydride site exchange into the signal at δ 4.57 due to free hydrogen were observed. In addition, a strong nOe connection from the hydride signal at δ −10.6 to an *ortho*-phenyl proton at δ 7.2 was detected; this corresponds to a resonance in the two equivalent axial phosphines. The mixing time used in this experiment was then varied and the intensity of the hydride signals modelled as a function of mixing time.[18] The associated rate constant for hydride-hydride exchange at 295 K was determined to be 1.9 s^{-1}, while that for the formation of free H_2 was found to be 1.38 s^{-1}.

A study of phosphine dissociation from $RhCl(H)_2(PPh_3)_3$, revealed that the PPh_3 ligand that is *trans* to hydride dissociates at a rate of 400 s^{-1} at 298 K.[20] This process was shown to proceeded *via* an intermediate with C_{2v} symmetry and results in hydride site interchange. The crystal structure of $RhCl(H)_2(P^tBu_3)_2$ confirmed this view.[21] It is therefore likely that hydride site interchange in $RhCl(H)_2(PBz_3)_3$ proceeds *via* phosphine loss.

When 5 μL of pyridine was introduced into a toluene-d_8 solution containing preformed $RhCl(H)_2(PBz_3)_3$, and the resulting sample degassed and refilled with 3 atm. *p*-H_2 the hydride signals from $RhCl(H)_2(PBz_3)_3$ disappeared. Two new hydride signals were, however, seen at δ −18.1 (H_a) and δ −18.6

Table 1 Key NMR data for metal dihydride products

Compound	^{1}H (metal–hydride) (δ, J/Hz)	^{31}P (δ, J/Hz)	^{103}Rh (δ)	^{15}N (δ)
$RhCl(H)_2(PBz_3)_2$ (295 K)	−10.6 (md) $^2J_{HH}$ = 8, $^1J_{HRh}$ = 12, $^2J_{HP_a}$ = 163	32.3 (dd) $^1J_{PRh}$ = 113, $^2J_{PP}$ = 22	−393	—
	−19.2 (m) $^2J_{HH}$ = 8, $^1J_{HRh}$ = 20, $^2J_{HP}$ = 14	−1.95(dt) $^1J_{PRh}$ = 93, $^2J_{PP}$ = 22		
$RhCl(H)_2(PBz_3)_2$(py) (255 K, py-d_5, stable)	−18.1 $^2J_{HH}$ = 11, $^1J_{HRh}$ = 14, $^2J_{HP_a}$ = 15	36.6 (d) $^1J_{PRh}$ = 120	119 (275 K)	−117(255 K)
	−18.6 $^2J_{HH}$ = 11, $^1J_{HRh}$ = 25, $^2J_{HP_b}$ = 13			
$RhCl(H)_2(PBz_3)$(py)$_2$ (255 K, py-d_5, stable)	−17.3 $^2J_{HH}$ = 11, $^1J_{HRh}$ = 14, $^2J_{HP_a}$ = 15	62.4 (d) $^1J_{PRh}$ = 155	856	—
	−18.3 $^2J_{HH}$ = 11, $^1J_{HRh}$ = 25, $^2J_{HP_b}$ = 13			
$RhCl(H)_2(PBz_3)_2$(4-Me-py) (255 K)	−18.1 (dtd) $^2J_{HH}$ = 11, $^1J_{RhH}$ = 15, $^2J_{HP}$ = 13	37.5 (d) $^1J_{RhP}$ = 120	—	—
	−18.6 (dtd) $^2J_{HH}$ = 11, $^1J_{RhH}$ = 24, $^2J_{HP}$ = 15			
$RhCl(H)_2(PPh_3)_2$ (295 K)	−9.3 (d, br), $^2J_{HP}$ = 159, $^2J_{HP}$ = 18, $^1J_{RhH}$ = 18.	−20.7 $^1J_{RhP}$ = 114	98.5 (275 K)	—
	−16.7 (q), $^2J_{HP}$ = *ca.* 15	−40.3 $^1J_{RhP}$ = 90		
$RhCl(H)_2(PPh_3)_2$(py) (263 K)	−16.5 $^2J_{HH}$ = 12, $^1J_{HRh}$ = 17, $^2J_{HP_a}$ = 12	45.7 (d) $^1J_{PRh}$ = 123	304 (275 K)	−111(263 K)
	−17.0 $^2J_{HH}$ = 10, $^1J_{HRh}$ = 21, $^2J_{HP_b}$ = 14			
$[RhCl(H)_2(PCy_3)_2]_2$	−22.6 (m) $^1J_{HRh}$ = 26.8, $^2J_{HP}$ = 13.7	51.8 (d) $^1J_{PRh}$ = 114	194 (295 K)	—
$RhCl(H)_2(PCy_3)_2$(py)	−18.9 (m) $^2J_{HH}$ = 10.4, $^1J_{HRh}$ = 30, $^2J_{HP}$ = 21.7	48.3 (d) $^1J_{PRh}$ = 114	337 (235 K)	−109(220 K)
	−19.7 (m) $^2J_{HH}$ = 10.4, $^1J_{HRh}$ = 30, $^2J_{HP_b}$ = 28.7			
$RhCl(H)_2(PCy_3)$(py)$_2$ (235 K py-d_5)	−18.3 (m) $^2J_{HH}$ = −10.7, $^1J_{HRh}$ = 24.7, $^2J_{HP}$ = 22.4	71.6 (d) $^1J_{PRh}$ = 142	408 (235 K)	−101(220 K)
	−19.0 (m) $^2J_{HH}$ = −10.7, $^1J_{HRh}$ = 24.6, $^2J_{HP}$ = 25.8			
$[Rh(H)_2(PCy_3)_2(py)_2]^+$ Cl^-	−19.6 (dt) $^1J_{HRh}$ = 15.2, $^2J_{HP}$ = 20.5	46.8 (d) $^1J_{PRh}$ = 112	—	—

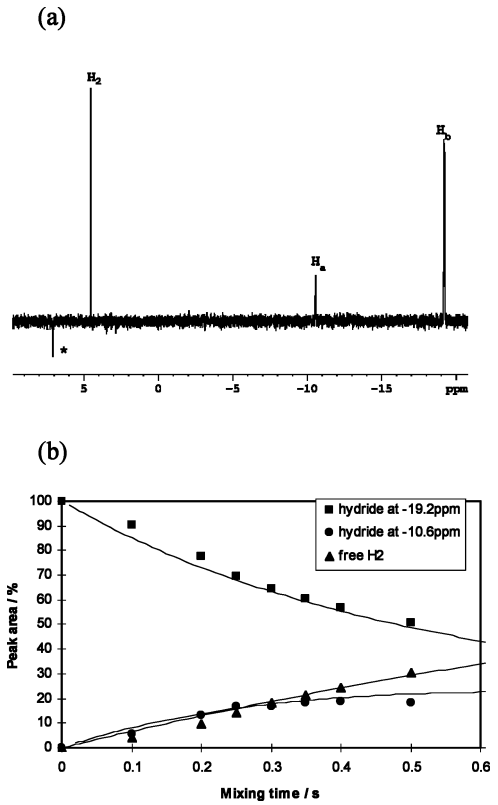


Fig. 2 (a) $^1H\{^{31}P\}$ nOe spectrum obtained when the hydride resonance for the site *trans* to chloride in $RhCl(H)_2(PBz_3)_3$ is excited (mixing time 0.25 s, at 295 K). Magnetisation transfer to H_2 and the hydride site *trans* to phosphine is indicated. The * indicates an nOe connection to the *ortho* phenyl protons of the benzyl group. (b) Kinetic profile showing the change in peak area as a function of mixing time for indicated species, with the continuous line indicating data obtained by simulation.

(H_b) which showed no enhancement. At 255 K, these hydride resonances appeared as pairs of doublets of doublets with J_{HH} = 11 Hz, J_{H_aRh} = 14 Hz, and J_{H_bRh} = 25 Hz in the corresponding $^1H\{^{31}P\}$ NMR spectrum. In the fully coupled ^{1}H spectrum each hydride showed an additional triplet splitting due to two ^{31}P nuclei where J_{H_aP} = 15 Hz and J_{H_bP} = 13 Hz respectively. The ^{31}P signal associated with the single phosphine environment in this product was located at δ 36.6 and appeared as a rhodium coupled doublet where J_{RhP} = 120 Hz. In addition, a signal for free phosphine was detected at δ −13.2. The corresponding 2D ^{1}H–^{103}Rh HMQC spectrum, shown in Fig. 3(a) (275 K), located a single ^{103}Rh resonance for this product at δ 119 which showed couplings to two ^{31}P centres. In order to confirm the presence of pyridine in this product, and define the chemical shift of the hydride ligand that is *trans* to pyridine, a further sample was prepared containing 5 μL of ^{15}N labelled pyridine. The corresponding $^1H\{^{31}P\}$ NMR spectrum revealed that the

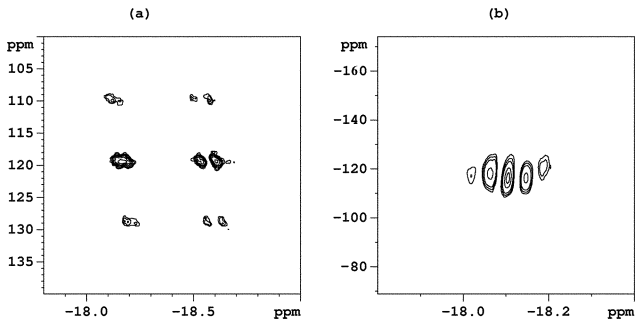
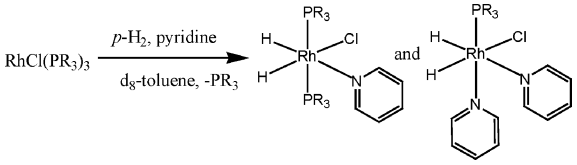


Fig. 3 Hydride region of 2D NMR spectra of $RhCl(H)_2(PBz_3)_2$(py) obtained *via* the reaction of $RhCl(H)_2(PBz_3)_3$ with pyridine in toluene-d_8 at 275 K. (a) ^{1}H–^{103}Rh HMQC spectrum obtained *via* hydride couplings, (b) ^{1}H–^{15}N HMQC spectrum of the ^{15}N labelled complex at 255 K.

resonance for H_a now possessed an additional 18 Hz coupling and thereby confirmed that this ligand is *trans* to pyridine.[22] A ^1H–^{15}N HMQC spectrum located the corresponding pyridine ^{15}N resonance at δ −117 (Fig. 3(b)). A signal for free pyridine was also located in this spectrum at δ −60.6. The product detected in these experiments has therefore been confirmed as $RhCl(H)_2(PBz_3)_2(py)$, with the ligand arrangement shown in Scheme 1.



Scheme 1 Reaction of $RhCl(PR_3)_3$ (R = benzyl, phenyl) with pyridine and H_2.

The hydride signals for $RhCl(H)_2(PBz_3)_2(py)$ failed to show any parahydrogen enhancement between 255 and 325 K, although the resonances themselves were strongly affected by temperature, coalescing at *ca.* 300 K. The hydride regions of a series of $^1H\{^{31}P\}$ NMR spectra recorded for this species between 265 and 325 K are shown in Fig. 4. The hydride ligands in this complex can therefore be concluded to interchange their positions on the NMR timescale. EXSY examination of $RhCl(H)_2(PBz_3)_2(py)$ system at 273 K, revealed the presence of only simple exchange from one hydride site to the other (Fig. 5). In addition, an nOe connection to a peak at δ 7.2 corresponding to a resonance for an *ortho*-phenyl proton of the phosphine was detected. Analysis of the magnetisation transfer data yielded a rate constant for hydride site interchange of 10.68 s^{-1} at 275 K when 5 μL of pyridine was employed. When this observation was repeated on a sample containing the same metal concentration and 40 μL of pyridine, the corresponding rate constant for hydride site exchange proved to be 10.38 s^{-1} and was hence identical to the earlier value within experimental error. This process is therefore independent of pyridine. This suggests the involvement of $RhCl(H)_2(PBz_3)_2$ and supports the view that it too has C_{2v} symmetry (Scheme 2). In order to

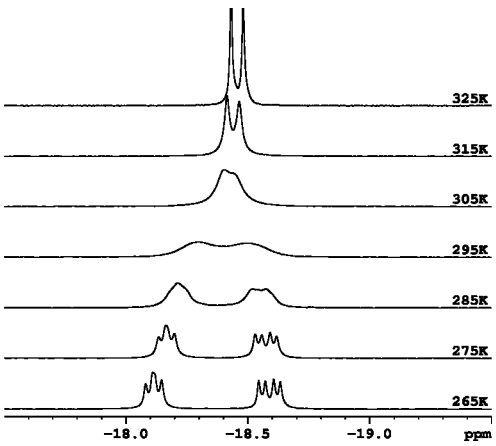
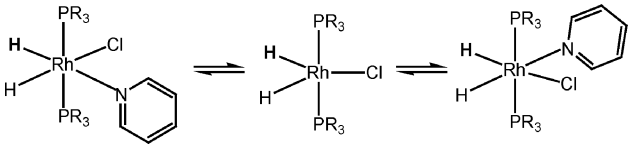


Fig. 4 The hydride region of $^1H\{^{31}P\}$ NMR spectra obtained from a pyridine doped sample of $RhCl(H)_2(PBz_3)_3$ and 3 atm pH_2 in toluene-d_8 between 265 and to 325 K Resonances for $RhCl(H)_2(PBz_3)_2(py)$ are visible.



Scheme 2 Mechanism for hydride site exchange observed in $RhCl(H)_2(PR_3)_2$(pyridine) (R = benzyl, phenyl).

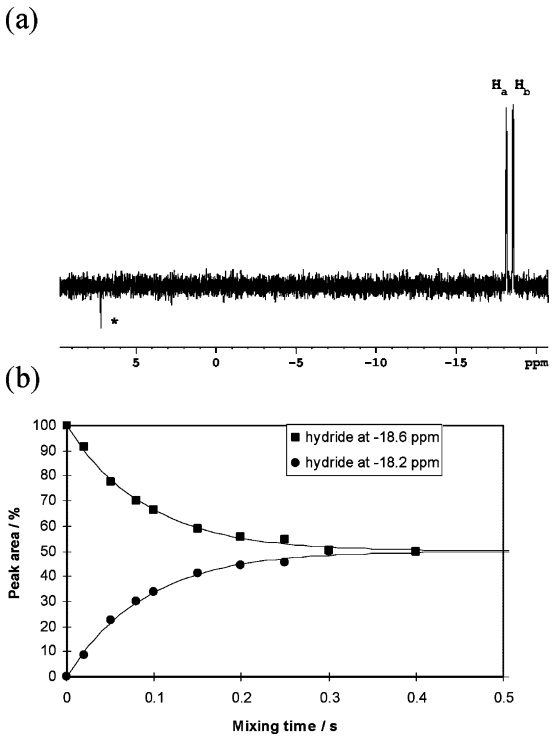


Fig. 5 (a) $^1H\{^{31}P\}$ nOe spectrum obtained when the resonance for the hydride ligand *trans* to chloride in $RhCl(H)_2(PBz_3)_2(py)$ is excited (mixing time 0.25 s, 275 K). The * indicates an nOe connection to the *ortho* phenyl protons of the benzyl group. (b) Kinetic trace showing the change in peak area as a function of mixing time for indicated species, with the continuous line indicating data obtained by simulation.

explore the dynamic behaviour of this system more fully, a combination of EXSY spectroscopy and line-shape analysis methods were employed. These data yielded the activation parameters $\Delta H^{\ddagger} = 98.6 \pm 3.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 137 \pm 12$ J K^{-1} mol^{-1} for the hydride–hydride exchange process. It should be noted, that at 273 K no hydride ligand exchange was observed for $RhCl(H)_2(PBz_3)_3$.

Pyridine was then replaced with 4-methylpyridine, and the analogous complex, $RhCl(H)_2(PBz_3)_2$(4-methylpyridine) characterised. The NMR data for this species can be found in Table 1. The variable temperature NMR spectra of $RhCl(H)_2(PBz_3)_2$(4-methylpyridine) revealed evidence for a similar dynamic process whereby the hydride ligands interchange identities. Line-shape analysis of appropriate spectra between 265 and 325 K yielded the activation parameters for the hydride-hydride exchange process, $\Delta H^{\ddagger} = 95.8 \pm 7.5$ kJ mol^{-1} and $\Delta S^{\ddagger} = 121 \pm 27$ J K^{-1} mol^{-1}. Unfortunately, the errors in these data suggest that no substantial differences exist between the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the two substrates. The rate of hydride exchange for the 4-methyl pyridine complex proved to be 1.6 s^{-1} while that of the pyridine system was 3.22 s^{-1} at 265 K. It is therefore clear that the rhodium 4-methylpyridine bond is less labile than the rhodium pyridine bond. This reflects the fact 4-methylpyridine is the stronger base and hence a better electron donor.

When 100% pyridine-d_5 was employed as the solvent, the NMR spectra obtained for the reaction of $RhCl(PBz_3)_3$ with H_2 contained evidence for a further product. In the corresponding ^1H NMR spectra (255 K) two pairs of hydride resonances were seen at δ −18.1, −18.6, due to $RhCl(H)_2(PBz_3)_2(py)$ and at δ −17.3 (H_c) and δ −18.3 (H_d) due to the new species. The resonances due to the new species appear as doublets of doublets upon ^{31}P decoupling with $J_{HH} = 11$ Hz, and $J_{HRh} = 25$ and $J_{HRh} = 14$ Hz, respectively. Comparison of the ^{31}P decoupled and fully coupled ^1H NMR spectra confirm that the new species contains one phosphine ligand, that is *cis* to both hydride ligands, and it is therefore identified as the double substitution product $RhCl(H)_2(PBz_3)(py)_2$ (Scheme 1).

We have previously reported that the size of the parahydrogen amplification observed for a series of binuclear dihydride complexes that were detected when $RhCl(CO)(PPh_3)_2$ was reacted with *p*-H_2 increased when a suitable hydrogen receptor such as styrene was added to the solution.[5g] We therefore examined the effect of adding styrene and 1-phenyl-1-propyne to the $RhCl(PBz_3)_3$–pyridine system. The addition of styrene proved to have no effect on the associated NMR spectra at 295 K, although, the addition of Ph–C≡C–Me led to the observation of broad parahydrogen enhanced hydride resonances at δ −18.3 and −18.6 at 295 K. When the reaction temperature was lowered to 273 K, the hydride signals resolved such that for the δ −18.1 signal (moved from δ −18.3 at 295 K) the coupling $J_{HH} = 11$ Hz, $J_{HRh} = 15$ Hz and $J_{HP} = 14$ Hz could be measured while for the signal at δ −18.6 the couplings $J_{HH} = 11$ Hz, $J_{HRh} = 25$ Hz and $J_{HP} = 13$ Hz could be determined (Fig. 6(a)). These spectral features, and additional ^{15}N, ^{31}P and ^{103}Rh data obtained for this species, match those obtained above for $RhCl(H)_2(PBz_3)_2(py)$ exactly. The observation of $RhCl(H)_2(PBz_3)_2(py)$ with parahydrogen enhanced hydride resonances therefore arises because the substrate, in this case 1-phenyl-1-propyne, promotes hydrogen cycling, and allows the $RhCl(H)_2(PBz_3)_2(py)$ to be detected before relaxation quenches the *p*-H_2 enhancement.

When the hydride exchange process was examined in the presence of Ph–C≡C–Me, the corresponding hydride exchange rate (275 K) proved to be 11.64 s^{-1} regardless of the excess of Ph–C≡C–Me (5–40 μL). The size of the observed parahydrogen enhancement seen for the hydride signals of $RhCl(H)_2(PBz_3)_2(py)$, however, increased as the proportion of Ph–C≡C–Me increased from 2 to 222 relative to $RhCl(PBz_3)_3$. There was, however, no evidence in these spectra for magnetisation transfer from the rhodium species into PhCH=CHMe, although, clearly more rapid hydrogen cycling is necessary to account for the parahydrogen amplification seen for the hydride resonances of $RhCl(H)_2(PBz_3)_2(py)$.

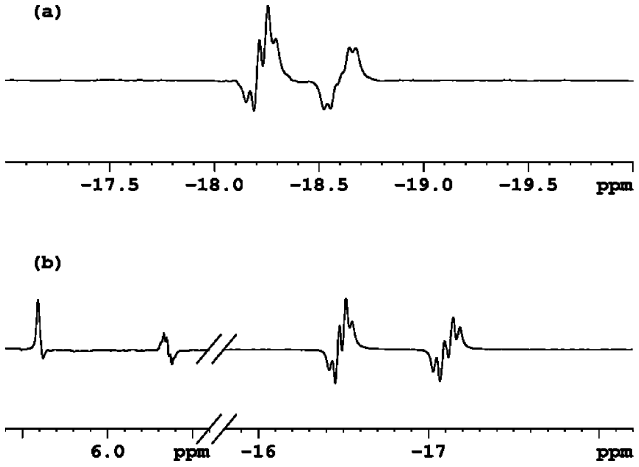


Fig. 6 (a). Hydride region of a ^1H NMR spectrum obtained when a sample of $RhCl(H)_2(PBz_3)_3$ was reacted with pyridine-^{15}N, phenylpropyne and 3 atm. of H_2 at 275 K (b) Hydride and alkyl regions of a $^1H\{^{31}P\}$ NMR spectrum obtained when a sample of $RhCl(H)_2(PPh_3)_3$ was reacted with pyridine-^{15}N, phenylpropyne and 3 atm of H_2 at 263 K.

Studies involving $RhCl(PPh_3)_3$

When a toluene-d_8 solution of $RhCl(PPh_3)_3$ was mixed with 3 atm H_2, and observed by NMR spectroscopy, the known dihydride $RhCl(H)_2(PPh_3)_3$ was detected *via* the associated hydride resonances at δ −9.3 and −16.7. A ^1H–^{103}Rh HMQC spectrum recorded on this sample at 275 K located a ^{103}Rh signal at δ 98.5 for this species. This samples was then taken into the glovebox and 5 μL of pyridine added before the NMR tube was refilled with 3 atm. of *p*-H_2. ^1H and $^1H\{^{31}P\}$ NMR spectra recorded at 295 K now contained two broad hydride resonances at δ −16.5 and −17.0 which showed no parahydrogen enhancement. At 263 K, these signals resolved upon ^{31}P decoupling into doublets of doublets for which $J_{HH} = 12$ Hz, $J_{HRh} = 17$ Hz and $J_{HRh} = 21$ Hz respectively. Additional J_{HP} triplet couplings of 12 and 14 Hz were then determined for the fully coupled spectra. A ^1H–^{103}Rh HMQC spectrum, recorded at 275 K, connected these two hydride signals to a ^{103}Rh signal at δ 304 which coupled to two ^{31}P centres. When ^{15}N labelled pyridine was employed, the δ −16.5 hydride showed an additional 15 Hz coupling at 263 K due to the *trans* ^{15}N label; the corresponding ^1H–^{15}N HMQC located a ^{15}N signal for this species at δ −111. The formation of $RhCl(H)_2(PPh_3)_2(py)$ is therefore indicated.[10,12]

This NMR tube was then opened and 10 μL of 1-phenyl-1-propyne, added, before being refilled with *p*-H_2. Monitoring of this sample by NMR spectroscopy then revealed that the hydride resonances of $RhCl(H)_2(PPh_3)_2(py)$ were polarised for ten minutes at 263 K (Fig. 6(b)). The NMR characteristics of this species were, however, again unaffected by the addition of the substrate. Small antiphase signals were now visible in these spectra at δ 6.4 and 5.6 (dq), due to the formation of the hydrogenation product Ph–CH=CH–Me (Fig. 6(b)).

Reactions of $Rh(Cl)(C_2H_4)(PCy_3)_2$

When $[RhCl(C_2H_4)_2]_2$ was reacted with four equivalents of the phosphine PCy_3 in toluene, the known complex $RhCl(PCy_3)_2(C_2H_4)$ was formed. NMR spectroscopy revealed that $RhCl(PCy_3)_2(C_2H_4)$ gave rise to a ^{31}P signal at δ 24.1 which possessed a 119 Hz Rh–P coupling to a ^{103}Rh signal that resonated at δ 357.

A toluene-d_8 solution containing $RhCl(PCy_3)_2(C_2H_4)$ was placed in an NMR tube fitted with a Young's tap, and 3 atm. of *p*-H_2 introduced. Spectra were then collected on this sample at 295 K. Normal hydride signals were immediately observed in the high field region of the ^1H NMR spectrum at δ −22.6 due to the formation of a stable product. This signal appears as a distorted doublet of triplets due to couplings to one rhodium ($J_{HRh} = 26.8$ Hz) and two phosphorus nuclei ($J_{HP} = 13.7$ Hz). In the corresponding ^{31}P NMR spectrum, a single peak is observed at δ 51.8 ($J_{RhP} = 114$ Hz) for this species while in the corresponding ^{103}Rh spectrum a triplet is observed at δ 194. Literature suggests that this product corresponds to $Rh(Cl)(H)_2(PCy_3)_2$,[23] but a tetrahydride dimer, analogous to $(H)_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(H)_2(PPh_3)_2$[5g] would also fit these data.

NMR methods involving diffusion measurements have been used to examine problems relating to molecular volume, hydrogen bonding and ion pairing.[24] This DOSY approach has recently been used to distinguish between mononuclear and binuclear products.[25] A series of DOSY spectra were therefore recorded on a sample containing hydrogen and a mixture of $RhCl(PPh_3)_3$ and $RhCl(PCy_3)_2(C_2H_4)$ at 295 K. Reaction with H_2 led to the rapid formation of $(H)_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$, and the product yielding the signal at δ −22.6. The diffusion coefficient of the known species $(H)_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2$ proved to be 5.3×10^{-9} m^2 s^{-1} while that for the unknown species yielded a very similar diffusion coefficient of 4.8×10^{-9} m^2 s^{-1}. The similarities in these values suggest that the molecules concerned have similar volumes. We therefore conclude that $Rh(Cl)(H)_2(PCy_3)_2$ is actually the tetrahydride dimer $(H)_2Rh(PCy_3)_2(\mu\text{-}Cl)_2Rh(H)_2(PCy_3)_2$. As a further control experiment, a sample of $RhCl(PCy_3)_2(C_2H_4)$ and H_2 alone was also examined under the same conditions, the δ −22.6 signal now corresponded to a species with diffusion coefficient 5.5×10^{-9} m^2 s^{-1}. The reproducibility of these data supports this conclusion.

When pyridine was added to this sample, the hydride resonance at δ −22.6 remained even when the sample was warmed to 333 K. This suggests that once $(H)_2Rh(PCy_3)_2(\mu\text{-}Cl)_2Rh(H)_2(PCy_3)_2$ is formed it is relatively stable. However,

when 5 μL of pyridine was added to a toluene-d_8 solution of the precursor, $RhCl(PCy_3)_2(C_2H_4)$, and the subsequent reaction with *p*–H_2 monitored at 235 K, three hydride resonances were observed; the signal at δ −22.6 described above, and a pair of doublets of triplets of doublets at δ −18.9 and −19.7. The logical identity of this species is $Rh(Cl)(H)_2(PCy_3)_2(py)$.

When the pyridine concentration was increased to 30 μL, the δ −22.6 signal disappeared, while those for $Rh(Cl)(H)_2(PCy_3)_2(py)$ remained, and a second pair of hydride resonances were observed at δ −18.2 and −18.7 which appeared as simple doublets of doublets of doublets. Signals for this species were clearly visible in neat d_5-pyridine solution. The corresponding hydride resonances appeared at δ −18.3 and −19.0 in pyridine-d_5, and showed strong parahydrogen enhancement at 235 K. Under these conditions, the signals appear as distorted antiphase doublets of doublets of doublets and proved to be coupled in the corresponding ^1H–^1H COSY NMR dataset. In the corresponding ^1H–^{31}P HMQC correlation, a single ^{31}P signal was located at δ 71.6 ($J_{RhP} = 142$ Hz). When a sample was prepared using ^{15}N labelled pyridine, the resonance at δ −18.3 showed an additional 20 Hz coupling due to the *trans* ^{15}N centre which resonates at δ −101. The structure of $Rh(Cl)(H)_2(PCy_3)(py)_2$ is indicated in Scheme 1.

Upon warming this sample to 335 K, a new species yielding a single hydride resonance at δ −19.6 was observed. This signal appeared as doublet of triplets due to a single HRh coupling and two equivalent *cis* HP splittings. A ^1H–^{31}P HMQC correlation spectrum revealed that this hydride resonance coupled to a ^{31}P signal at δ 46.8. On the basis of this data and studies of Heaton *et al.*,[12] the product yielding these signals in assigned to the ionic complex $[Rh(H)_2(PCy_3)_2(py)_2]^+Cl^-$.

In-situ reaction of $RhCl(PCy_3)_2(C_2H_4)$ with *p*-H_2 in the presence of PMe_3 and pyridine

^1H NMR observation of a toluene-d_8 solution containing 1 equivalent of PMe_3, 3 atm. *p*-H_2, and a mixture of $[Rh(Cl)(PCy_3)_2]_2$ and $RhCl(PCy_3)_2(C_2H_4)$, led to the observation of strong *p*-H_2 based signals at δ −9.4 and −18.6. The NMR data for the product giving rise to these signals matched that previously reported for $Rh(Cl)(H)_2(PMe_3)_3$ with $[Rh(H)_2(PMe_3)_4]Cl$ being detected at greater PMe_3 loadings.[14] The addition of pyridine to these systems failed to enable the detection of any further species. This suggests that the Rh–PMe_3 bond is too strong to be readily broken and that systems based on $Rh(Cl)(PMe_3)_3$ or $[Rh(PMe_3)_4]Cl$ are unsuitable as precursors for a pyridine sensor.

Conclusions

In this paper, we have used the fact that both $RhCl(PBz_3)_3$ and $RhCl(PPh_3)_3$ add H_2 to form Rh(III) dihydrides with labile phosphine ligands to enable the detection of $RhCl(H)_2(PR_3)_2$(pyridine). The corresponding pyridine adducts have been characterised by multinuclear NMR spectroscopy. In the case of the PBz_3 ligand system we also employed 4-methylpyridine as a substrate. EXSY spectroscopy revealed that these $RhCl(H)_2(PBz_3)_2(L)$ systems undergo hydride site interchange *via* nitrogen donor dissociation and the formation of the 16-electron intermediate $RhCl(H)_2(PR_3)_2$ with equivalent hydride ligands. The activation parameters for this process were very similar for both pyridine and 4-methylpyridine. The large positive $\Delta S^{\ddagger}$ values of 137 ± 12 and 121 ± 27 J K^{-1} mol^{-1} respectively are consistent with a dissociative process. For these systems, the activation free energy, $\Delta G^{\ddagger}_{300}$, proved better defined, and corresponds to 57.4 ± 0.1 kJ mol^{-1} while for 4-methylpyridine the value is 59.6 ± 0.3 kJ mol^{-1}. This confirms that the barrier to the loss of 4-methylpyridine is 2.2 ± 0.4 kJ mol^{-1} higher than that for pyridine and accounts for the higher kinetic stability of such complexes.[26]

In this study we aimed to demonstrate that parahydrogen can be used to facilitate the detection of weakly bound ligands *via* the observation of substantially enhanced and diagnostic hydride signals in a suitable receptor complex. The intrinsic chemistry of these systems however means that they proved unsuitable for this role since they fail to exchange free and bound hydrogen at a sufficient rate. Nonetheless, the addition of a sacrificial substrate that acts to pull hydrogen through the metal-based manifold does enable enhanced hydride resonance to be observed for the pyridine containing dihydride adducts.

In an effort to activate the system to H_2 addition, we also studied the effect of replacing PPh_3 with both PCy_3 and PMe_3. Because of the large cone angle of PCy_3 and the desire to start with a pure complex we selected $RhCl(PCy_3)_2(C_2H_4)$ as a suitable precursor. We were therefore surprised when the preformed $Rh(Cl)(H)_2(PCy_3)_2$ we expected to obtain *via* H_2 addition to $RhCl(PCy_3)_2(C_2H_4)$ failed to coordinate the added pyridine ligand. This proved to be consistent with a revised formulation of the stable H_2 addition product as the tetrahydride dimer $(H)_2Rh(PCy_3)_2(\mu\text{-}Cl)_2Rh(H)_2(PCy_3)_2$.[23] The order of ligand addition, proved to be critical since when $RhCl(PCy_3)_2(C_2H_4)$ was reacted with pyridine first and H_2 added later, the formation of $Rh(Cl)(H)_2(PCy_3)_2(py)$ was indicated. This suggests that $RhCl(PCy_3)_2(py)$ was formed,[12,13] and H_2 addition to form $Rh(Cl)(H)_2(PCy_3)_2(py)$ becomes possible. Neither $Rh(Cl)(H)_2(PMe_3)_3$ nor $[Rh(H)_2(PMe_3)_4]Cl$, however, showed any sign of reacting with pyridine.

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