Reaction of iodocarbonylbis(trimethylphosphine)rhodium(I) with parahydrogen leads to the observation of five characterisable H₂ addition products

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The complex $RhI(CO)(PMe_3)_2$ reacts with dihydrogen to generate five different products that have been identified and structurally assigned through the use of parahydrogen induced polarisation.

When the addition of hydrogen to a metal centre is monitored by NMR spectroscopy in conjunction with dihydrogen specially enriched in the para or anti-symmetric spin state,[1] the observation of previously unseen hydride products becomes possible.[2] In this approach, the spin-correlated activation of parahydrogen leads to non-Boltzmann spin populations for the product hydride nuclei and consequent enhanced absorptions and emissions in their ^{1}H NMR signals.[3] The reaction chemistry presented here concerns the addition of H_2 to $RhI(CO)(PMe_3)_2$ **1**, and shows the power of this method in detecting and identifying different dihydrogen products, including very minor components, from a reaction mixture. It has previously been reported that when $RhCl(CO)(PPh_3)_2$ is warmed with parahydrogen only the binuclear product **2** is detected, whereas with the PMe_3 analogue, only the hydride-bridged product **3** was seen.[4] Products **2** and **3** are related by interchange of a bridging chloride for hydride.
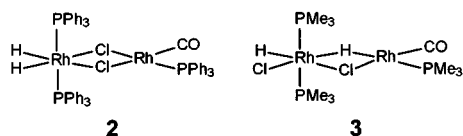

When a C_6D_6 solution of $RhI(CO)(PMe_3)_2$, **1**, under 3 atm of para-enriched hydrogen (p-H_2) is monitored by ^{1}H NMR spectroscopy at 348 K, the spectrum shown in Fig. 1(a) is obtained. Close examination reveals the presence of 10 hydride resonances belonging to five reaction products (Table 1). We show below that three of the products, **4**, **5** and **6**, are isomeric analogues of **2** and **3**. Each pair of product resonances exhibits anti-phase lines (emission/absorption or *E/A*) characteristic of parahydrogen induced polarisation (PHIP) with the sense of the anti-phase lines indicating that all of the hydride–hydride spin–spin couplings are negative. In the corresponding ^{1}H-{^{31}P} NMR spectrum, the resonances at δ -10.00, -14.63, -14.75, -14.80, -15.83, -17.70, and -18.02 simplify into anti-phase doublets of doublets, showing that each is coupled to one [103]Rh nucleus as a terminal hydride ligand, while the three resonances at δ -11.18, -14.46 and -16.73 couple to two rhodium centres indicating that they correspond to bridging hydride ligands [Fig. 1(b)]. The connectivity of the hydride ligands was established by a gradient assisted [1]H–^{1}H correlation spectrum (COSY) employing a 45° starting pulse and a 90° read pulse. The resulting spectrum [Fig. 1(c)] reveals the connectivity of five pairs of hydride resonances (Table 1). In order to fully characterise the reaction products, a series of [1]H–[31]P, [1]H–[13]C and [1]H–[103]Rh spectra were then recorded.
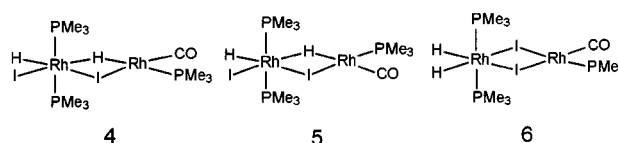
At 348 K the most intense signals originate from the mutually coupled hydride resonances at δ -14.46 and δ -14.63. The terminal hydride resonance at δ -14.63 connects with a single [103]Rh nucleus, δ -210 (J_{RhH} = 23 Hz), and two equivalent ^{31}P nuclei (J_{PH} = 15.5 Hz) which resonate at δ -15.9 in the corresponding HMQC experiments. In addition, the [1]H–[31]P HMQC experiment reveals that the hydride partner at δ -14.46, identified above as bridging, couples to two separate sets of ^{31}P nuclei, which are themselves not coupled, at δ -6.0 (J_{PH} = 14, J_{RhP} = 155 Hz) and -15.9 (J_{PH} = 32, J_{RhP} = 96 Hz) respectively. The change in J_{RhP} from 155 Hz to 96 Hz for these resonances is consistent with an oxidation state change from I to III for the corresponding rhodium centre. The rhodium(I) centre, located in a [1]H–[103]Rh spectrum at δ -733, couples to this hydride only. When compound **1** is specifically labelled with [13]CO, the resonance due to the bridging hydride of this product possesses an additional coupling of 3 Hz and correlates with a ^{13}C resonance at δ 186.1 in the corresponding [1]H–[13]C spectrum. The identity of the product is therefore clearly established as $(H)(I)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}I)Rh(CO)(PMe_3)$ **4**, analogous to **3**. Although the iodide ligands are NMR silent, their presence is required to satisfy the rhodium oxidation state requirements.

A minor reaction product, **5**, with hydride resonances at δ -14.80 and -16.73, possesses similar spectral features to those of **4** which indicate similar ligand spheres and the presence of Rh(I) and Rh(III) centres. However, in this isomer, the couplings from phosphorus to the bridging hydride are 13.5 and 14 Hz, while the hydride coupling to [13]CO has increased to 11 Hz. The decrease in J_{PH}, from 32 to 13.5 Hz, and increase in $J_{([13]CO)H}$, from 3 to 11 Hz, on moving from **4** to **5** is consistent with the argument that **4** contains a μ-hydride which is *trans* to the PMe_3 ligand of the Rh(I) centre, while in **5** the μ-hydride is *trans* to CO. The small size of J_{PH} associated with a *trans* P–Rh(I)–H arrangement is consistent with that previously observed for $(H)_2Rh_2\{P[N(CH_3)_2]_3\}_4$.[5]

At 313 K the remaining resonances become sharper and are hence easier to monitor. Four of these resonances are assigned to the products $(H)_2Rh(PMe_3)_2(\mu\text{-}I)Rh(CO)(PMe_3)$ **6**, and $Rh(H)_2I(PMe_3)_3$ **7**. The mutually coupled hydride resonances of **6** appear at δ -17.70 and -18.02, and possess additional couplings due to one rhodium and two phosphorus nuclei, the resonances of which were located at δ 74 and -16.4 (J_{RhP} = 113 Hz) in the corresponding [1]H–[103]Rh and [1]H–[31]P correlation experiments, respectively. Evidence for the iodide bridges comes directly from the chemical shifts of the hydride ligands of **6**, δ -17.70 and -18.02, which require the presence of *trans* electronegative groups. Furthermore, the
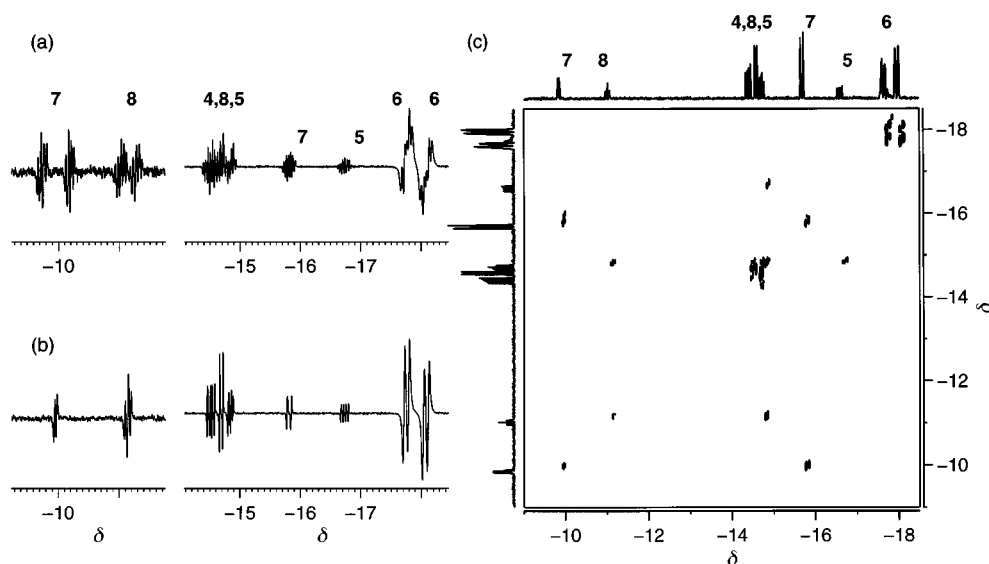
Fig. 1 ^{1}H NMR spectra showing the hydride region after warming a sample of RhI(CO)(PMe$_3$)$_2$ **1** with p-H$_2$ in C$_6$D$_6$. (a) ^{1}H spectrum at 348 K; (b) [1]H-{[31]P} spectrum at 333 K; (c) selected cross peaks (absolute value display) and projections in the [1]H–[1]H correlation spectrum, using gradients and ^{31}P decoupling showing hydride–hydride connectivity.

Table 1 Selected ^{1}H, ^{31}P, ^{13}C and [103]Rh NMR spectral data for the reaction products of RhI(CO)(PMe$_3$)$_2$ with H$_2$ (all ^{1}H data tested by simulation)[a]

Complex	[1]H	[31]P	[13]C	[103]Rh
4	−14.46 (ddddt, $^2J_{HH}$ = −3.5, $^1J_{RhH}$ = 19 and 30, $^2J_{PH}$ = 14 and 32, $^2J_{HCO}$ = 3) −14.63 (ddt, $^2J_{HH}$ = −3.5, $^1J_{RhH}$ = 23, $^2J_{PH}$ = 15.5)	−6.0 ($^1J_{RhP}$ = 155) −15.9 ($^1J_{RhP}$ = 96)	186.1 ($^2J_{PC}$ = 16.9, $^1J_{RhC}$ = 79.8)	−210 −733
5	−16.73 (ddddt, $^2J_{HH}$ = −3.5, $^1J_{RhH}$ = 16.7 and 31.5, $^2J_{PH}$ = 14 and 13.5, $^2J_{HCO}$ = 11) −14.80 (ddt, $^2J_{HH}$ = −3.5, $^1J_{RhH}$ = 21, $^2J_{PH}$ = 16)	−0.6 ($^1J_{RhP}$ = 151) −16.5 ($^1J_{RhP}$ = 97)	183.8	—
6	−17.70 (ddt, $^2J_{HH}$ = −9, $^1J_{RhH}$ = 32, $^2J_{PH}$ = 15.6) −18.02 (ddt, $^2J_{HH}$ = −9, $^1J_{RhH}$ = 30.7, $^2J_{PH}$ = 16.3)	−16.4 ($^1J_{RhP}$ = 113)	—	74
7	−10.0 (dddt, $^2J_{HH}$ = −7, $^1J_{RhH}$ = 14.4, $^2J_{PH}$ = 176, $^2J_{PH}$ = 17.4) −15.83 (ddq, $^2J_{HH}$ = −7, $^1J_{RhH}$ = 28.1, $^2J_{PH}$ = 36)	−13.6 ($^1J_{RhP}$ = 102) −31.3 ($^1J_{RhP}$ = 94)	—	−644
8	−11.18 (dddt, $^2J_{HH}$ = −6, $^1J_{RhH}$ = 19 and 19, $^2J_{PH}$ = 99.5, 21 and 16) −14.75 (ddt, $^2J_{HH}$ = −6, $^1J_{RhH}$ = 28, $^2J_{PH}$ = 15 and 15)	−10.34 (*trans* to hydride, $^1J_{RhP}$ = 120, $^4J_{PP}$ = 70, $^2J_{PP}$ = 40) 0.6 ($^1J_{RhP}$ = 145, $^4J_{PP}$ = 70) 10.38 ($^1J_{RhP}$ = 126, $^2J_{PP}$ = 40)	—	—

[a] δ in ppm, J in Hz magnitudes of couplings only for $^2J_{HH}$.
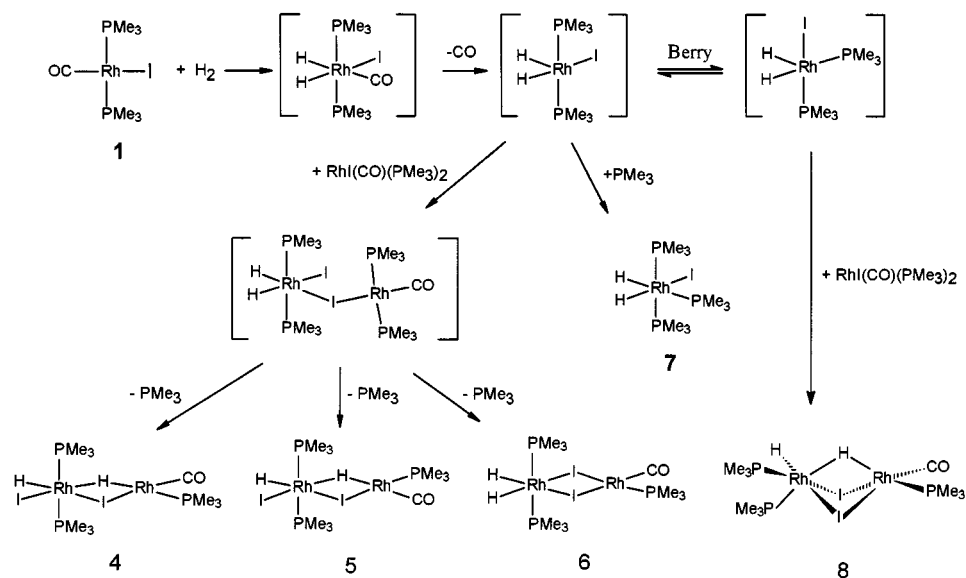
Scheme 1

similarity of these chemical shifts to those previously reported for the related complex (H)$_2$Rh(PPh$_3$)$_2$(μ-I)$_2$Rh(CO)(PPh$_3$) points to the presence of a second Rh(I) centre.[4] Additionally, the rhodium chemical shift, δ 74, is very similar to that of

δ 32 observed for the related complex (H)$_2$Rh(PPh$_3$)$_2$(μ-I)$_2$-Rh(CO)(PPh$_3$).

For **7**, the hydride resonances appear at δ −10.00 and −15.83 and contain splittings which imply the presence of one rhodium

and three phosphorus nuclei. The resonance at δ -10.00 possesses a large P–H coupling of 176 Hz, requiring the corresponding hydride ligand to be located *trans* to phosphine. The higher field resonance, δ -15.83, arises from the hydride ligand which is *trans* to the iodide group.

The final product contains a terminal hydride (δ -14.75) *cis* to two phosphorus centres and a bridging hydride ligand which resonates at δ -11.18 and possesses a large phosphorus coupling, $J_{PH} = 99.5$ Hz, indicative of an essentially *trans* H–Rh–PMe$_3$ arrangement. Further couplings to two other phosphorus nuclei, $J_{PH} = 21$ and 16 Hz, and essentially equal couplings to two rhodium centres, $J_{RhH} = 19$ Hz, are observed to the bridging hydride. The terminal hydride resonance at δ -14.75 does not connect with the ^{31}P nucleus at δ 0.6 in the corresponding ^{1}H–^{31}P HMQC spectrum which confirms its location on the second rhodium centre. In the complexes, (μ-H)$_2$Rh$_2$-{P[N(CH$_3$)$_2$]$_3$}$_4$ and (μ-H)$_2$Rh$_2${P[OPr^i]$_3$}$_4$, containing rhodium(I) centres with near coplanar framework atoms P$_2$Rh-H$_2$RhP$_2$, reported by Muetterties, the corresponding H$_{bridge}$–P couplings are established at around 30 Hz.[5,6] The related complex **9**, shown below, was also detected with P[OPr^i]$_3$ and has been reported to possess hydride resonances for H$_a$ at δ -11.1 ($J_{PH} = 89$ Hz, 1H) and H$_b$ at δ -14.5 (1H).[6] Based on the similarities between the J_{PH} couplings and the chemical shifts of the terminal and bridging hydride ligands observed for the new species we suggest that it is most likely to adopt the structure shown as **8**. When RhI(^{13}CO)(PMe$_3$)$_2$ is employed, no additional hydride–^{13}C couplings are visible; however, the resonance line width is sufficient to hide a small *cis* coupling indicating that the bridging hydride in **8** is *cis* to the carbonyl of the second rhodium centre.

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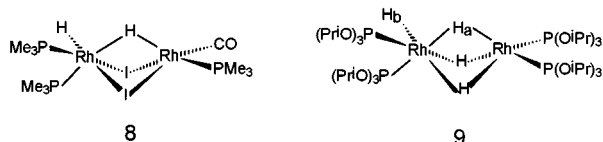
The formation of products **4**–**8** can be envisioned to proceed according to Scheme 1 in which oxidative addition of H$_2$ to **1** is followed by rapid CO loss. Subsequent addition of excess **1** to the unsaturated species Rh(H)$_2$I(PMe$_3$)$_2$ leads to the binuclear products while addition of PMe$_3$ generates **7**. Consistent with

this view, the signals due to **7** decrease substantially as the concentration of **1** is increased. Since the binuclear products **4**, **5** and **6** arise from a common intermediate, it is possible to assess the relative rates of the product forming steps from the relative magnitudes of the observed polarisation. For **4** and **5** for example, the intensity difference is 15:1 at 358 K reflecting a $\Delta G^{\ddagger}$ of 8.1 kJ mol^{-1} in the key product forming step.[6] The same analysis involving **6** is more ambiguous because facile dihydride interchange broadens the hydride resonances significantly at this temperature.

In this paper we have shown that parahydrogen induced polarisation can be used to monitor complex thermal reactions that are not normally decipherable or even observable. The complexity of a reaction system, as apparently simple as H$_2$ addition to **1**, is surprising and underscores the pitfalls in drawing up catalytic reaction mechanisms in which isomeric structures of intermediates are ignored.

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