Hydrogenation Studies Involving Halobis(phosphine)–Rhodium(I) Dimers: Use of Parahydrogen Induced Polarisation To Detect Species Present at Low Concentration

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Abstract: Reaction of $[RhCl(PPh_3)_2]_2$ with parahydrogen revealed that the binuclear dihydride $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ and the tetrahydride complex $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)]_2$ are readily formed. While magnetisation transfer from free H_2 into both the hydride resonances of the tetrahydride and $[Rh(H)_2Cl(PPh_3)_3]$ is observable, neither transfer into $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ nor transfer between the two binuclear complexes is seen. Consequently $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)]_2$ and $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ are not connected on the NMR timescale by simple elimination or addition of H_2. The rapid exchange of free H_2 into the tetrahydride proceeds via reversible halide bridge rupture and the formation of $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)RhCl(H)_2(PPh_3)_2]$. When these reactions are examined in CD_2Cl_2, the formation of the solvent complex $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(CD_2Cl_2)(PPh_3)]$ and the deactivation products $[Rh(Cl)(H)(PPh_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(Cl)(H)(PPh_3)_2]$ and $[Rh(Cl)(H)(CD_2Cl_2)(PPh_3)(\mu\text{-}Cl)(\mu\text{-}H)Rh(Cl)(H)(PPh_3)_2]$ is indicated. In the presence of an alkene and parahydrogen, signals corresponding to binuclear complexes of the type $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2(Rh)(PPh_3)(alkene)]$ are detected. These complexes undergo intramolecular hydride interchange in a process that is independent of the concentration of styrene and catalyst and involves halide bridge rupture, followed by rotation about the remaining Rh–Cl bridge, and bridge reestablishment. This process is facilitated by electron rich alkenes. Magnetisation transfer from the hydride ligands of these complexes into the alkyl group of the hydrogenation product is also observed. Hydrogenation is proposed to proceed via binuclear complex fragmentation and trapping of the resultant intermediate $[RhCl(H)_2(PPh_3)_2]$ by the alkene. Studies on a number of other binuclear dihydride complexes including $[(H)(Cl)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Rh(CO)(PMe_3)]$, $[(H)_2Rh(PMe_3)_2(\mu\text{-}Cl)_2Rh(CO)(PMe_3)]$ and $[HRh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)_2Rh(CO)(PMe_3)]$ reveal that such species are able to play a similar role in hydrogenation catalysis. When the analogous iodide complexes $[RhI(PPh_3)_2]_2$ and $[RhI(PPh_3)_3]$ are examined, $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)_2]$, $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)]_2$ and $[Rh(H)_2I(PPh_3)_3]$ are observed in addition to the corresponding binuclear alkene–dihydride products. The higher initial activity of these precursors is offset by the formation of the trirhodium phosphide bridged deactivation product, $[\{(H)(PPh_3)Rh(\mu\text{-}H)(\mu\text{-}I)(\mu\text{-}PPh_2)Rh(H)(PPh_3)\}(\mu\text{-}I)_2Rh(H)_2(PPh_3)_2]$

Keywords: homogeneous catalysis · hydrogenation · NMR spectroscopy · parahydrogen · rhodium

Introduction

Transition-metal complexes are used to catalyse an enormous range of chemical reactions in solution, many of which are of considerable industrial or synthetic significance. However, probably the most extensively studied group of homogeneous catalysts are those associated with the hydrogenation of unsaturated carbon–carbon bonds, with by far the best known and most widely used of these being $[RhCl(PPh_3)_3]$.[1] Discovered by Wilkinson and his co-workers in 1965 (and often referred to as Wilkinson's catalyst), this species was found to be capable of effecting the rapid homogeneous hydrogenation of alkenes at ambient temper-

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atures and pressures,[2,3] and although the slow reduction of unsaturated alkenes by H_2 in the presence of metal ions such as Ag^+ or Cu^{2+} was already known,[4] $[RhCl(PPh_3)_3]$ represented the first practical catalyst system. The chemistry of $[RhCl(PPh_3)_3]$ is dominated by reactions involving either the substitution of one phosphine ligand to yield *trans* products of the form $[RhCl(CO)(PPh_3)_2]$ or $[RhCl(C_2H_4)(PPh_3)_2]$, or the oxidative addition of small molecules producing Rh^{III} complexes. In addition to facilitating efficient hydrogenation under ambient conditions, $[RhCl(PPh_3)_3]$ is capable of promoting selective hydrogenation of C=C or C≡C groups in the presence of other easily reducible functionalities such NO_2 or CHO.[1,3] At the same time, interest in $[RhCl(PPh_3)_3]$ is not solely limited to hydrogenation since hydrosilation, decarbonylation, and transfer dehydrogenation reactions can also be initiated.[1]

The mechanism by which $[RhCl(PPh_3)_3]$ catalyses the hydrogenation of alkenes has been the subject of extensive research with the core mechanistic pathway proposed to involve four key intermediates, $[RhCl(PPh_3)_2]$, $[RhCl(H)_2(PPh_3)_2]$, $[RhCl(H)_2(alkene)(PPh_3)_2]$ and $[RhCl(alkyl)(H)(PPh_3)_2]$. Whilst the extremely reactive 14 electron species, $[RhCl(PPh_3)_2]$, is never observed in solution under hydrogenation conditions, it has been generated during flash photolysis studies[5] on $[RhCl(CO)(PPh_3)_2]$ and a solid sample of $[RhCl(PtBu_3)_2]$, stabilised by the bulky phosphine ligands, has been prepared.[6] Despite the resultant low concentration of $[RhCl(PPh_3)_2]$,[7,8] it remains kinetically significant since H_2 addition to it is 10^4 times faster than that to $[RhCl(PPh_3)_3]$.[9] Indeed, based on results with $[RhCl[P(p\text{-tolyl})_3]_3]$, Tolman proposed that about 90% of the $[RhCl(H)_2(PPh_3)_3]$ in solution is formed via $[RhCl(PPh_3)_2]$.[10] A number of related species have been synthesised using bulky phosphines that mimic the H_2 addition product $[RhCl(H)_2(PPh_3)_2]$ and these culminated in a crystal structure for $[RhCl(H)_2(PtBu_3)_2]$.[6] This complex possesses approximately C_{2v} symmetry, with equivalent and mutually *trans*-$PtBu_3$ ligands and matches that proposed by Brown for $[RhCl(H)_2(PPh_3)_2]$.[7] Alkene coordination to the resultant 16 electron dihydride species corresponds to the next step in the cycle, and a number of geometries for $[RhCl(H)_2(alkene)(PPh_3)_2]$ are possible, even though this complex has traditionally been depicted with *trans* phosphines. However, when crystal structure data results were used to enable the energies of potential $[RhCl(H)_2(alkene)(PPh_3)_2]$ intermediates to be quantified for many substrates (such as cyclohexene and bicylco[2.2.1]heptene), complexes with *trans* phosphine arrangements were found to be highly sterically strained due to interactions between the coordinated alkene and the other ligands.[11] Only with much smaller alkenes such as *cis*-but-2-ene do alkene dihydride complexes with *trans* phosphines result in viable intermediates. Thus, intermediates with *cis* phosphines may exist at greater concentrations than those with *trans* arrangements, and based on modelling studies with cyclohexene, they may even have the higher activity.[12] A further complication arises from the fact that coordination of alkene to $[RhCl(H)_2(PPh_3)_2]$ is reversible.[11] However, it should also be noted that in the case of alkenes that coordinate more strongly than cyclohexene such as styrene, Halpern proposed that an additional parallel route to hydrogenation exists, via a complex containing two alkene ligands and only one phosphine.[13] Indeed, the kinetic studies of Halpern suggest that under the catalytic conditions usually employed with $[RhCl(PPh_3)_3]$, the majority of the hydrogenation proceeds via this bis(alkene) route.

Theoretical methods using PH_3 as the phosphine have also been applied to this problem by Dedieu, Morukuma and others.[14–16] On the basis of these studies, two pathways involving intermediates with *cis*- or *trans*-phosphine ligands were validated, with the *trans* pathway typically corresponding to the lower energy route. Interestingly, the *cis*- and *trans*-phosphine pathways were shown to have different rate limiting steps corresponding to reductive elimination in the former and alkene insertion in the latter. It was also noted that the relative energies of the species might change when bulkier PPh_3 ligands were involved along with alkenes other than C_2H_4.

There is a further twist to these descriptions since in the initial publications concerning solutions of $[RhCl(PPh_3)_3]$, Wilkinson noted the gradual formation of the virtually insoluble dimeric complex $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$.[2] This complex has been shown to react with hydrogen according to UV and ^{31}P NMR spectroscopy to form $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ rather than $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)]_2$ as originally proposed by Wilkinson. The $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ dimer thus provides access to another potential hydride containing intermediate.[2] Indeed, Tolman revealed that the equilibrium constant for the formation of $[Rh(H)_2\{P(p\text{-tolyl}_3)_2\}_2(\mu\text{-}Cl)_2Rh\{P(p\text{-tolyl})_2\}_2]$ from $[RhCl[P(p\text{-tolyl})_3]_2]_2$ and H_2 is only 3.6 times lower than that for the formation of $[RhCl(H)_2(PPh_3)_3]$ from $[RhCl(PPh_3)_3]$. In addition, he also obtained evidence for the transfer of the hydride ligands of $[Rh(H)_2\{P(p\text{-tolyl}_3)_2\}_2(\mu\text{-}Cl)_2Rh\{P(p\text{-tolyl})_2\}_2]$ to cyclohexene while reforming $[RhCl[P(p\text{-tolyl})_3]_2]_2$, and subsequently estimated that as much as 25% of the cyclohexene hydrogenation might occur via this route.

These studies clearly reveal that the detailed study of reaction mechanisms requires the direct detection and monitoring of the key reaction intermediates. Since these species are by their nature present in low concentration, NMR might initially be thought to be unsuitable for this work. One route to achieving high concentrations of reactive species is to use photochemistry to prepare them at temperatures where they are stable. Through the use of this approach, Ball recently characterized the first σ-alkane complex by NMR spectroscopy.[17] However, another method exists involving the independent synthesis of molecules in specific nuclear spin states. Under these conditions, the observable NMR signals have strengths that are not governed by Boltzmann statistics but rather by the efficiency of the initial nuclear spin state preparation. In this study, the technique first described by Bowers and Weitekamp involving the addition of dihydrogen enriched in the *para*-spin state is employed to achieve this.[18] To date, *p*ara*h*ydrogen *i*nduced *p*olarisation or PHIP has been used to characterise metal dihydrides formed by H_2 oxidative addition in a rapidly expanding number of systems which include complexes of Ru^0, Rh^I,

Ta^{III}, Ir^{I} and Pt^{0}, and a number of reviews describe the benefits of this approach.[19] Studies of $[RhCl(PPh_3)_3]$ have been featured in this area, with complexes of the type $[RhCl(alkene)(H)_2(PPh_3)_2]$ having *cis*-phosphine ligands and coordinated styrenes being previously described.[20] Here we describe how parahydrogen induced polarisation, and normal NMR methods can be employed with $[RhCl(PPh_3)_2]_2$, $[RhCl(PPh_3)_3]$, $[RhI(PPh_3)_2]_2$ and $[RhI(PPh_3)_3]$ to detect a number of previously unseen species and demonstrate their involvement in hydrogenation. The primary thrust of this work focuses on exploring the role that binuclear intermediates play in the hydrogenation reaction. Some of this work has already been published in preliminary communication form.[21]

Experimental Section

All sample preparations were performed using either a nitrogen filled glove box or a Schlenk line. Solvents were dried and degassed prior to use using potassium for the C_6D_6 and C_7C_8 and molecular sieves for CD_2Cl_2 and $CDCl_3$. NMR measurements were made using NMR tubes that were fitted with J. Young Teflon valves and solvents were added by vacuum transfer on a high vacuum line. Triphenyl phosphine (Aldrich), trimethyl phosphine (Aldrich) and hydrogen (99.99%, BOC) were used as received. $[RhCl(PPh_3)_2]_2$, $[RhCl(PPh_3)_3]$, $[RhCl(CO)(PMe_3)_2]$ and $[RhI(CO)(PMe_3)_2]$ were prepared according to established methods.[22] $[RhI(PPh_3)_3]$ was prepared by refluxing an ethanol solution containing PPh_3 (3.0 g), $RhCl_3{\cdot}3H_2O$ (0.5150 g) and LiI (2.0 g) under an N_2 atmosphere. Selected spectroscopic data: ^1H NMR (C_7D_8, 273 K): $\delta = 7.71$ (m, *o*-H), 7.25 (m, *m*-H), 6.87 (m, *p*-H); ^{31}P NMR (CD_2Cl_2, 263 K): $\delta =$ 44.35 (dt, $^1J_{P,Rh} = 195.6$ Hz, $^2J_{P,P} = 34.7$ Hz, *P*Ph_3/*trans* to iodide), 28.62 (dd, $^1J_{P,Rh} = 138.8$ Hz, $^2J_{P,P} = 34.7$ Hz, *P*Ph_3/*trans* to P). Although $[RhI(PPh_3)_2]_2$ could be produced by warming solutions of $[RhI(PPh_3)_3]$, the best results were obtained by refluxing a toluene solution containing $[RhCl(PPh_3)_3]$ (100 mg) and LiI (0.15 g) for 18 h. After cooling, the fine deep red product was separated by filtration and purified by washing with dry toluene or hexane. Selected spectroscopic data: ^1H NMR (C_7D_8, 273 K): $\delta = 7.92$ (m, *o*-H), 7.72 (m, *m*-H), 7.00 (m, *p*-H); ^{31}P NMR (C_6D_6, 295 K): $\delta = 50.2$ (d, $^1J_{PRh} = 190.0$ Hz, *P*Ph_3)].

For the PHIP experiments, hydrogen enriched in the *para* spin state was prepared by cooling H_2 to 77 K over a paramagnetic catalyst as described previously.[23] A pressure of H_2 equivalent to ca. 3 atm at 298 K was introduced into the NMR tube on a high vacuum line. The samples were thawed immediately prior to use and introduced into the NMR spectrometer at the pre-set temperature. parahydrogen-enhanced NMR spectra were recorded on a Bruker DRX-400 spectrometer with ^1H at 400.130, ^{31}P at 161.975, ^{13}C at 100.613, and ^{103}Rh at 12.594 MHz, respectively. ^1H NMR chemical shifts are reported in ppm relative to residual ^1H NMR signals in the deuterated solvents ([D_5]benzene, $\delta = 7.13$, and [D_7]toluene, $\delta = 2.13$). $^{31}P\{^1H\}$ NMR spectra are reported in ppm downfield of an external 85% solution of phosphoric acid, ^{13}C NMR spectra are reported relative to [D_6]benzene, $\delta = 128.0$, and [D_8]toluene, $\delta = 21.3$, and ^{103}Rh spectra are reported relative to 12.64 MHz, $\delta = 0$. Modified ^1H-^1H, -COSY, -HMQC, and -NOESY pulse sequences were used as previously described.[24]

The NOE spectra were analysed according to standard methods.[25] Importantly, no exchange cross peaks to free hydrogen were observed for the range of mixing times used to extract rate information and a simple two-site exchange mechanism was assumed. The rate of hydride interchange, k [s^{-1}], was determined for a mixing time, t_m, using Equation (1), where I is the ratio of intensities of the diagonal and exchange cross peaks.

$$k = \frac{1}{t_m}\left(\frac{I+1}{I-1}\right) \quad (1)$$

Results and Discussion

Observations on the reaction of $[RhCl(PPh_3)_2]_2$ (1) with H_2—Characterisation and dynamic behaviour of $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)]_2$: When a C_6D_6 solution of $[RhCl(PPh_3)_2]_2$ (**1**) is observed by ^1H NMR spectroscopy under *n*-H_2 (*n* = normal) at 295 K, two distinct hydride resonances are observed in the high-field region of the spectrum at δ −19.45 and −20.01, respectively. Figure 1a illustrates the corresponding $^1H\{^{31}P\}$ spectrum where both these resonances appear as rhodium coupled doublets and can hence be deduced to arise from terminal hydride ligands. Surprisingly, the signal intensity of the δ −20.01 resonance was temporarily increased relative to that of the δ −19.45 peak if the NMR sample was shaken and immediately returned to the probe. This imbalance rapidly decays until after approximately 30 seconds the initial signal intensities are restored. It should also be noted that the observation of the δ −20.01 resonance is totally suppressed during the hydrogenation experiments described later.

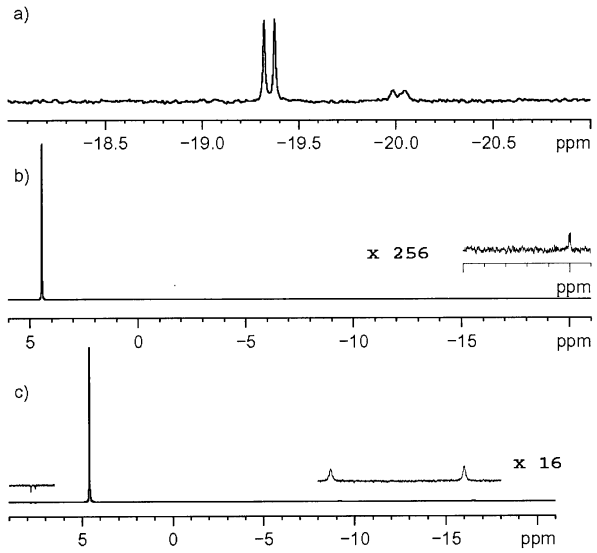
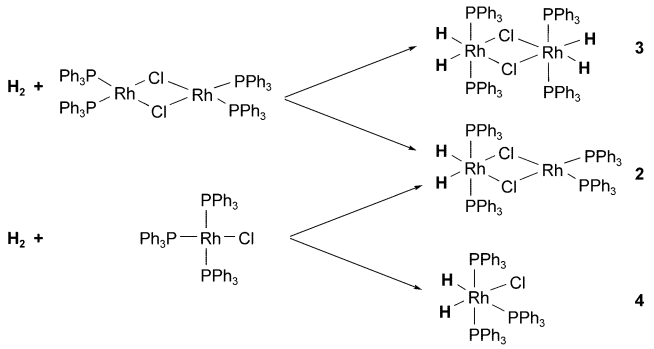


Figure 1. a) $^1H\{^{31}P\}$ spectrum showing high field resonances of **2** and **3** obtained from the reaction of $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ with normal hydrogen in [D_8]toluene at 295 K. b) 1D ^1H NOE spectrum at 295 K on the same sample acquired following the selective excitation of the free H_2 signal and a 400 ms mixing time, magnetisation transfer into the hydride ligands of **3** is indicated; c) 1D NOE spectrum acquired at 295 K following the selective excitation of the free H_2 signal with magnetisation transfer into the hydrides of **4** indicated. NOE connections to the *ortho*-phenyl protons are also illustrated. This corresponds to monitoring the reaction of $[Rh(Cl)(PPh_3)_3]$ with H_2.

The chemical shift of the hydride signal at δ −19.45 matches that previously reported for $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ (**2**),[3] with the high-field chemical shift proving to be indicative of a hydride ligand positioned *trans* to bridging chloride ligand. Since the δ −20.01 hydride resonance of species **3** is comparable to that of **2** it is also likely to arise from a hydride ligand positioned *trans* to a bridging chloride; however, since its line-width is 20 Hz at 295 K complete characterisation was not possible in this solvent.

The line-width of the hydride resonance for **2** is 2.5 Hz under the same conditions. In order to characterise **3** more fully, the solvent was changed to CD_2Cl_2 where the solubility of **1** is significantly higher.

The reaction of $[RhCl(PPh_3)_2]_2$ with *n*-H_2 in CD_2Cl_2 yields hydride signals due to **2** and **3** at δ −19.92 and −20.16, respectively. The hydride resonance of **3** was again considerably broader than that of **2** but a series of $^1H\{^{31}P\}$ spectra, recorded at progressively lower temperatures, resulted in a gradual reduction in the line-width of this resonance as it moved to higher frequency. At 203 K, in the fully coupled ^1H NMR spectrum, the hydride resonance of **3** appears at δ −18.96 and exhibits a doublet of triplet multiplicity where two equivalent phosphines provide a $J_{H,P}$ value of 13.5 Hz and the value of $J_{H,Rh}$ is 25.2 Hz. In the corresponding $^1H,^{103}Rh$ HMQC spectrum, this hydride resonance connects to a single ^{103}Rh resonance at δ 661 which exhibited passive coupling to two equivalent ^{31}P nuclei which resonate at δ 39.1 in the ^{31}P NMR spectrum. These data clearly confirm that **3** corresponds to the highly symmetrical tetrahydride complex, $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)]_2$, with the structure shown in Scheme 1.



Scheme 1. H_2 addition products of $[Rh(PPh_3)Cl]$ and $[Rh(PPh_3)_2(\mu\text{-}Cl)]_2$.

Both the associated hydride resonance line-widths, and the temperature dependence of the hydride ligand's chemical shift require that **3** is undergoing a fluxional process. When the hydride resonance of **3** was selected in a 1D-EXSY sequence at 285 K, and a mixing time of 100 ms used to monitor chemical exchange, the resulting spectrum contained a single resonance at δ 4.47 corresponding to the detection of free H_2. Reducing the mixing time to 10 ms led to the observation of resonances due to both the irradiated hydride and free H_2 in a 1:0.1 ratio in accord with a rate of H_2 elimination of 10 s^{-1} at 285 K. Interestingly, while the reverse process—exchange of free H_2 into **3**—could also be observed using the same 1D-EXSY method ($k_{obs}=0.025$ s^{-1} at 285 K, Figure 1b), no transfer of H_2 into **2**, or H_2 elimination from **2**, was seen until 312.5 K. At this point, the rate of H_2 loss from **2** was determined to be 0.025 s^{-1}. It can therefore be concluded that the rate of hydrogen elimination from **2** at 312.5 K is around 400 times slower than that for **3** at 285 K.

The dynamic processes involving the interchange of the hydride ligands of $[RhCl(H)_2(PPh_3)_3]$, **4** and their reversible exchange with H_2 have already been investigated extensively by Brown.[7] We note here that irradiation of either hydride signal for **4** in a 1D-EXSY sequence at 295 K led to the observation of hydride interchange and H_2 elimination with a rate of 3.3 s^{-1}. When the resonance of free H_2 was selected in this experiment, at 295 K, exchange peaks were observed into both hydride positions in **4** (Figure 1c). Importantly, no evidence for the interconversion of **4**, **2** and **3** was obtained in these EXSY spectra for mixing times up to 500 ms; it should be noted that **4** and **3** were not observed simultaneously since **3** is not observed during the reaction of $[RhCl(PPh_3)_3]$ with H_2 or when **1** reacts with H_2 in the presence of an excess of PPh_3. A point of particular interest relates to the absence of exchange peaks connecting the hydride resonances of **2** and **3**. This enables the conclusion to be drawn that the tetrahydride is not formed on the NMR timescale by the direct addition of hydrogen to the Rh^I centre of **2**; this proposal supports Tolman's early suggestion that the addition of H_2 to **2** would be inhibited by electronic factors.[2] Furthermore, since the formation of **2** from $[RhCl(PPh_3)_3]$ and H_2 coincides with the generation of free PPh_3 it is clear that free PPh_3 suppresses the formation of **3**.

If **3** undergoes rapid and reversible rupture of one of the halide bridges, then the chemical environment of the hydride ligands will fluctuate between that of the dimer and those typical of the corresponding unsaturated intermediate $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)RhCl(H)_2(PPh_3)_2]$ (**5**). In this species, the unsaturated rhodium centre could either adopt a square based pyramidal structure where one hydride is *trans* to a vacant site[26,27] or a trigonal-bipyramidal geometry where both hydrides are in equatorial positions without a direct *trans* ligand.[28] Both of these situations will result in the resonance of the associated hydride ligands moving to higher field (lower frequency) and thus reversible halide bridge rupture in **3** will shift the hydride resonance to high field. At lower temperatures, the rate of this process would be expected to reduce and the contribution of the chemical shift of unsaturated intermediate to the observed chemical shift would fall, with resonances moving to higher frequency. This is consistent with the observation that on cooling, the hydride resonance of **3** is observed at progressively higher frequencies. The failure to observe hydride exchange from **3** to **2**, and the observation of free H_2 exchange with **3** indicates that H_2 must add to the Rh^I Centre of the product formed by H_2 loss from **5** rapidly, and preserve **3**, before **2** is formed or fragmentation occurs. This is further supported by the fact that while the rates of hydrogen addition to $[RhCl(PPh_3)_3]$ and $[RhCl(PPh_3)_2]_2$ have been found to be similar ($k=4.81$ $mol^{-1}s^{-1}$ for the monomer), they are considerably lower than the rate of addition to the 14 electron species $[RhCl(PPh_3)_2]$, which was estimated to be 7×10^4 $mol^{-1}s^{-1}$.[3]

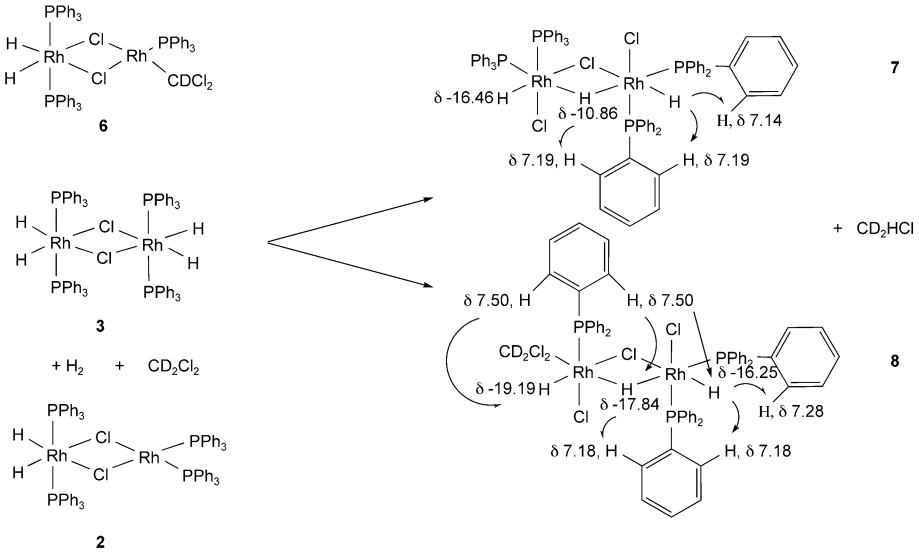
Utilisation of transfer NOE protocols to probe the ligand sphere of $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)]_2$ (3) and $[RhCl(H)_2(PPh_3)_3]$ (4): During the 1D-EXSY experiments involving **4** in C_6D_6 when the peak for free H_2 was selected, and a mixing time of 400 ms employed, two further resonances, possessing opposite phase to the irradiated signal were

seen at δ 7.79 and 7.55 in the final spectrum. ^{1}H NMR resonances in this region are characteristic of phenyl protons in metal bound phosphine ligands. Indeed, the same two resonances are observed when the hydride signal at δ −16.63 is selected and a 400 ms mixing time utilised. From this result, the origin of the signals at δ 7.79 and 7.55 can be attributed to NOE interactions between the irradiated hydride nuclei and the *ortho*-phenyl protons in the two types of PPh_3 ligands of **4**. A mechanism accounting for this observation has been reported previously and termed *transfer NOE*. Transfer NOE methods have been developed for predominantly biochemical applications, with particular emphasis being placed on the investigation of ligands binding to proteins.[29,30] Thus, under conditions where rapid chemical exchange occurs between free and coordinated ligand molecules, information concerning the bound state of a ligand–protein complex can be deduced by probing NOE interactions via nuclei in the free ligand.[30–34] The chemistry of the rapid addition and elimination of H_2 to **4** is analogous to that of a protein and a reversibly coordinating ligand and irradiation of the H_2 resonance results in the observation of NOE interactions reflecting the environment of the proton nuclei originating from H_2 in the "bound state". We note that increasing the temperature and hence rate of H_2–RhH_2 exchange increases the intensity of these NOE connections. The opposite trend was produced by the addition of 2 mg of free PPh_3 to a solution of $[RhCl(PPh_3)_3]$ in toluene; Halpern has demonstrated that the rate of H_2 addition to form **4** is approximately 10^5 times slower than that to generate the unsaturated species $[RhCl(H)_2(PPh_3)_2]$. Under these conditions no NOE or exchange connections were observed to **4** when the H_2 resonance was selected. We also note that for an equivalent number of scans and mixing time, the intensity of the NOE peaks in **4** were greater when the free H_2 resonance, rather than the hydride resonance, was irradiated. Furthermore, at 325 K the line-width of the hydride signals for **4** exceeds 600 Hz and only irradiation of the free H_2 signal led to NOE connections being observed to the phosphine. Clearly the monitoring of the ligand sphere of minor, or highly fluxional, complexes is readily facilitated by this approach.

When the free hydrogen peak is irradiated in this way for a sample of **1** and H_2 in C_6D_6 at 305 K, a negative NOE peak is visible in the corresponding ^{1}H NMR spectrum at δ 7.82. Since the chemical shift of this new resonance does not match those expected for **4** or **2** it must correspond to the *ortho*-phenyl proton resonance of the tetrahydride **3**.

Reactions of $[RhCl(PPh_3)_2]_2$ (1) with H_2 in chlorinated solvents: We described above how *n*-H_2 reacts with **1** at 295 K in CD_2Cl_2 to form both **2** and **3**. We now note that at very early reaction times, a further pair of weak hydride resonances, both of the same intensity, could be detected at δ −19.77 and −20.50. These chemicals shifts are characteristic of those found for hydride ligands in binuclear structures that are located *trans* to bridging chlorides. These resonances are only visible within the first ten minutes of starting the reaction and their signal intensity did not permit the acquisition of ^{31}P nor ^{103}Rh NMR data. Nonetheless, in the ^{1}H{^{31}P} spectrum these resonances appear as simple doublets of doublets of 22 and 10.2 Hz couplings, and in the ^{31}P coupled ^{1}H NMR spectrum, each resonance shows an additional triplet splitting of approximately 15 Hz consistent with the presence of two *cis* phosphines. The formation of $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(CD_2Cl_2)(PPh_3)]$ (**6**), a species that contains inequivalent hydride ligands is totally consistent with these observations. We note that even though the hydride resonances for **6** were sharp, they did not display PHIP with *p*-H_2. This observation can be explained by the fact that complex **3** rapidly quenches the *p*-H_2 reservoir due to its extremely high reactivity.

A more noteworthy feature of this reaction is the fact that five additional hydride resonances become visible after 25 minutes. These resonances appear at δ −10.86, −16.26, −16.46, −17.84, and −19.19 and while they continue to increase in intensity at the expense of signals due to **2** and **3**, over time their appearance in the corresponding ^{1}H NMR spectra is unchanged between 310 and 203 K. The full characterisation of these species by NMR spectroscopy is described in the Supporting Information. This details how the two hydride signals of relative intensity 1:2 at δ −10.86 and −16.46 arise from $[Rh(Cl)(H)(PPh_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(Cl)(H)(PPh_3)_2]$ (**7**). Those at δ −17.84, −16.26 and −19.19, with identical intensities, arise from the solvent complex $[Rh(Cl)(H)(PPh_3)(CD_2Cl_2)(\mu\text{-}Cl)(\mu\text{-}H)Rh(Cl)(H)(PPh_3)_2]$ (**8**). Scheme 2 illustrates the structures of these species and includes key NOE connections that support the assignments.



Scheme 2. NOE connectivities in **7** and **8**.

One of the most notable differences in the NMR properties of **7** and **8** is the chemical shift of the bridging hydride. It shifts from δ −10.86 when it is *trans* to two phosphines, to δ −17.84 when it is *trans* to only one, and hence is also *trans* to chloride or coordinated CD_2Cl_2. A number of rhodium hydride complexes containing ligated solvent molecules have been reported including some with dimeric structures.[35,36] The role of the solvent was subsequently confirmed by the fact that in 50% CD_2Cl_2/CH_2Cl_2 an additional NOE interaction between this hydride and a signal at δ 4.57 is observed. Further evidence supporting a solvated structure was obtained by adding $CDCl_3$ into a CD_2Cl_2 solution containing **7** and **8**. While the terminal resonance at δ −19.19 moves by 56 Hz for a 1:4 solvent ratio, the 4 other resonances shift by less than 10 Hz.

It should be noted that **7** and **8** are only formed in chlorinated solvents, and the formation of CD_2HCl is indicated by the observation of a quintet at δ 3.37. The chemical shift of the proton in CD_2HCl has been reported as δ 3.05 in CCl_4.[37] In addition, when $[RhCl(PPh_3)_3]$ reacts with *n*-H_2 in CD_2Cl_2 solution only **2**, **4** and **7** were observed. Thus, the generation of **8** is suppressed by added PPh_3 which is consistent with solvent coordination in this species. It should be noted that direct exchange between **7** and **8** was not observable on the NMR timescale.[38]

The reactivity of these trihydrides was further investigated by placing an NMR sample containing both **7** and **8** under an atmosphere of D_2. When a ^1H NMR spectrum was acquired, a 1:1:1 triplet at δ 4.57 (superimposed upon the resonance of H_2) was observed. This triplet is due to the formation of HD, the $^1J_{H,D}$ coupling being 42.4 Hz, and requires the existence of a pathway for D_2/H, HD/D exchange. During this process, all the hydride resonances in each complex were found to decrease in intensity at essentially the same rate, although the rate of deuterium incorporation into **8**, the solvent stabilised complex, substantially exceeded that for **7**. Interestingly, placing a benzene solution of **8** and **7** under *p*-H_2 did not yield any polarisation in the hydride resonances of these species. Thus, although the deuterium experiment confirms that these complexes undergo exchange with H_2, the rate is insufficient to see enhancement of these resonances.

Observations on the reaction of $[RhCl(PPh_3)_2]_2$, 1, with H_2 in the presence of an alkene: A number of studies have demonstrated that when the hydrogenation of styrene catalysed by **1** or $[RhCl(PPh_3)_3]$ is examined with *p*-H_2, polarised resonances are readily observed in the hydrogenation product ethylbenzene due to the pairwise hydrogenation of the substrate by the catalyst, as shown in Figure 2a. However, when **1** is employed, close examination of the hydride region of the associated ^1H NMR spectrum reveals the presence of two additional polarised resonances at δ −18.72 and −19.51 (Figure 2b). These resonances have previously been reported to arise from terminal hydride ligands in the binuclear species $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(styrene)]$ (**9a**).[20,21] Consequently, when the corresponding ^1H NMR spectrum is acquired with broadband phosphorus decoupling during data acquisition, both hydride resonances simplify into doublets of antiphase doublets from which $J_{H,H}$ = −10.9 Hz and $J_{Rh,H}$ ≈22.5 Hz can be determined. The location of these hydride resonances as high-field signals confirms the presence of the two halide bridges, and by comparison with the position of those in the related complexes $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ and $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(CO)(PPh_3)]$, it can be deduced that the δ −19.51 resonance arises from the hydride that is cisoid to the PPh_3 ligand on the Rh^I centre. The NMR data for **9** can be found in Table 1.

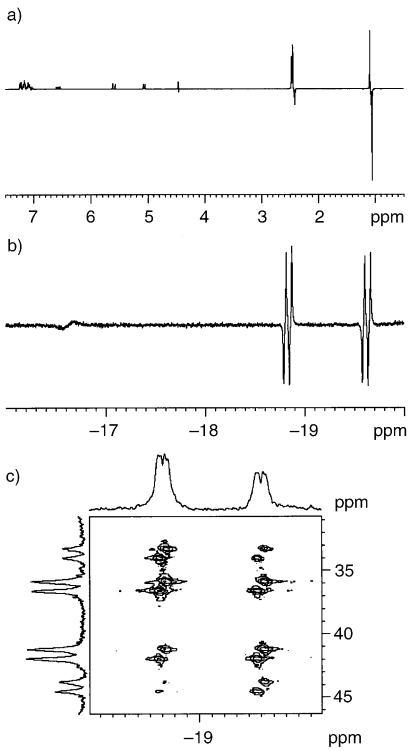


Figure 2. a) The hydride region of the ^1H NMR spectrum obtained when **1** reacts with H_2 in $[D_8]$toluene at 298 K with signals for **2** and **3** illustrated; a) ^1H NMR spectrum illustrating the effect of utilising *p*-H_2 as a substrate during the hydrogenation of styrene by **1**; b) expansion of the hydride region of a $^1H\{^{31}P\}$ NMR spectrum obtained for the sample used in a) revealing signals due to **9a**; c) selected cross peaks (absolute value display) and projections in the $^1H,^{31}P$ HMQC correlation spectrum of **9a** (^{31}P decoupled).

Since the observation of this species was first described[20] we have developed a high sensitivity approach to observe heteronuclei signals via heteronuclear multiple quantum correlation (HMQC) spectroscopy. Surprisingly, when the hydride resonances of **9a** are used in this way to learn about the associated ^{31}P chemical shifts, the resultant spectrum, illustrated in Figure 2c, indicates that each hydride ligand couples to two different phosphorus centres. Consequently, the ^{31}P domain contains two resonances with distorted doublet of doublets multiplicity from which passive couplings of 127 and 417 Hz can be determined. These couplings correspond to $^1J_{Rh,P}$ and $^2J_{P,P}$, respectively and suggest that the two phosphine ligands giving rise to these signals are *trans* and inequivalent.

The observation of **9a** was not unique. When styrene was replaced with *para*-methylstyrene, *para*-chlorostyrene and 1-

Table 1. Selected NMR Data for complexes **2**–**12**.

Complex (L = PPh_3)	Nucleus, Solvent, T [K]	δ (multiplicity)	Assignment J [Hz]	δ (multiplicity)	Assignment J [Hz]
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)_2]$ (**2**)	^1H C_6D_6, 295	7.96 (m)	(*o*-H)/P_bPh_3 5.6 $^3J_{H,H}$	−19.35 (dt)	H_a 21.6 $^1J_{H,Rh}$, 17.5 $^2J_{H,P}$
	^{31}P C_6D_6, 295	54.57 (d)	P_a 195.1 $^1J_{P,Rh}$	37.47 (d)	P_b 119.0 $^1J_{P,Rh}$
	^{103}Rh C_6D_6, 295	957 (t)	Rh^{III} 110[a] $^1J_{Rh,P}$		
	^1H CD_2Cl_2, 295	−19.92 (dt)	H_a 21.6 $^1J_{H,Rh}$, 17.5 $^2J_{H,P}$		
	^{31}P CD_2Cl_2, 295	54.38 (d)	P_a 195.1 $^1J_{P,Rh}$	38.32 (d)	P_b 119.0 $^1J_{P,Rh}$
	^{103}Rh CD_2Cl_2, 213	909 (t)	Rh^{III} 110[a] $^1J_{Rh,P}$		
$[H_2Rh(L)_2(\mu\text{-}I)_2Rh(L)_2]$ (**2-I**)	^1H C_7D_8, 295	8.05 (m)	(*o*-H)/P_bPh_3 7.5 $^3J_{H,H}$	−16.06 (dt)	H_a 22.3 $^1J_{H,Rh}$, 13.7 $^2J_{H,P}$
	^{31}P C_7D_8, 295	50.7 (d)	P_a 186.9 $^1J_{P,Rh}$	39.9 (d)	P_b 114.9 $^1J_{P,Rh}$
	^{103}Rh C_7D_8, 295	387(t)	Rh^{III} 114.9 $^1J_{Rh,P}$		
$[H_2Rh(L)_2(\mu\text{-}I)(\mu\text{-}Cl)Rh(L)_2]$ (**2-Cl-I**)	^1H C_6D_6, 295	−15.86 (ddt)	H_a 9.7 $^2J_{H,H}$, 22.5 $^1J_{H,Rh}$, 15 $^2J_{H,P}$	−19.45 (ddt)	H_b 9.7 $^2J_{H,H}$, 20.9 $^1J_{H,Rh}$, 17 $^2J_{H,P}$
	^{31}P C_6D_6, 295	38.23 (d)	P_a 111.2 $^1J_{P,Rh}$		
	^{103}Rh C_6D_6, 295	710 (t)	Rh^{III} 110[a] $^1J_{Rh,P}$		
$[H_2Rh(L)_2(\mu\text{-}Cl)_2(L)_2RhH_2]$ (**3**)	^1H C_6D_6, 295	7.82 (m)	(*o*-H)/P_aPh_3	−20.01 (dt)	H_a 25.2 $^1J_{H,Rh}$, br
	^{31}P C_6D_6, 295	39.1 (d)	P_a 118.8 $^1J_{Rh,P}$		
	^1H CD_2Cl_2, 295	−20.16 (dt)	H_a 25.2 $^1J_{H,Rh}$, 13.5 $^2J_{H,P}$		
	^{31}P CD_2Cl_2, 203	43.16 (d)	P_a 140[a] $^1J_{P,Rh}$		
	^{103}Rh CD_2Cl_2, 213	661 (t)	Rh^{III} 118.8 $^1J_{Rh,P}$		
$[H_2Rh(L)_2(\mu\text{-}I)_2Rh(H)_2(L)_2]$ (**3-I**)	^1H C_7D_8, 295	−15.91 (m)	H_a 24.8 $^1J_{H,Rh}$, br		
	^{103}Rh C_7D_8, 295	246 (m)	Rh^{III}		
$[H_2RhCl(L)_3]$ (**4**)	^1H C_7D_8, 273	−9.33 (dddt)	H_a −7.6 $^2J_{H,H}$, 11.7 $^1J_{H,Rh}$, 154.4 $^2J_{H,P(a)}$, 13.5 $^2J_{H,P(b)}$	−16.60 (ddq)	H_b −7.6 $^2J_{H,H}$, 19.2 $^1J_{H,Rh}$, 15.5 $^2J_{H,P}$
	^{31}P C_7D_8, 273	39.52 (dd)	P_a 115.2 $^1J_{P,Rh}$, 21.5 $^2J_{P,P}$	20.48 (dt)	P_b 98.7 $^1J_{P,Rh}$, 21.5 $^2J_{P,P}$
	^{103}Rh C_7D_8, 268	260	Rh^{III}		
	^1H, C_6D_6, 295	7.79 (m)	(*o*-H)/P_aPh_3 7.3 $^3J_{H,H}$	7.55 (m)	(*o*-H)/P_bPh_3 8.7 $^3J_{H,H}$
		−9.31 (dddt)	H_a 155 $^2J_{H,P(a)}$	−16.63 (ddq)	H_b br
$[H_2RhI(L)_3]$ (**4-I**)	^1H C_7D_8, 270	−9.56 (dddt)	H_a −8.5 $^2J_{H,H}$, 19.3 $^1J_{H,Rh}$, 149.3 $^2J_{H,P(a)}$, 11.6 $^2J_{H,P(b)}$	−13.71 (ddq)	H_b −8.5 $^2J_{H,H}$, 19.7 $^1J_{H,Rh}$, 14.5 $^2J_{H,P}$
	^{31}P C_7D_8, 270	37.03 (dd)	P_a 114.1 $^1J_{PR,h}$, 18.6 $^2J_{P,P}$	19.90 (dt)	P_b 91.2 $^1J_{P,Rh}$, 18.6 $^2J_{P,P}$
	^{103}Rh C_7D_8, 268	−80 (m)	Rh^{III}		
	^1H C_7D_8, 295	7.70 (m)	(*o*-H)/P_aPh_3 5.7 $^3J_{H,H}$	7.36 (m)	(*o*-H)/P_bPh_3
		−9.80 (dddt)	H_a 150 $^2J_{H,P}$	−13.89 (ddq)	H_b br
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)(CD_2Cl_2)]$ (**6**)	^1H CD_2Cl_2, 295	−19.77 (m)	H_a 10.2 $^2J_{H,H}$, 22.4 $^1J_{H,Rh}$	−20.50 (m)	H_b 10.2 $^2J_{H,H}$, 23.2 $^1J_{H,Rh}$
$[(L)_2RhHCl(\mu\text{-}Cl)(\mu\text{-}H)ClHRh(L)_2]$ (**7**)	^1H CD_2Cl_2, 295	7.19 (m)	(*o*-H)/P_aPh_3	7.14 (m)	(*o*-H)/P_bPh_3
		−10.86 (ttt)	H_a 21.3 $^1J_{H,Rh}$, 74.9 $^2J_{H,P(a)}$, 9.8 $^2J_{H,P(b)}$	−16.46 (dt)	H_b 18.1 $^1J_{H,Rh}$, 18 $^2J_{H,P}$, 18 $^2J_{H,P}$
	^{31}P CD_2Cl_2, 295	51.58 (dd)	P_a 140 $^1J_{P,Rh}$, 28.5 $^2J_{P,P}$	36.30 (dd)	P_b 120 $^1J_{P,Rh}$, 28.5 $^2J_{P,P}$
	^{103}Rh CD_2Cl_2, 263	814 (dd)	Rh^{III} 120 $^1J_{Rh,P}$, 140 $^1J_{Rh,P}$		
$[(L)_2RhHCl(\mu\text{-}Cl)(\mu\text{-}H)H(solv)RhCl(L)]$ (**8**)	^1H CD_2Cl_2, 295	7.50 (m)	(*o*-H)/P_aPh_3	7.33 (m)	(*m*-H)/P_aPh_3
		7.28 (m)	(*o*-H)/P_cPh_3	7.18 (m)	(*o*-H)/P_bPh_3
		7.08 (m)	(*m*-H)/P_bPh_3		
		−16.26 (dt)	H_a 16.6 $^1J_{H,Rh}$, 21.7 $^2J_{H,P(a)}$, 14.5, $^2J_{H,P(b)}$	−17.84 (m)	H_b 27.4 $^1J_{H,Rh}$, 20.8 $^1J_{H,Rh}$, 64 $^2J_{H,P(c)}$, 9 $^2J_{H,P}$, 9 $^2J_{H,P}$
		−19.19 (dd)	H_c 17.4 $^1J_{H,Rh}$, 16.9 $^2J_{H,P}$		
	^{31}P CD_2Cl_2, 295	52.77 (d)	P_aPh_3 151.9 $^1J_{P,Rh}$	49.51 (dd)	P_bPh_3 123.4 $^1J_{P,Rh}$, 50 $^2J_{P,P}$
		36.62 (dd)	P_cPh_3 123.4 $^1J_{P,Rh}$, 50 $^2J_{P,P}$		
	^{103}Rh CD_2Cl_2, 263	1645 (d)	Rh_a^{III} 150[a] $^1J_{Rh,P}$	861 (dd)	Rh_b^{III} 140[a] $^1J_{Rh,P}$, 120[a] $^1J_{Rh,P}$
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)(styrene)]$ (**9a**)	^1H C_6D_6, 295	8.20 (m)	(*o*-H)/L 6.5 $^3J_{H,H}$, 6.5 $^3J_{H,P}$	7.85 (m)	(*o*-H)/L 6.5 $^3J_{H,H}$
		−18.72 (ddt)	H_a −10.9 $^2J_{H,H}$, 22.1 $^1J_{H,Rh}$, 17 $^2J_{H,P}$	−19.51 (ddt)	H_b −10.9 $^2J_{H,H}$, 22.7 $^1J_{H,Rh}$, 17 $^2J_{H,P}$
	^{31}P C_6D_6, 295	42.73 (dd)	(L-Rh^{III}) 127 $^1J_{P,Rh}$, 417 $^2J_{P,P}$	35.23 (dd)	(L-Rh^{III}) 127 $^1J_{P,Rh}$, 417 $^2J_{P,P}$
	^{103}Rh C_6D_6, 300	950	Rh^{III}		

Table 1. (Continued)

Complex (L = PPh_3)	Nucleus, Solvent, T [K]	δ (multiplicity)	Assignment J [Hz]	δ (multiplicity)	Assignment J [Hz]
$[H_2Rh(L)_2(\mu\text{-}I)_2Rh(L)$-(styrene)] (**9a-I**)	^1H C_7D_8, 268	−15.79 (m)	H_a −11.5 $^2J_{H,H}$, 20.8 $^1J_{H,Rh}$	−16.03 (m)	H_b −11.5 $^2J_{H,H}$, 20.1 $^1J_{H,Rh}$
$[H_2Rh(L)_2(\mu\text{-}Cl)(\mu\text{-}I)Rh(L)$-(styrene)] (**9a-Cl-I**)	^1H C_7D_8, 290	−15.85 (m)	H_a −9.8 $^2J_{H,H}$, 20.2 $^1J_{H,Rh}$	−19.20 (m)	H_b −9.8 $^2J_{H,H}$, 22.0 $^1J_{H,Rh}$
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)$-(*p*-Me-styrene)] (**9b**)	^1H C_6D_6, 295	8.09 (m)	(*o*-H)/L	7.74 (m)	(*o*-H)/L 7.9 $^3J_{H,H}$
		−18.82 (ddt)	H_a −11.0 $^2J_{H,H}$, 22.3 $^1J_{H,Rh}$, 20 $^2J_{H,P}$	−19.59 (ddt)	H_b −11.0 $^2J_{H,H}$, 22.9 $^1J_{H,Rh}$, 17 $^2J_{H,P}$
	^{31}P C_6D_6, 295	42.38 (dd)	(L-Rh^{III}) 125 $^1J_{P,Rh}$, 427 $^2J_{P,P}$	33.96 (dd)	(L-Rh^{III}) 125 $^1J_{P,Rh}$, 427 $^2J_{P,P}$
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)$-(*p*-Cl-styrene)] (**9c**)	^1H C_6D_6, 295	8.08 (m)	(*o*-H)/L 9.0 $^3J_{H,H}$	7.74 (m)	(*o*-H)/L 6.6 $^3J_{H,H}$
		−18.89 (ddt)	H_a −11.0 $^2J_{H,H}$, 22.3 $^1J_{H,Rh}$, 20 $^2J_{H,P}$	−19.73 (ddt)	H_b −11.0 $^2J_{H,H}$, 23.0 $^1J_{H,Rh}$, 17 $^2J_{H,P}$
	^{31}P C_6D_6, 295	43.44 (dd)	(L-Rh^{III}) 122 $^1J_{P,Rh}$, 425 $^2J_{P,P}$	34.43 (dd)	(L-Rh^{III}) 125 $^1J_{P,Rh}$, 425 $^2J_{P,P}$
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)$-(1-hexene)] (**9d**)	^1H C_6D_6, 295	8.24 (m)	(*o*-H)/L	8.09 (m)	(*o*-H)/L
		−18.66 (ddt)	H_a −11.0 $^2J_{H,H}$, 22.6 $^1J_{H,Rh}$, 17 $^2J_{H,P}$	−19.46 (ddt)	H_b −11.0 $^2J_{H,H}$, 22.4 $^1J_{H,Rh}$, 17 $^2J_{H,P}$
	^{31}P C_6D_6, 295	40.42 (dd)	(L-Rh^{III}) 121 $^1J_{P,Rh,}$ 417 $^2J_{P,P}$	36.78 (dd)	(L-Rh^{III}) 128 $^1J_{P,Rh}$, 417 $^2J_{P,P}$
$[H_2Rh(L)_2(\mu\text{-}I)_2Rh(L)$-(1-hexene)] (**9d-I**)	^1H C_7D_8, 268	−15.85 (m)	H_a −10.8 $^2J_{H,H}$, 22.0 $^1J_{H,Rh}$	−15.93 (m)	H_b −10.8 $^2J_{H,H}$, 24.6 $^1J_{H,Rh}$
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)$-(*cis*-stilb)] (**9e**)	^1H C_6D_6, 295	−18.73 (ddt)	H_a −10.8 $^2J_{H,H}$, 23.4 $^1J_{H,Rh}$, 17 $^2J_{H,P}$	−19.46 (ddt)	H_b −10.8 $^2J_{H,H}$, 23.0 $^1J_{H,Rh}$, 17 $^2J_{H,P}$
	^{31}P C_6D_6, 295	39.6 (d)	P_a 126.6 $^1J_{P,Rh}$		
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)$-(diphen-eth)] (**9f**)	^1H C_6D_6, 295	−19.12 (ddt)	H_a −10.5 $^2J_{H,H}$, 23.7 $^1J_{H,Rh}$, 16 $^2J_{H,P}$	−19.43 (ddt)	H_b −10.5 $^2J_{H,H}$, 23.8 $^1J_{H,Rh}$, 16 $^2J_{H,P}$
	^{31}P C_6D_6, 295	41.2 (d)	P_a 132.9 $^1J_{P,Rh}$		
$[H_2Rh(L)_2(\mu\text{-}Cl)_2Rh(L)$-(F-styrene)] (**9g**)	^1H CD_2Cl_2, 263	−19.61 (ddt)	H_a 10.8 $^2J_{H,H}$, 23.1 $^1J_{H,Rh}$, 12 $^2J_{H,P}$	−20.56 (ddt)	H_b 10.8 $^2J_{H,H}$, 23.8 $^1J_{H,Rh}$, 12 $^2J_{H,P}$
	^{31}P CD_2Cl_2, 280	50.34 (d)	P_a 178.0 $^1J_{P,Rh}$		
	^{31}P CD_2Cl_2, 263	44.56 (dd)	(L-Rh^{III}) 123.4 $^1J_{P,Rh}$, 427.1 $^2J_{P,P}$	37.41 (dd)	(L-Rh^{III}) 123.4 $^1J_{P,Rh}$, 427.1 $^2J_{P,P}$
	^{103}Rh CD_2Cl_2, 268	910 (m)	Rh^{III}		
	^1H C_6D_6, 295	−19.05 (dt)	H_a −10.8 $^1J_{H,Rh}$, 23.0 $^2J_{H,H}$	−20.21 (dt)	H_b −10.8 $^2J_{H,H}$, 23.8 $^1J_{H,Rh}$
$[H_2Rh(L)_2(\mu\text{-}I)_2Rh(L)$-(F-styrene)] (**9g-I**)	^1H CD_2Cl_2, 263	−16.47 (ddt)	H_a 8.6 $^2J_{H,H}$, 23.7 $^1J_{H,Rh}$	−16.76 (ddt)	H_b 8.6 $^2J_{H,H}$, 23.0 $^1J_{H,Rh}$
	^{31}P CD_2Cl_2, 263	40 (m)	P_a 2nd order		
	^1H C_7D_8, 280	−15.92 (ddt)	H_a 8.6 $^2J_{H,H}$, 23.7 $^1J_{H,Rh}$	−16.46 (ddt)	H_b 8.6 $^2J_{H,H}$, 23.0 $^1J_{H,Rh}$
$[H_2Rh(L)_2(\mu\text{-}Cl)(\mu\text{-}I)Rh(L)$-(F-styrene)] (**9g-Cl-I**)	^1H CD_2Cl_2, 263	−16.91 (ddt)	H_a 9.5 $^2J_{H,H}$, 24.7 $^1J_{H,Rh}$, 11 $^2J_{H,P}$	−20.01 (ddt)	H_b 9.5 $^2J_{H,H}$, 22.5 $^1J_{H,Rh}$, 11 $^2J_{H,P}$
	^{31}P CD_2Cl_2, 280	54.11 (d)	P_a 172.6 $^1J_{P,Rh}$		
	^{31}P CD_2Cl_2, 263	43.16 (dd)	(L-Rh^{III}) 117 $^1J_{P,Rh}$, 402 $^2J_{P,P}$	39.47 (dd)	(L-Rh^{III}) 120 $^1J_{P,Rh}$, 402 $^2J_{P,P}$
	^{103}Rh CD_2Cl_2, 268	680 (m)	Rh^{III}		
$[H_2Rh(L)_2(\mu\text{-}I)_2Rh_2H_2(L)_2(\mu\text{-}I)(\mu\text{-}H)(\mu\text{-}PPh_2)]$ (**10**)	^1H C_7D_8, 295	7.86 (m)	(*o*-H)/P_cPh_3	7.83 (m)	(*o*-H)/P_cPh_3
		7.57 (m)	(*o*-H)/P_bPh_3	7.21 (m)	(*o*-H)/P_aPh_3
		−10.31 (dtt)	H_a 14.1 $^1J_{H,Rh}$, 69.9 $^2J_{H,P(a)}$, 14.2 $^2J_{H,P(b)}$	−15.11 (dt)	H_b 21.2 $^1J_{H,Rh}$, 14.4 $^2J_{H,P}$
		−16.88 (m)	H_c 18.2 $^1J_{H,Rh}$, 16.6 $^2J_{H,P(a)}$, 4 $^2J_{H,P(c)}$		
	^{31}P C_7D_8, 295	203.1 (t)	P_a 113 $^1J_{P,Rh}$	44.4 (m)	P_b 2nd order ABX
		37.8 (m)	P_c 2nd order AA′MXX′		
	^{103}Rh C_7D_8, 295	172 (t)	Rh_a^{III} 120 $^1J_{P,Rh}$	84 (m)	Rh_b^{III} 2nd order AA′MXX′
$[H_2Rh(L)_2(\mu\text{-}I)_2Rh_2H_2(L)_2\text{-}(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}PPh_2)]$ (**11**)	^1H C_7D_8, 295	−9.90 (dtt)	H_a 16.5 $^1J_{H,Rh}$, 73.7 $^2J_{H,P(a)}$, 16.6 $^2J_{H,P(b)}$	−14.82 (dt)	H_b 21.6 $^1J_{H,Rh}$, 14.7 $^2J_{H,P}$
		−19.25	H_c 19.1 $^1J_{H,Rh}$, 20.4 $^2J_{H,P(a)}$, 5.8 $^2J_{H,P(c)}$		
	^{31}P C_7D_8, 295	196.8 (t)	P_a 118.5 $^1J_{P,Rh}$	44.0	P_b 2nd order ABX
		37.9	P_c 2nd order AA′MXX′		
	^{103}Rh C_7D_8, 295	316 (m)	Rh_a^{III}	117 (m)	Rh_b^{III}
$[HClRh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Rh(CO)(PMe_3)]$ (**12**)	^1H C_6D_6, 295	−17.09 (ddddt)	H_a −3.2 $^2J_{H,H}$, 29 $^1J_{H,Rh}$, 19 $^1J_{H,Rh}$ 30 $^2J_{H,P(a)}$, 15.5 $^2J_{H,P(b)}$	−17.57 (ddt)	H_b −3.2 $^2J_{H,H}$, 24.8 $^1J_{H,Rh}$, 15.5 $^2J_{H,P}$

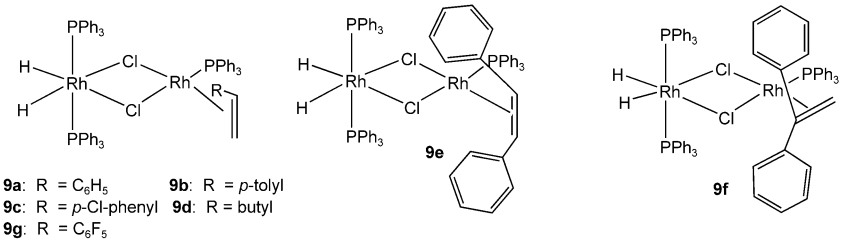
Table 1. (Continued)

Complex (L = PPh_3)	Nucleus, Solvent, T [K]	δ (multiplicity)	Assignment J [Hz]	δ (multiplicity)	Assignment J [Hz]
	^{31}P C_6D_6, 333	−1.5 (d)	P_a 160 $^1J_{P,Rh}$	−5.7 (d)	P_b 120 $^1J_{P,Rh}$
$[H_2Rh(PMe_3)_2$-$(\mu\text{-}Cl)_2Rh(PMe_3)$-$(CO)]$ (**13**)	^1H C_6D_6, 295	−20.75 (ddt)	H_a −11 $^2J_{H,H}$, 30.9 $^1J_{H,Rh}$, 19 $^2J_{H,P}$	−21.36 (ddt)	H_b −11 $^2J_{H,H}$, 30.0 $^1J_{H,Rh}$, 22 $^2J_{H,P}$
	^{31}P C_6D_6, 295	−5.76 (d)	P_a 98.1 $^1J_{P,Rh}$		
$[(PMe_3)_2HRh(\mu\text{-}Cl)_2$-$(\mu\text{-}H)Rh(PMe_3)(CO)]$ (**14**)	^1H C_6D_6, 295	−10.14 (ddddt)	H_a −7 $^2J_{H,H}$, 20.2 $^1J_{H,Rh}$, 20.2 $^1J_{H,Rh}$, 115 $^2J_{H,P}$, 20 $^2J_{H,P}$, 17 $^2J_{H,P}$	−17.95 (dddd)	H_b −7 $^2J_{H,H}$, 18.5 $^1J_{H,Rh}$, 19 $^2J_{H,P}$, 11 $^2J_{H,P}$
	^{31}P C_6D_6, 295	−2.95 (m)		−20.63 (m)	
$[HClRh(PMe_3)_2(\mu\text{-}H)$-$(\mu\text{-}Cl)Rh(PMe_3)(CO)]$ (**15**)	^1H C_6D_6, 295	−14.46 (m)	H_a −3.9 $^2J_{H,H}$, 19.1 $^1J_{H,Rh}$, 31.7 $^1J_{H,Rh}$	−17.21 (m)	H_b −3.9 $^2J_{H,H}$, 22.4 $^1J_{H,Rh}$
	^{31}P C_6D_6, 295	−3.50 (d)	P_a 170 $^1J_{P,Rh}$	−10.37 (d)	P_b 90 $^1J_{P,Rh}$
$[HIRh(PMe_3)(styrene)$-$(\mu\text{-}H)(\mu\text{-}I)Rh(PMe_3)(CO)]$ (**16**)	^1H C_6D_6, 323	−15.53 (m)	H_a −5.4 $^2J_{H,H}$, 29.1 $^1J_{H,Rh}$, 7.7 $^1J_{H,Rh}$, 66.3 $^2J_{H,P(b)}$, 10 $^2J_{H,P(a)}$	−17.18 (m)	H_b −5.4 $^2J_{H,H}$, 18.3 $^1J_{H,Rh}$, 18.5 $^2J_{H,P}$
	^{31}P C_6D_6, 323	22.34 (d)	P_a 133 $^1J_{P,Rh}$	−5.21 (m)	P_b -not seen
$[H_2Rh(L)_2$-$(\mu\text{-}I)_2Rh(L)(CO)]$	^1H C_6D_6, 333	−16.28 (ddt)	H_a −8.9 $^2J_{H,H}$, 24.7 $^1J_{H,Rh}$, 14.2 $^2J_{H,P}$	−16.64 (ddt)	H_b −8.9 $^2J_{H,H}$, 24.8 $^1J_{H,Rh}$, 14.7 $^2J_{H,P}$
	^{31}P C_6D_6, 333	39.73 (d)	P_a 118.7 $^1J_{P,Rh}$		
$[Rh(H)_2(I)(L)_2$-$(\mu\text{-}I)_2Rh(L)_3]$	^1H C_7D_8, 258	−15.29 (ddt)	H_a −9.7 $^2J_{H,H}$, 23.4 $^1J_{H,Rh}$,13.5 $^2J_{H,P}$	−16.19 (ddt)	H_b −9.7 $^2J_{H,H}$, 17.1 $^1J_{H,Rh}$
	^{31}P C_7D_8, 258	48.98 (d)	P_a 122.8 $^1J_{PRh}$		
$[Rh(H)_2(I)(L)_2$-$(\mu\text{-}I)Rh(L)_2]$	^1H C_7D_8, 258	−13.49 (ddt)	H_a −9.1 $^2J_{H,H}$, 24.6 $^1J_{H,Rh}$, 13.5 $^2J_{H,P}$	−16.11 (ddt)	H_b −9.1 $^2J_{H,H}$, 15.8 $^1J_{H,Rh}$, 14.6 $^2J_{H,P}$
	^{31}P C_7D_8, 258	47.69 (d)	P_a 108.9 $^1J_{PRh}$		
$[Rh(H)_2(I)(L)_2$-$(\mu\text{-}I)Rh(L)_3]$	^1H C_7D_8, 258	−13.95 (ddt)	H_a −9.1 $^2J_{H,H}$, 24.2 $^1J_{H,Rh}$, 10.5 $^2J_{H,P}$	−16.71 (ddt)	H_b −9.1 $^2J_{H,H}$, 15.0 $^1J_{H,Rh}$, 13.5 $^2J_{H,P}$
	^{31}P C_7D_8, 258	47.67 (d)	P_a 115.2 $^1J_{P,Rh}$		

[a] Accuracy of the coupling limited by resolution of ^1H,^{103}Rh HMQC experiment.

hexene, hydrogenation with p-H_2 at 298 K led to the detection of the analogous species **9b**, **9c** and **9d**, respectively (Scheme 3). In the corresponding ^1H,^{31}P HMQC spectra, second order phosphine resonances of an AB type representation are again observed. However, the frequency separation between the signals falls from 1210 Hz in **9a** to 590 Hz in **9d** (400 MHz for ^1H). Furthermore, when **1** catalysed the hydrogenation of *cis*-stilbene and 1,1-diphenyl ethylene, the corresponding products **9e** and **9f** yielded only single ^{31}P signals at δ 39.6 and 41.2, respectively, which suggests that the corresponding phosphine ligands are now in apparently equivalent environments. When *trans*-stilbene was employed, no evidence for a species corresponding to **9** was observed. These results are consistent with the fact that when **9** contains a prochiral alkene, the two *trans* phosphines of the Rh^I centre are diastereotopic and hence inequivalent, whereas with both 1,1-diphenylethene and *cis*-stilbene, equivalence will exist between the two phosphines. This view holds true regardless of whether the alkene is rigid or undergoing rotation. Unfortunately we were unable to demonstrate whether the phosphines in **9** interconvert and we are therefore unable to exclude either of these options.

Additional structural information concerning **9a–f** was obtained using NOE measurements to probe the spatial arrangement of ligands within each complex as described in the supplementary section. However, peaks indicative of site-exchange were also observed from the selected hydride to signals corresponding to free H_2 and the second hydride ligand in these complexes. These features require **9** to undergo a fluxional process whereby the hydride ligands can interchange their identities. A second reaction involving the reductive elimination of H_2 is also required. Data were measured for a number of mixing times and the change in magnetisation intensity modelled to determine the rate of hydride interchange (see Experimental Section). Since the concentration of free alkene falls due to hydrogenation during these experiments, a number of observations were undertaken with a common 400 ms mixing time and varying excesses of free styrene relative to **1** (from 1500:1 to 100:1). These spectra revealed that the magnitude of the intramolecular hydride–hydride exchange peak was independent of styrene concentration.



Scheme 3. Structures of binuclear alkene dihydride complexes.

Varying the concentration of rhodium by a factor of three also had no visible effect. These results therefore suggest that hydride–hydride exchange occurs without dinuclear complex break-up and alkene loss. These findings are consistent with those previously reported for $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(CO)]$.[40] Table 2 lists the associated rates at 296 K and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for hydride exchange in complexes **9a–d**.

Table 2. Hydride exchange rates and activation parameters for hydride interchange in **9a–d**.

Complex	k [s^{-1}] (296 K)	$\Delta H^{\neq}$ [$kJ\,mol^{-1}$]	$\Delta S^{\neq}$ [$J^{-1}K^{-1}mol^{-1}$]
9a	0.94 ± 0.04	42 ± 4	-100 ± 12
9b	1.43 ± 0.76	32 ± 14	-131 ± 45
9c	1.40 ± 0.27	25 ± 11	-157 ± 35
9d	1.63 ± 0.27	34 ± 5	-127 ± 17

Experimental evidence for solvent participation in this process was obtained when the exchange in **9a** was monitored in [D_5]nitrobenzene rather than [D_8]toluene. Under these conditions, no exchange was observed at 295 K within 400 ms. This would suggest that exchange proceeds via the formation of a 16 electron rhodium centre that is capable of facile solvation.

Direct evidence for hydrogenation catalysis by $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(L)(PPh_3)]$ [L = alkene]: The exchange processes involving the hydride ligands of **9** were then monitored at the point where the ratio of **1** to styrene was 1:1200. Under these conditions, after a mixing time of 400 ms, 6% of the total hydride peak intensity of the selected hydride resonance due to **9a** had moved into a position corresponding to free H_2 and k_{obs}, the rate of hydride transfer into free H_2, was calculated as $0.15\,s^{-1}$. However, when the corresponding ratio of **1** to styrene was 100:1, the H_2 exchange peak area increased to 17% of the total peak area, which corresponds to k_{obs} for hydrogen elimination of $0.75\,s^{-1}$. Consequently, it can be stated that the observed rate of H_2 elimination from **9a** increases as the alkene concentration falls.

Interestingly, the absolute intensity of the hydride signals of **9a** also increases as the concentration of styrene falls. This change is illustrated qualitatively in Figure 3 where the associated ^1H NMR spectra correspond to eight scan averages in order to ensure that the [H_2] in solution remains essentially constant during data measurement. Interpreting these results is complicated by the fact that the absolute size of the hydride resonance relates both to the concentration of the species yielding the signal and to the purity of the parahydrogen derived spin-state. The latter parameter relates to the lifetime of the metal dihydride product and the extent of relaxation prior to the read pulse which creates the observable magnetic state. Since these experiments are recorded with the same delay between repetitions, the effects of relaxation in the absence of enhanced hydride exchange should be identical, and the lower alkene concentrations should inherently act to reduce the concentration of **9a**.

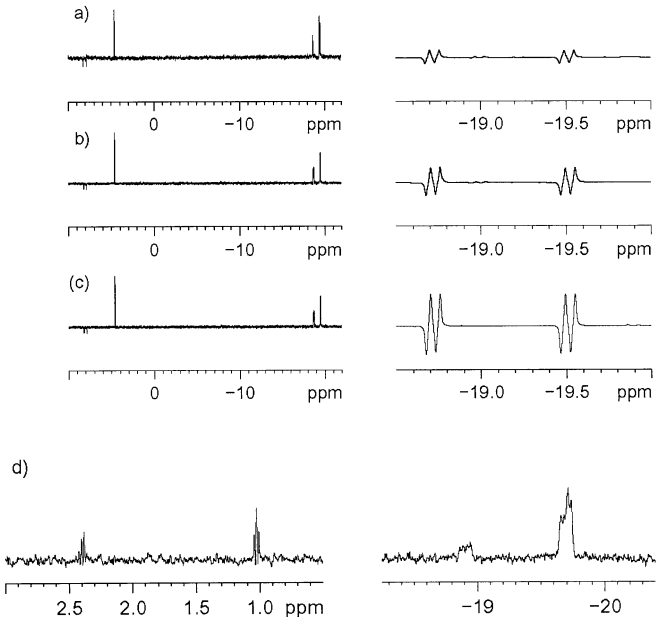


Figure 3. Series of selective 1D-EXSY (left trace, mixing time 400 ms), and $^1H\{^{31}P\}$ spectra (right trace, constant vertical expansion) acquired when styrene to $[RhCl(PPh_3)_2]_2$ (**1**) ratios were: a) 1200:1, b) 550:1, c) 190:1. (d) $^1H\{^{31}P\}$ 1D-NOE spectrum of *p*-H_2 enhanced **9a** at 295 K with resonance selection at δ −19.51 and a mixing time of 200 ms at the point where there is a 20-fold excess of styrene relative to **1**. Positive signals arise due to intramolecular hydride interchange and conversion to ethylbenzene. The negative signals in traces a)–c) at $\approx\delta$ 7 arise from NOE interaction between the hydride to *ortho*-phenyl protons.

Clearly, the promotion of hydride exchange is the only factor that can account for this effect.

A third process is observed in these spectra that has a direct impact on this view. This process involves the hydride ligands of **9a** moving into positions that yield NMR signals at δ 2.43 and 1.06 (Figure 3d). These chemical shifts match those of the hydrogenation product ethylbenzene and only become visible when there is a relatively small alkene excess relative to **1**. The observed rate of hydrogen transfer from **9a** into ethylbenzene for the situation illustrated in Figure 3d corresponds to $1\pm0.5\,s^{-1}$ at 295 K. In the light of this result it is clear that **9a** can function as an intermediate in alkene hydrogenation involving **1** and that its effectiveness as a hydrogenation catalyst increases as the concentration of alkene falls. Since it has previously been estimated that rate limiting hydride migration to the alkene in $[Rh(H)_2(Cl)(cyclohexene)(PPh_3)_2]$ proceeds at a rate of $0.22\,s^{-1}$ at 298 K,[13] it can be deduced that under the right conditions hydrogenation via binuclear complexes of type **9a** is significant.

Reactions of $[RhCl(CO)(PMe_3)_2]$ with H_2—Demonstration of a role for binuclear dihydride complexes during hydrogenation catalysis: In a number of related studies it has been shown that the complexes $[RhX(CO)(PR_3)_2]$ [X = Cl, Br, I; R = Ph] react thermally with H_2 to form binuclear complexes of the type $[Rh(H)_2(PR_3)_2(\mu\text{-}X)_2Rh(CO)(PR_3)]$.[40] However, upon replacing PPh_3 by PMe_3, complexes with a bridging hydride, $[H(X)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}X)Rh(PMe_3)$

(CO)] (X = Cl, Br and I), are most readily observed. The effect of added alkene on this reaction is remarkable. When a solution containing a 1.5-fold excess of styrene relative to $[RhCl(CO)(PMe_3)_2]$, is monitored with *p*-H_2, the hydride resonances of $[(Cl)(H)(Rh)(PMe_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(CO)(PMe_3)]$ (**12**) become enhanced by a factor of 16 over those observed for the same species without styrene (Figure 4a). Furthermore, the new species $[Rh(H)_2(PMe_3)_2(\mu\text{-}Cl)Rh(CO)(PMe_3)]$ (**13**) $[(H)(PMe_3)_2Rh(\mu\text{-}Cl)_2(\mu\text{-}H)Rh(CO)(PMe_3)]$ (**14**) and a second isomer of $[(Cl)(H)Rh(PMe_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(CO)(PMe_3)]$ (**15**) are detected (Scheme 4, NMR data Table 1 and similar to that previously reported for the analogous iodide complexes[40]). These data require that the addition of styrene enhances the rate of hydrogen cycling through the system via sacrificial hydrogenation (visible as polarised ethylbenzene), and consequently enables the detection of additional species that normally undergo relatively slow exchange with free H_2.

When a sample of the more reactive complex $[RhI(CO)(PMe_3)_2]$ is monitored with *p*-H_2 and styrene, signals corresponding to $[Rh(H)_2(PMe_3)_2(\mu\text{-}I)_2Rh(CO)(PMe_3)]$ (**13-I**), two isomers of $[(H)(I)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}I)Rh(CO)(PMe_3)]$ (**12-I** and **14-I**), $[Rh(H)_2I(PMe_3)_3]$ and $(PMe_3)_2HRh(\mu\text{-}H)(\mu\text{-}I)_2Rh(CO)(PMe_3)]$ (**15-I**), which are all visible without free alkene, are detected. In addition, signals for a new rhodium-based product are observed at δ −15.53 and −17.18 (Figure 4b). Since these resonances couple to two rhodium and two phosphorus centres and one rhodium and one phosphorus centre, respectively, the product must contain the fragment $[H(I)Rh(PMe_3)(\mu\text{-}H)(\mu\text{-}I)Rh(PMe_3)]$. In earlier studies, **12-I** and **14-I** were distinguished by introducing a ^{13}CO label; the isomer where the bridging hydride is *trans* to CO yields a $J_{H,C}$ coupling of 11 Hz and a *cis* $J_{H,P}$ coupling of 14 Hz while that where the bridging hydride is *trans* to PMe_3 and *cis* to CO yielded couplings of 3 and 32 Hz, respectively.[40] When $[Rh(I)(^{13}CO)(PMe_3)_2]$ was employed here, no evidence for ^{13}C coupling to the bridging hydride was observed, and therefore $J_{H,^{13}C}$ can be concluded to be <2 Hz; however, the corresponding $J_{H,P}$ value of 66.3 Hz confirms that the bridging hydride lies *trans* to PMe_3. When these experiments were repeated with 1-hexene or *para*-methylstyrene, species with hydride resonances with apparently identical chemical shifts were observed. The identity

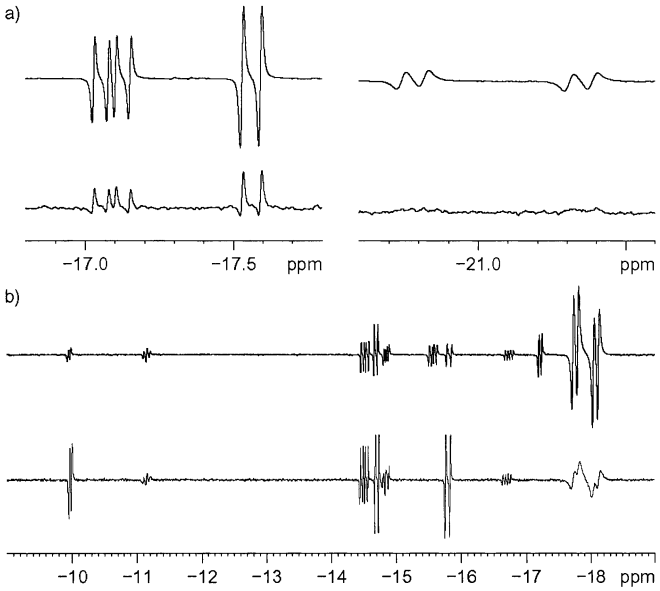
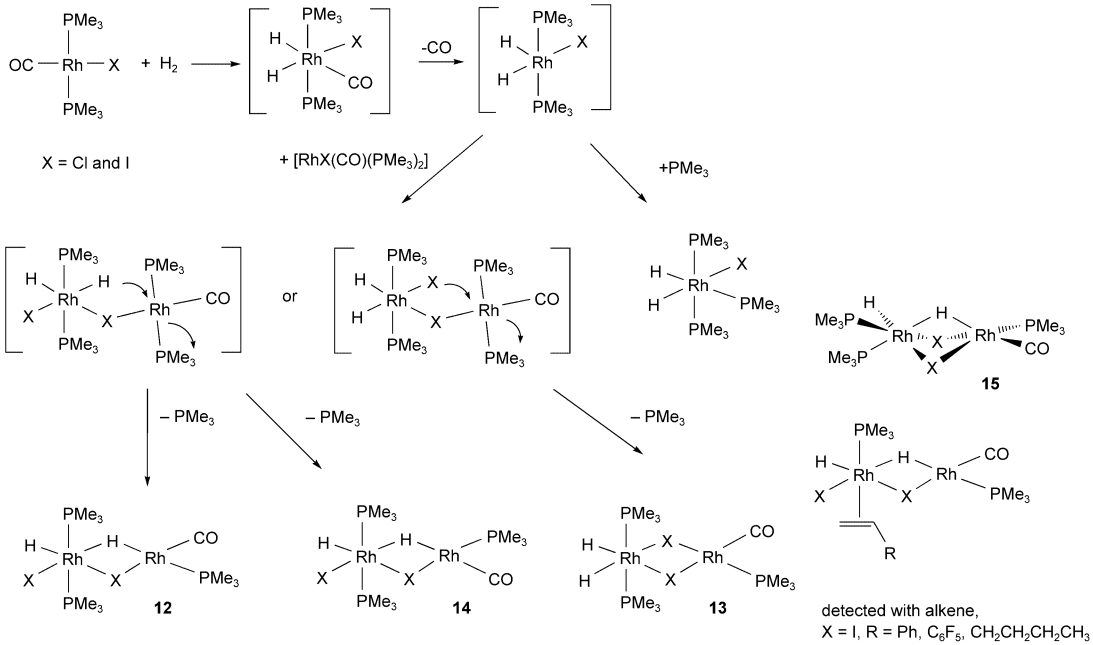


Figure 4. a) ^1H NMR spectrum (lower trace) showing the hydride region of a sample containing $[RhCl(CO)(PMe_3)_2]$ and *p*-H_2 in C_6D_6 at 295 K, upper trace corresponds to the spectrum obtained after introducing styrene. b) ^1H NMR spectrum showing the hydride region of a sample containing $[RhI(CO)(PMe_3)_2]$ and *p*-H_2 in C_6D_6 at 295 K in the absence (lower trace) and presence of styrene (upper trace).



Scheme 4. For X = I products A, B, C and D, and for X = Cl product C only, are detected using *p*-H_2 in the absence of an alkene. For X = Cl products A and B and D are detected at 295 K in the presence of *p*-H_2 and alkene.

of this product most likely corresponds to the binuclear complex $[H(I)Rh(alkene)(PMe_3)(\mu\text{-}H)(\mu\text{-}I)Rh(CO)(PMe_3)]$ (**16**). In view of the apparent insensitivity of the terminal hydride ligands chemical shift to the identity of the alkene, it is likely that alkene binding to the Rh^{III} centre is rapid and reversible. This is further supported by the dramatic high field shift of the ^{31}P signal of the PMe_3 group *trans* to this site that now appears at δ 22.34 rather than δ −6 in the analogous $[H(I)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}I)Rh(CO)(PMe_3)]$ complex.

It proved possible to demonstrate that **13-I** plays a direct role during hydrogenation by showing that selective excitation of the associated hydride resonances at 333 K leads to the observation of magnetisation transfer into the corresponding alkane. In contrast, when the hydride resonances of the remaining four binuclear species are interrogated in a similar way, no direct transfer of the magnetisation in to the alkane is observed. This establishes the fact that $[Rh(H)_2(PMe_3)_2(\mu\text{-}I)_2Rh(CO)(PMe_3)]$ (**13-I**) is the most active of the five potential binuclear hydrogenation catalysts described here. It should be remembered, however, that the results described above for $[RhCl(CO)(PMe_3)_2]$ confirm that **13**, **12** and **14** are indeed active, albeit much less efficient, hydrogenation catalysts than their mononuclear analogues.

In order to probe the role of **9** more closely, **1** was treated with pentafluorostyrene and the analogous complex **9g**, $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(C_2H_3C_6F_5)]$, was characterised at 263 K in CD_2Cl_2 where it is visible without the need for p-H_2 amplification. At 295 K, in C_6D_6, while the same species is produced, alkene hydrogenation is extremely slow, and very weak polarisation is observed in the associated hydride resonances. Significantly, when 1 μL of styrene is added to the system, a considerable increase in the rate of hydrogen cycling is observed with polarised resonances for ethylbenzene being detected. In addition, the signals due to the hydride resonances of **9g** dramatically increase in size. This result suggests that while **9g** participates in alkene hydrogenation, the hydrogenated alkene does not originate from the Rh^I centre (see Figure 5a and b).

Reactions of $[RhI(PPh_3)_3]$ and $[RhI(PPh_3)_2]_2$ with H_2: In view of the fact that binuclear complexes were more readily observed during the reaction of $[RhI(CO)(PMe_3)_2]$ with p-H_2 than in the corresponding case with $[RhCl(CO)(PMe_3)_2]$, a logical extension of the present study involved the examination of $[RhI(PPh_3)_3]$ and $[RhI(PPh_3)_2]_2$. It is interesting to note that despite being synthesised along with the well known chloride complexes in 1966,[39] relatively little work has been performed using these iodide derivatives. When the reaction of p-H_2 with $[RhI(PPh_3)_3]$ is followed in C_6D_6 at 295 K, very broad hydride resonances are observed for $[Rh(H)_2I(PPh_3)_3]$ (**4-I**), which precludes the observation of PHIP at this temperature. However, transfer NOE methods involving free H_2 enable the location of the corresponding *ortho*-phenyl resonances at δ 7.70 and 7.36 in an analogous way to that described earlier for **4**. It should be noted at this point that these results are complicated by the fact that $[RhI(PPh_3)_3]$ undergoes substantial phosphine dissociation even at 295 K and appreciable amounts of $[RhI(PPh_3)_2]_2$ and

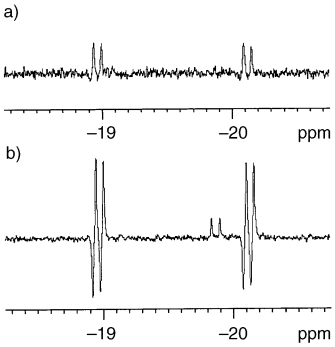


Figure 5. a) Expansion of the hydride region of a $^1H\{^{31}P\}$ NMR spectrum obtained when **1** catalyses the p-H_2 based hydrogenation of pentaflurostyrene, visible signals due to **9h**. b) Expansion of the hydride region of a $^1H\{^{31}P\}$ NMR spectrum obtained when **1** catalyses the p-H_2 based hydrogenation of pentaflurostyrene and sytrene illustrating that the hydride resonances for **9h** are now substantially enhanced.

PPh_3 are visible in the initial $^{31}P\{^1H\}$ spectrum recorded prior to H_2 addition. Furthermore, in this reaction no evidence for the formation of **2-I** was obtained at 295 K even though $[RhI(PPh_3)_2]_2$ was clearly visible in the corresponding $^{31}P\{^1H\}$ spectrum (at higher temperatures **2-I** is also observed).

When the reaction of a toluene solution of $[RhI(PPh_3)_2]_2$ with hydrogen was monitored by NMR spectroscopy at 295 K, two unpolarised hydride resonances were observed immediately at δ −16.06 and −15.91 due to **2-I** and **3-I**, respectively. These assignments are supported by the fact that resonances at δ −16.35 and −16.72 have been reported for the hydrides ligands in the related complex $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(CO)(PPh_3)]$.[40] The NMR characteristics of **2-I**, **3-I** and **4-I** are described in Table 1.

Observation of intermediates involved in the formation of $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)_2]$: Although no polarised hydride signals were detected during the reaction of $[RhI(PPh_3)_2]_2$ (**1-I**) with p-H_2 at room temperature, the same experiment at 268 K in toluene solution enabled the observation of eight polarised hydride signals. The corresponding $^1H\{^{31}P\}$ spectrum is shown in Figure 6a. By comparison with the data obtained using $[RhI(PPh_3)_3]$, two of these resonances, located at δ −9.66 (not shown in Figure 6a) and δ −13.80, can immediately be assigned to the tris(phosphine) complex **4-I**; the observation of **4-I** indicates that there are traces amounts of free PPh_3 in this sample. The remaining resonances, occurring at δ −13.49, −13.96, −15.30, −16.11, −16.19 and −16.71 were less intense, with each corresponding to a terminal hydride ligand. The fact that each of these signals couples to two equivalent phosphorus nuclei, and that the $J_{H,H}$ splitting is of the order of −10 Hz, is reminiscent of many of the binuclear complexes already described. COSY Spectroscopy confirmed that the resonances at δ −13.49 and −16.11, −13.95 and −16.71, and −15.29 and −16.18 were coupled. We note that the resonances at δ −13.49 and −13.95 sandwich the resonance of **4-I** corresponding to the hydride that is *trans* to iodide. This suggests that they arise from a similar arrangement. Furthermore,

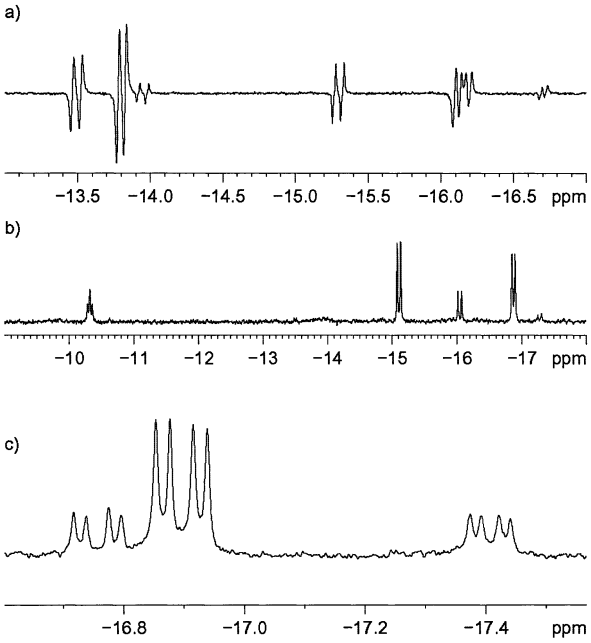
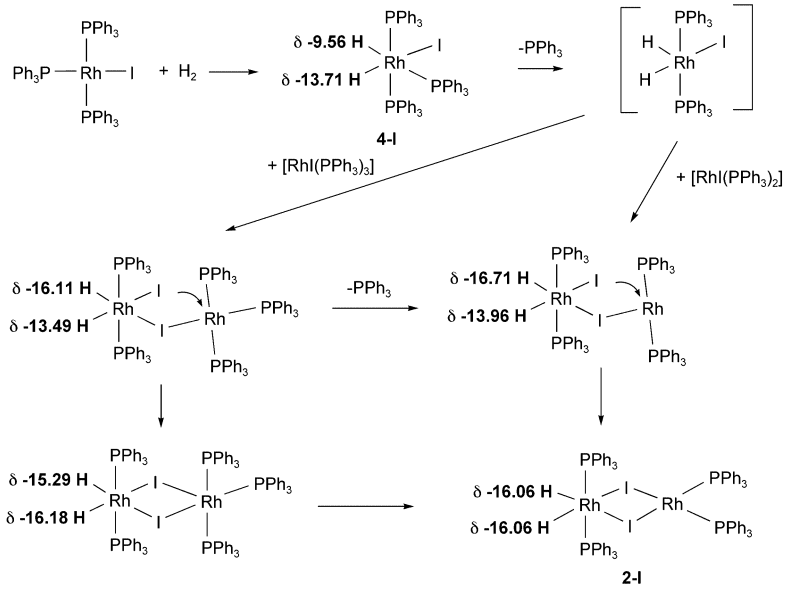


Figure 6. a) The hydride region of the ^{1}H NMR spectrum obtained when $[RhI(PPh_3)_2]_2$ reacts with p-H_2 in [D_8]toluene at 268 K b) The hydride region of the ^{1}H NMR spectrum obtained 24 h after $[RhI(PPh_3)_2]_2$ was placed under p-H_2 in [D_8]toluene and left at 295 K. c) The hydride region of the ^{1}H NMR spectrum obtained when a mixture of $[RhI(PPh_3)_2]_2$ and $[RhCl(PPh_3)_2]_2$ reacts with pentafluorostyrene with H_2 in CD_2Cl_2 at 263 K.

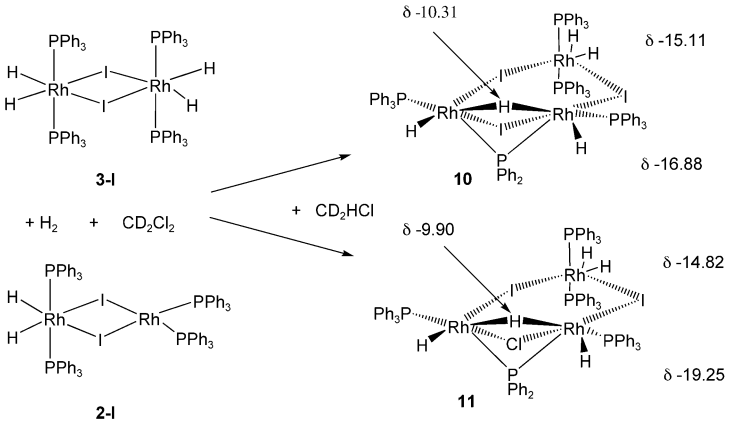
their respective partners at δ −16.11 and 16.71 are very close to those of **2-I** or **3-I**. We interpret this to suggest that these three species most likely correspond to the $[Rh(H)_2(I)(PPh_3)_2(\mu\text{-}I)Rh(PPh_3)_2]$, $[Rh(H)_2(I)(PPh_3)_2(\mu\text{-}I)Rh(PPh_3)_3]$ and $[Rh(H)_2(I)(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)_3]$ which are involved in the formation of **2-I**. A reaction sequence accounting for the formation of **2-I** is shown in Scheme 5 where $[RhI(PPh_3)_3]$ is the precursor. When this reaction was repeated in the presence of a slight excess of PPh_3,[41] the signal intensity of the δ −13.96 and −16.71 resonances were reduced relative to those at δ −13.49 and −16.11. This is consistent with the phosphine deficient structure indicated.

Observation of binuclear complexes during hydrogenation catalysis with $[RhI(PPh_3)_2]_2$: When a ^{1}H{^{31}P} spectrum was recorded on a sample of **1-I** at 268 K in the presence of p-H_2 and styrene, two additional, but extremely weak, polarised terminal hydride resonances were detected at δ −15.79 and δ −16.03 which were not observed when $[RhI(PPh_3)_2]_2$ alone was reacted with p-H_2. A pair of enhanced hydride resonances, at δ −15.85 and −15.93, were detected during the analogous reaction with 1-hexene, and with pentafluorostyrene, the corresponding resonances appear at δ −15.92 and −16.46. Although the intensity of these resonances were too low to allow the acquisition of heteronuclear NMR data, the detection of $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)$(styrene)] (**9a-I**), $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)$(1-hexene)] (**9d-I**) and $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)$(pentafluorostyrene)] (**9g-I**) can be proposed by analogy with the results described for **1** above. It should be noted that when **9g-I** was detected using n-H_2, a second-order multiplet centred at δ 40 was seen in the corresponding ^{31}P NMR spectrum.

Characterisation of the trirhodium phosphide bridged deactivation product $[(H)(PPh_3)Rh(\mu\text{-}H)(\mu\text{-}I)(\mu\text{-}PPh_2)Rh(H)(PPh_3)](\mu\text{-}I)_2Rh(H)_2(PPh_3)_2$: We note that when the toluene solutions of $[RhI(PPh_3)_2]$ were left under H_2 for extended periods of time, signals at δ −10.31, −15.11 and −16.88 appeared in the ratio 1:2:2 due to species **10** with structure shown in Scheme 6. The hydride region of the corresponding ^{1}H{^{31}P} NMR spectrum is shown in Figure 6b. A notable feature of the NMR characteristics of **10** corresponds to the observation of cross-peaks between the δ −10.31 and −16.88 hydride ligand resonances in the corresponding ^{1}H,^{31}P HMQC experiment to a ^{31}P signal with the unusual chemical shift of δ 203.1. ^{31}P NMR resonances with similar chemical shifts have been observed before and are characteristic of phosphide complexes possessing bridging (μ-PR_2) ligands.[42] The full NMR characterisation of **10** is described in the Supporting Information. Complex **10** is a trinuclear compound, which possesses two equivalent rhodium centres (bridged by the phosphide) and a third, distinct rhodium centre to which the hydrides resonating at δ −15.11 are coordinated. The bridging hydride spans the same rhodium nuclei as does the phosphide ligand and is approximately *trans* to two PPh_3 groups, one of which is con-



Scheme 5. Route to the formation of $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)_2]$ from the reaction of $[Rh(PPh_3)_3(I)]$ with H_2.



Scheme 6. Deactivation products observed in the reaction chemistry of $[Rh(PPh_3)_3(I)]$ with H_2.

nected to each of the equivalent metal centres. Two mutually *trans* phosphines are attached to the unique rhodium centre and a total of three iodide bridges are indicated by virtue of the number of hydride ligands and their associated chemical shifts.

In order to learn more about this result, a sample containing both $[RhI(PPh_3)_2]_2$ and $[RhCl(PPh_3)_2]_2$ was also studied. After 24 h resonances due to **10** and the chloride substituted derivative **11** were observed. The dramatic 2.4 ppm shift in the δ −16.88 resonance to δ −19.25 reflects the change in bridging iodide to chloride and is consistent with previous deductions.[40]

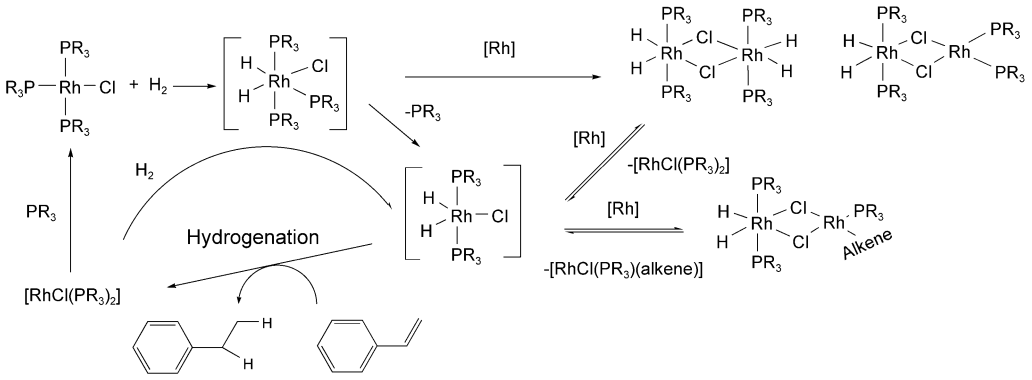
Conclusion

This paper has described the characterisation of a number of new hydride complexes detected during the reactions of $[RhCl(PPh_3)_2]_2$ and $[RhCl(PPh_3)_3]$ with hydrogen. The distribution of products that is obtained has been shown to depend upon the identity of the catalyst precursor, the nature of the solvent and the temperature. The solvents employed in this study correspond in the main to toluene, benzene and methylenechloride which have been featured in previous mechanistic studies as described in the introduction. Ethanol provides another example of a suitable solvent, used because of the enhanced solubility of $[RhCl(PPh_3)_3]$, and we expect the results presented here to be relevant to both hydrocarbon and polar media. In both solvent types when the precursor is $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$, the major hydride containing products that are visible in solution correspond to the dihydride $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ (**2**) and the tetrahydride $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)]_2$ (**3**). However, when $[RhCl(PPh_3)_3]$ is employed, the major hydrogen addition product is $[Rh(H)_2Cl(PPh_3)_3]$ (**4**) with $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)_2]$ (**2**) produced to a lesser extent. While magnetisation transfer from free H_2 into the hydride resonances of **3** and **4** is observable on the NMR timescale, direct transfer of H_2 into **2** is not observed, nor is exchange between **2** and **3**. We conclude that **3** is not formed on the NMR timescale by the direct addition of H_2 to **2** and propose that exchange of free H_2 into **3** proceeds via reversible halide bridge rupture to form **5**, $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)RhCl(H)_2(PPh_3)_2]$, which subsequently undergoes rapid H_2 exchange before reformation of **3**. Since exchange of **3** into **2** is not observed at this stage, H_2 addition to $[Rh(PPh_3)_2(\mu\text{-}Cl)RhCl(H)_2(PPh_3)_2]$ must be significantly faster than halide bridge closure.

We fully characterised these species in CD_2Cl_2 where the solubility of the precursors is much higher. Under these conditions there is evidence for the formation of the solvent complex $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(CD_2Cl_2)(PPh_3)]$ (**6**) in addition to **2** and **3**. Reaction of these complexes via hydride exchange with the solvent leads to the corresponding trihydride complexes $[Rh(Cl)(H)(PPh_3)_2(\mu\text{-}Cl)(\mu\text{-}H)Rh(Cl)(H)(PPh_3)_2]$ (**7**) and $[Rh(Cl)(H)(CD_2Cl_2)(PPh_3)(\mu\text{-}Cl)(\mu\text{-}H)Rh(Cl)(H)(PPh_3)_2]$ (**8**) being generated.

When the reaction of $[RhCl(PPh_3)_2]_2$ with H_2 in the presence of a number of alkenes is examined, the formation of $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)_2(Rh)(PPh_3)(alkene)]$ (**9**) is indicated. When **9** contains a prochiral alkene, the two *trans* phosphines of the Rh^I centre are diastereotopic and hence inequivalent, whereas with both 1,1-diphenylethene and *cis*-stilbene, equivalence between the two phosphines is observed. Hydride interchange was observed to occur in **9** in a process that was independent of the concentration of styrene and catalyst, suggesting that the hydride interchange process is intramolecular. Eyring data for this process is listed in Table 2 with $\Delta H^{\neq}$ consistently falling as the alkene changes from styrene through *para*-methyl to *para*-chlorostyrene. A process involving halide bridge rupture, followed by rotation about the remaining Rh–Cl bridge, and bridge re-establishment is consistent with this information. This process is facilitated as the alkene becomes electron rich, and the large negative values of $\Delta S^{\neq}$ for this process imply a degree of solvent participation.

In these studies, the observed hydride signals for species of type **9** decay rapidly as the hydrogen present in solution is consumed by alkane formation. The absolute intensity of the hydride signals for **9**, however, increased consistently when solutions were examined that contained a lower alkene concentration but the same rhodium and *p*-H_2 concentrations. Surprisingly, as the concentration of alkene in solution decreases the significance of the reductive elimination of H_2 from **9** also increased. At even lower alkene concentrations magnetisation transfer from the hydrides of **9a** to the alkyl protons of the hydrogenation product ethylbenzene was observed. This corresponds to direct evidence for the corresponding binuclear metal dihydride complex being linked to alkene hydrogenation. In order to account for the complex kinetic behaviour, the hydrogenation process cannot simply involve bridge opening followed by alkene binding. A logical option would be for hydrogenation to proceed via binuclear complex fragmentation with trapping of the resultant $[RhCl(H)_2(PPh_3)_2]$ fragment by the alkene. This would be consistent with the fact that the binuclear complexes act as a hydrogen reservoir during catalysis and a reduced stability for the potential intermediate $[Rh(H)_2(PPh_3)_2(\mu\text{-}Cl)RhCl(PPh_3)(alkene)]$ with fall in alkene concentration as summarised in Scheme 7.



Scheme 7. Products observed when $[Rh(PPh_3)_3Cl]$ reacts with H_2 and an alkene.

The role of binuclear complexes in the hydrogenation cycle was even more clearly illustrated when the precursor $[RhCl(CO)(PMe_3)_2]$ was examined. In a control experiment, the reaction of $[RhCl(CO)(PMe_3)_2]$ with *p*-H_2 at 295 K essentially yielded only polarised signals due to $[(H)(Cl)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Rh(CO)(PMe_3)]$ (**12**). However, when an identical sample was prepared and monitored in the presence of 1.5-fold excess of styrene relative to $[RhCl(CO)(PMe_3)_2]$, the new species $[(H)_2Rh(PMe_3)_2(\mu\text{-}Cl)_2Rh(CO)(PMe_3)]$ (**13**) and $[HRh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)_2Rh(CO)(PMe_3)]$ (**14**) were clearly visible, and there was a dramatic 16-fold increase in size of the associated hydride signal intensities of $[(H)(Cl)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Rh(CO)(PMe_3)]$ (**12**). The observation of these additional complexes is possible due to the fact that hydrogenation acts to pull the hydrogen through the system and thereby promote *p*-H_2 cycling which in turn leads to a corresponding gain in the time averaged non-Boltzmann spin populations associated with the hydride nuclear spin states in these products. This effect was also observed when the analogous complex $[RhI(CO)(PMe_3)_2]$ was examined and in related studies involving $[Ru_3(CO)_{10}(PPh_3)_2]$ where a more quantitative link was demonstrated.[43] In these experiments the new dihydride complex $[H(I)Rh(alkene)(PMe_3)(\mu\text{-}H)(\mu\text{-}I)Rh(CO)(PMe_3)]$ (**16**) was also detected. This deduction is further supported by the fact that direct transfer of H_2 from $[Rh(H)_2(PMe_3)_3(\mu\text{-}I)_2Rh(CO)(PMe_3)]$ (**12-I**) into ethylbenzene was visible in suitable magnetisation transfer experiments.

When the analogous iodide complexes $[RhI(PPh_3)_2]_2$ and $[RhI(PPh_3)_3]$ were examined, hydrogenation was observed and $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)_2Rh(PPh_3)_2]$ (**2-I**), $[Rh(H)_2(PPh_3)_2(\mu\text{-}I)]_2$ (**3-I**) and $[Rh(H)_2I(PPh_3)_3]$ (**4-I**) were characterised. Although no polarised hydride signals were detected during the reaction of $[RhI(PPh_3)_2]_2$ with *p*-H_2 alone at 295 K, when this reaction was repeated at 268 K, three new complexes were observed, corresponding to intermediates involved in the formation of **2-I**. The catalytic studies involving $[RhI(PPh_3)_2]_2$ were complicated by the high initial hydrogenation activity but the observation of a number of analogous complexes to **9** was achieved. This further supports the suggestion that binuclear complexes play a significant role in hydrogenation in these systems. In these reactions, formation of the trirhodium phosphide bridged deactivation product, $[(H)(PPh_3)Rh(\mu\text{-}H)(\mu\text{-}I)(\mu\text{-}PPh_2)\text{-}Rh(H)(PPh_3)](\mu\text{-}I)_2Rh(H)_2(PPh_3)_2$ (**10**) was observed at longer reaction times. This product arises via P–C bond cleavage and the elimination of benzene, and accounts for the fact that although the iodide system shows a higher initial activity deactivation is facile.

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[1] F. H. Jardine, *Prog. Inorg. Chem.* **1981**, *28*, 63.
[2] J. F. Young, J. A. Osborn, F. H. Jardine, G. Wilkinson, *J. Chem. Soc. Chem. Commun.* **1965**, 131; J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1711.
[3] C. A. Tolman, P. Z. Meakin, D. L. Lindner, J. P. Jesson, *J. Am. Chem. Soc.* **1974**, *96*, 2762.
[4] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, **1986**.
[5] D. A. Wink, P. C. Ford, *J. Am. Chem. Soc.* **1987**, *109*, 436.
[6] T. Yoshida, S. Otsuka, M. Matsumoto, K. Nakatsu, *Inorg. Chim. Acta* **1978**, *29*, L257.
[7] J. M. Brown, P. L. Evans, A. R. Lucy, *J. Chem. Soc. Perkin Trans. 2* **1987**, 1589.
[8] H. Arai, J. Halpern, *J. Chem. Soc. Chem. Commun.* **1971**, 1571.
[9] J. Halpern, C. S. Wong, *J. Chem. Soc. Chem. Commun.* **1973**, 629.
[10] C. A. Tolman, P. Z. Meakin, D. L. Lindner, J. P. Jesson, *J. Am. Chem. Soc.* **1974**, *96*, 2762.
[11] J. M. Brown, A. R. Lucy, *J. Chem. Soc. Chem. Commun.* **1984**, 914.
[12] J. M. Brown, L. R. Canning, A. R. Lucy, *J. Chem. Soc. Chem. Commun.* **1984**, 915.
[13] J. Halpern, *Inorg. Chim. Acta* **1981**, *50*, 11.
[14] N. Koga, K. Morokuma, *Chem. Rev.* **1991**, *91*, 823.
[15] A. Dedieu, *Inorg. Chem.* **1980**, *19*, 375.
[16] C. Daniel, N. Koga, J. Han, X. Y. Fu, K. Morokuma, *J. Am. Chem. Soc.* **1988**, *110*, 3773.
[17] S. Geftakis, G. E. Ball, *J. Am. Chem. Soc.* **1999**, *121*, 6336.
[18] C. R. Bowers, D. P. Weitekamp, *Phys. Rev. Lett.* **1986**, *57*, 2645.
[19] S. Hasnip, S. B. Duckett, D. R. Taylor, M. J. Taylor, *Chem. Commun.* **1998**, 923; S. P. Millar, D. L. Zubris, J. E. Bercaw, R. Eisenberg, *J. Am. Chem. Soc.* **1998**, *120*, 5329.
[20] S. B. Duckett, C. L. Newell, R. Eisenberg, *J. Am. Chem. Soc.*, **1994**, *116*, 10548.
[21] S. A. Colebrooke, S. B. Duckett, J. A. B. Lohman, *Chem. Commun.* **2000**, 685–686.

[22] J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1711; L. Vallarino, *J. Chem. Soc.* **1957**, 2287.
[23] R. Eisenberg, *Acc. Chem. Res.* **1991**, *24*, 110.
[24] S. B. Duckett, G. K. Barlow, M. G. Partridge, B. A. Messerle, *J. Chem. Soc. Dalton Trans.* **1995**, 3427; S. B. Duckett, R. J. Mawby, M. G. Partridge, *J. Chem. Soc. Chem. Commun.* **1996**, 383; S. P. Millar, M. Jang, R. J. Lachicotte, R. Eisenberg, *Inorg. Chim. Acta* **1998**, **270**, 363; B. A. Messerle, C. J. Sleigh, M. G. Partridge, S. B. Duckett. *Dalton. Trans.* **1999**, 1429.
[25] G. Bodenhausen, R. R. Ernst *J. Am. Chem. Soc.* **1982**, *104*, 1304.
[26] C. Masters, B. L. Shaw, R. E. Stainbank, *J. Chem. Soc. Chem. Commun.* **1971**, 209.
[27] C. Masters, W. S. McDonald, G. Raper, B. L. Shaw, *J. Chem. Soc. Chem. Commun.* **1971**, 210.
[28] T. Yoshida, S. Otsuka, M. Matsumoto, K. Nakatsu, *Inorg. Chim. Acta* **1978**, *29*, L257.
[29] G. Wagner, *J. Magn. Reson.* **1984**, *57*, 497.
[30] G. M. Clore, A. M. Gronenborn, *J. Magn. Reson.* **1982**, *48*, 402.
[31] N. Nirmala, G. M. Lippens, K. Hallenga, *J. Magn. Reson.* **1992**, *100*, 25.
[32] G. M. Clore, A. M. Gronenborn, *J. Magn. Reson.* **1983**, *53*, 423.
[33] A. P. Campbell, B. D. Sykes, *J. Magn. Reson.* **1991**, *93*, 77.
[34] D. Henrichsen, B. Ernst, J. L. Magnani, W. T. Wang, B. Meyer, T. Peters, *Angew. Chem.* **1999**, *111*, 106; Angew. Chem. Int. Ed. **1999**, *38*, 98.
[35] A. Koch, J. Bargon, *Inorg. Chem.* **2001**, *40*, 533
[36] O. W. Howarth, C. H. McAteer, P. Moore, G. E. Morris, *J. Chem. Soc. Dalton Trans.* **1981**, 1481.
[37] W. Brüger, *Handbook of NMR spectral parameters*, **1979**, Heyden, London.
[38] We note that this data does not fully rule out swapping the CD_2Cl_2 and Cl ligand positions in **8**.
[39] J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1711.
[40] P. D. Morran, S. B. Duckett, P. R. Howe, J. E. McGrady, S. A. Colebrooke, R. Eisenberg, M. G. Partridge, J. A. B. Lohman, *J. Chem. Soc. Dalton Trans.* **1999**, 3949.
[41] This was achieved in practice by the addition of a small quantity of $[RhI(PPh_3)_3]$ or $[RhCl(PPh_3)_3]$.
[42] P. E. Garrou, *Chem. Rev.* **1985**, *85*, 171.
[43] D. Blazina, S. B. Duckett, J. A. B. Lohman, P. J. Dyson, *Angew. Chem.* **2000**, *113*, 3992–3995; *Angew. Chem. Int. Ed.* **2001**, *40*, 3874–3877; D. Blazina, S. B. Duckett, J. A. B. Lohman, P. J. Dyson, *Chem. Eur. J.* **2003**, *9*, 1045–1061.

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