

Activation of H₂ by Chlorocarbonylbis(trimethylphosphine)rhodium(I) labilizes CO and produces the New Binuclear Complex H(Cl)Rh(PMe₃)₂(μ-H)(μ-Cl)Rh(PMe₃)(CO)

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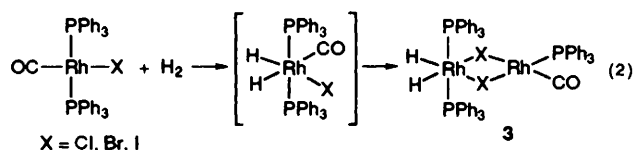
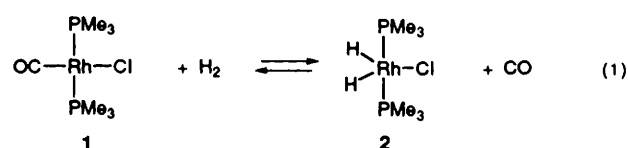
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The oxidative addition of H₂ to [RhCl(CO)(PMe₃)₂] is followed using NMR spectroscopy in conjunction with *para*-enriched hydrogen and leads to CO labilization and formation of an unusual binuclear complex.

The Rh^I complex [RhCl(CO)(PMe₃)₂], **1** is an active catalyst for photochemically driven alkane functionalization and thermal transfer hydrogenation.¹⁻⁷ In these processes that involve C-H bond activation, a critical step is eqn. (1) wherein oxidative addition of H₂ to **1** and the reverse reaction of CO addition to [RhH₂Cl(PMe₃)₂], **2**, proceed in an associative way *via* a Rh^{III} six-coordinate species that is necessarily labile. In this communication, we describe an NMR study of eqn. (1) using *para*-enriched H₂ (*p*-H₂) that allows us to identify previously undetected species in the reaction system and provides strong and unambiguous support for CO lability in

the initial six-coordinate Rh^{III} product. The species are observed through *p*-H₂ induced polarization which has been shown to yield strongly enhanced hydride resonances in H₂ addition products.⁸⁻¹⁴ Recently, this method has been employed to examine H₂ oxidative addition to the well-known PPh₃ analogue of **1** and has detected the binuclear complex [H₂Rh(PPh₃)₂(μ-Cl)₂Rh(CO)(PPh₃)] **3** in the formerly unobserved reaction shown as eqn. (2).¹⁵

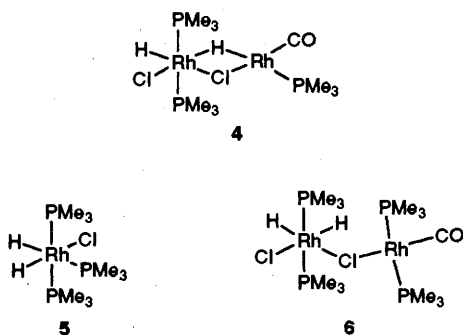
When a C₆D₆ solution of **1** under 3 atm (1 atm = 101.3 kPa) of *p*-H₂ is thawed rapidly, shaken and introduced into the probe of a 400 MHz NMR spectrometer at 342 K, the



spectrum shown in Fig. 1(a) is obtained within 60 s.† The spectrum shows two new resonances at $\delta -17.06$ and -17.60 , assigned to the hydride ligands, H_b and H_a of complex **4**, respectively. The antiphase character of these signals is a consequence of parahydrogen induced polarization, in which a 3.5 Hz separation between absorption and emission maxima corresponds to the coupling between H_b and H_a of **4**. In addition to J_{H-H} , the hydrides exhibit couplings to phosphorus and rhodium such that the resonance due to H_a appears as a doublet of triplets while a more complicated pattern exists for H_b .

A $^{31}\text{P}\{\text{INEPT}\}$ spectrum of **4** acquired with concurrent decoupling of the PMe_3 protons exhibits a doublet ($J_{\text{Rh-P}} 95.6$ Hz) of triplet structure ($J_{\text{P-H}} 15.5$ Hz) centred at $\delta -5.36$, assigned to P_a , with the outer lines of each triplet having opposite phase and half the intensity of the central line. When a ^1H NMR spectrum of **4** is obtained while selectively decoupling P_a , the H_a resonance collapses into a doublet of antiphase doublets [Fig. 1(b)] with a 24.9 Hz coupling corresponding to $J_{\text{Rh-H}}$, while the H_b resonance simplifies to a doublet of triplets of antiphase doublets. Upon expanding the ^{31}P decoupled region through utilization of a garp pulse sequence,¹⁶ an additional coupling is removed from H_b , yielding a doublet of doublets of antiphase doublets with couplings 29.5, 20 and -3.5 Hz, respectively [(Fig. 1(c)).

When the H_2 addition reaction is repeated with ^{13}CO -labelled $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$, the H_b hydride resonance clearly shows an additional doublet coupling ($J_{\text{HC}} 2.6$ Hz) in the $^1\text{H}\{^{31}\text{P}\}$ spectrum, whereas the H_a resonance is unaffected by the labelling [Fig. 1(d)]. The NMR results thus reveal that: (i) the signal due to H_a of **4** at $\delta -17.60$ is coupled to a single rhodium centre, two equivalent phosphines (P_a) and the second hydride (H_b), and from the magnitude of the coupling constants, the two phosphines and the other hydride are in *cis* positions, and (ii) the more complex signal due to H_b of **4** at $\delta -17.06$ couples to the same Rh and P_a nuclei while possessing additional couplings to a second, inequivalent Rh centre, a single phosphine ligand coordinated to that centre (P_b), and when $1\text{-}^{13}\text{CO}$ is used, a *cis* carbonyl ligand.‡ Based on these results, it is possible to assign the structure of **4**, the product observed in the reaction of $[\text{RhCl}(\text{CO})(\text{PMe}_3)_2]$ with hydrogen as, $[\text{H}(\text{Cl})\text{Rh}(\text{PMe}_3)_2(\mu\text{-H})(\mu\text{-Cl})\text{Rh}(\text{PMe}_3)(\text{CO})]$, **4**. The binuclear structure of **4** is similar to that of **3** found in eqn. (2) except that one hydride and one chloride are interchanged.



† The maximum signal enhancement observed for a single transient occurs at 362 K but because the rate of *p*- H_2 relaxation increases with increasing temperature, signal averaging is carried out at 342 K.

‡ Selected spectroscopic data for compound **4**: ^1H NMR (C_6D_6 , 342 K, 400 MHz); $\delta -17.60$ (H_a , m, $J_{\text{RhH}} 24.9$, $J_{\text{PH}} 15.5$, $J_{\text{HH}} -3.5$ Hz), $\delta -17.06$ (H_b , m, $J_{\text{RhH}} 29.5$, $J_{\text{RH}} 20$, $J_{\text{PH}} 15.5$, $J_{\text{PH}} 30$, $J_{\text{HH}} -3.5$ Hz). ^{31}P NMR (162 MHz): $\delta -5.36$ (P_a , dt, $J_{\text{RhP}} 95.6$, $J_{\text{PH}} 15.5$ Hz). The ^{31}P resonance of the Rh^I coordinated PMe_3 , P_b , was not observed since its signal was not enhanced by polarization transfer.

Since the Rh^{III} centre in **4** does not have CO coordinated to it, its formation suggests the lability of CO in the initial H_2 oxidative addition product. Indeed the presence of free PMe_3 in the reaction of **1** with *p*- H_2 completely inhibits the formation of **4** and leads instead to the appearance of polarized hydride resonances corresponding to $[\text{RhH}_2\text{Cl}(\text{PMe}_3)_3]$ **5**.¹⁷ The enhancement of signal when *p*- H_2 is reacted directly with $\text{RhCl}(\text{PMe}_3)_3$ ¹⁸ is impressive, with an increase in signal-to-noise of more than 200-fold relative to that obtained under normal H_2 [Fig. 2(a)]. Via the INEPT pulse sequence, this enhancement can be transferred to ^{31}P , yielding the spectrum shown in Fig. 2(b). The levels of ^1H signal enhancement for **5** permit its detection when present in even very small amounts and both **5** and **4** are in fact seen

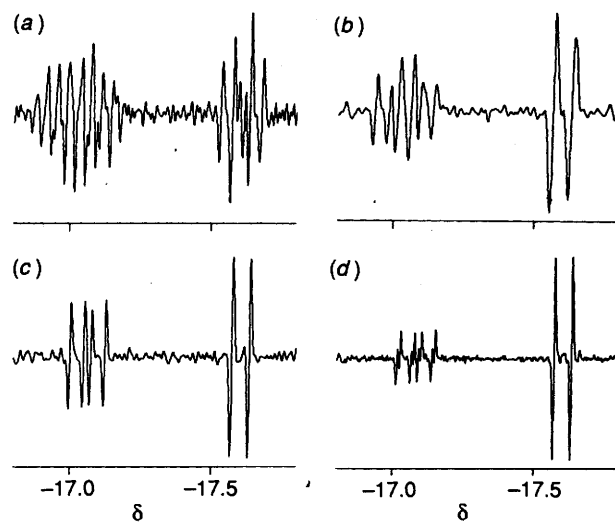


Fig. 1 ^1H NMR spectra of **4** obtained with *p*- H_2 in $[\text{D}_6]$ benzene at 342 K. The antiphase components arise in transitions involving protons that were correlated in parahydrogen. (a) ^1H spectrum; (b) $^1\text{H}\{^{31}\text{P}\}$ spectrum with the ^{31}P resonance at $\delta -5.36$ selectively decoupled; (c) $^1\text{H}\{^{31}\text{P}\}$ spectrum with complete ^{31}P decoupling; (d) $^1\text{H}\{^{31}\text{P}\}$ spectrum produced from ^{13}CO labelled $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ with complete ^{31}P decoupling.

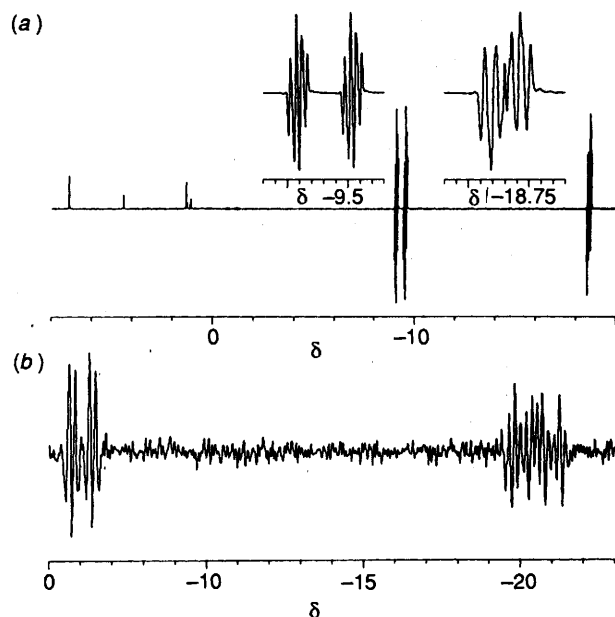


Fig. 2 NMR spectra showing enhanced signals of **5** formed in the reaction of $\text{RhCl}(\text{PMe}_3)_3$ with *p*- H_2 in $[\text{D}_6]$ benzene at 342 K. (a) ^1H spectrum with hydride resonances expanded as insets; (b) $^{31}\text{P}\{\text{INEPT}\}$ spectrum with the CH_3 resonances selectively decoupled.

when the sample of **1** used in reaction with *p*-H₂ contains trace amounts of PMe₃. Therefore, samples of **1** were routinely dissolved in benzene and reprecipitated upon evacuation, thereby removing trace amounts of free PMe₃.

The formation of **4** and the formation of **3** in eqn. (2) provide good evidence that CO is easily liberated from the initial Rh^{III} oxidative addition product, [RhH₂Cl(CO)(PR₃)₂]. It appears that the resultant five-coordinate species **2** completes its coordination shell by the addition of a chloride ligand of a second [RhCl(CO)(PR₃)₂] molecule as shown in **6**. The arrangement of **6** facilitates an internal displacement reaction on the Rh^I centre through which either hydride or halide substitute for one of the phosphine ligands, yielding the (μ-H, μ-Cl) or (μ-Cl)₂ structures of **4** and **3**, respectively. The notion of CO labilization *via* oxidative addition of H₂ to [RhX(CO)(PR₃)₂] is important in C-H bond activation and transfer hydrogenation catalysis by **1** and obtains direct spectroscopic support from the present study. Indeed, the observation of binuclear complexes **4** and **3** which are clearly related to Tolman's dihydride [(H)₂Rh(PPh₃)₂(μ-Cl)₂Rh(PPh₃)₂] seen in hydrogen addition to [RhCl(PPh₃)₃]¹⁹ poses interesting questions of whether such binuclear complexes of rhodium are generally accessible, and what role do they play in rhodium catalysed hydrogenations.

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