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Characterisation and kinetic behaviour of $H_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(alkene) and related binuclear complexes detected during hydrogenation studies involving parahydrogen induced polarisation

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When parahydrogen induced polarisation is used to examine hydrogenation reactions involving $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ and $RhCl(CO)(PMe_3)_2$, binuclear dihydride complexes are detected, characterised, and shown to be capable of alkene hydrogenation.

The *in situ* study of H_2 oxidative addition reactions using NMR spectroscopy in conjunction with para-enriched hydrogen (p-H_2)[1] has led to the detection of many new dihydride complexes.[2,3] This phenomenon enables the generation of a non-Boltzmann spin population for the ensemble of nuclei originally in p-H_2 which in turn allows their detection *via* signal strengths that often exceed the norm by 1000 times.[2] Prior work in this area has shown that monitoring the oxidative addition of p-H_2 to $RhCl(CO)L_2$ and $RhClL_3$ (L = PPh_3, PMe_3) enables the detection of binuclear dihydride species.[4] Here, we demonstrate how p-H_2 can be used to monitor the hydrogenation process directly and facilitate the detailed characterisation of species such as $(H)_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(alkene). We also show that the addition of a sacrificial alkene can facilitate the characterisation of previously uncharacterised dihydrides.

Initially, a series of C_6D_6 solutions containing *ca.* 1 mg of $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ and varying amounts of styrene were monitored by ^1H NMR spectroscopy at 295 K while under 3 atm of p-H_2. At early reaction times these solutions immediately yielded polarised hydride resonances at δ −18.72 and −19.51, arising from the previously reported complex $(H)_2Rh(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)$(styrene) **2a**.[4] A 2D-^1H–^{31}P HMQC experiment [Fig. 1(a)] revealed that this product contains two mutually coupled phosphorus resonances separated by 1210 Hz, at δ 35.23 and 42.73.† The large J_{PP} coupling of 427 Hz confirms that the two detected phosphines are located in a *trans* arrangement in the product.[7] The analogous species formed with hex-1-ene, **2b**, also possesses inequivalent phosphines, although the separation between the ^{31}P signals is reduced to 590 Hz. However, the corresponding species with *cis*-stilbene, **2c**, yields a single ^{31}P resonance in the same experiment which requires the two phosphines to be equivalent.†

Hence for **2a** and **2b** the alkene substituents are unsymmetrically displaced about the plane containing the Rh centres and thereby render the PPh_3 ligands inequivalent. For the *cis*-stilbene complex **2c** the presence of a mirror plane makes the phosphines equivalent. These experimental results are consistent with calculations that show it is favourable for an alkene to bind to a ML_3 fragment with the C=C bond arranged perpendicular to the plane containing the framework atoms.[5] Surprisingly, when 1,2 diphenylethene is employed, the analogous product **2d** also contains equivalent phosphines. This suggests that steric interactions can force the alkene to bind with the C=C bond arranged in the plane of the two metal centres.

In these studies, the observed hydride signals for species of type **2** decay rapidly as the hydrogen present in solution is consumed by alkane formation. However, the absolute intensity of the hydride signals for **2** increased consistently when solutions were examined which contain lower alkene, and identical rhodium and p-H_2, concentrations. In order to learn more about this effect we adapted the 1D NOE sequence of Keeler for use with p-H_2.[6] Selective pulses were used in conjunction with a suitable mixing time (for chemical exchange and NOE build-up) to probe the behaviour of a single, pre-selected, hydride resonance. We note that there are several possibilities for dynamic behaviour involving the hydride

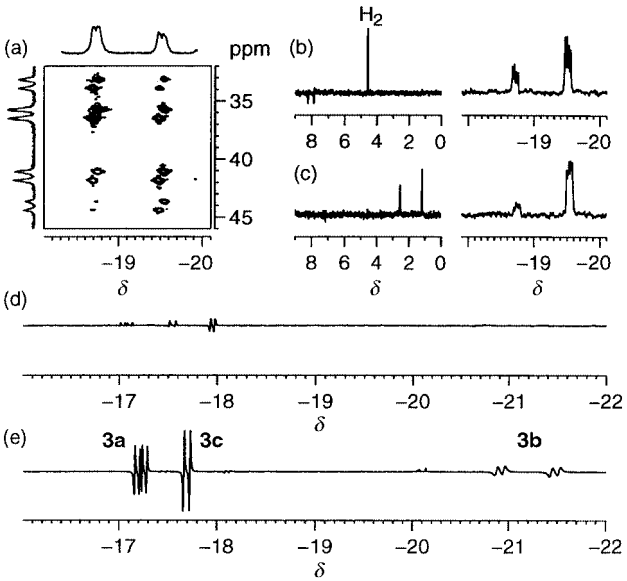

Fig. 1 (a) Selected cross peaks (absolute value display) and projections of the ^1H–^{31}P HMQC spectrum of **2a** showing hydride and phosphorus connectivity. (b) $^1H\{^{31}P\}$ 1D-NOE spectrum of p-H_2 enhanced **2a** at 295 K with resonance selection at δ −19.51 and a mixing time of 400 ms. Intramolecular hydride interchange is indicated. (c) $^1H\{^{31}P\}$ 1D-NOE spectrum of parahydrogen enhanced **2a** at 295 K with resonance selection at δ −19.51, mixing time of 200 ms, and *ca.* 20-fold reduction in [styrene]. Peaks indicate intramolecular hydride interchange, conversion to ethylbenzene and exchange with free H_2. (d) ^1H NMR spectrum showing the hydride region of a sample containing $RhCl(CO)(PMe_3)_2$ and p-H_2 in C_6D_6 at 295 K. (e) ^1H NMR spectrum at 295 K showing the same sample used in recording (d) but after introducing styrene in addition to the p-H_2.

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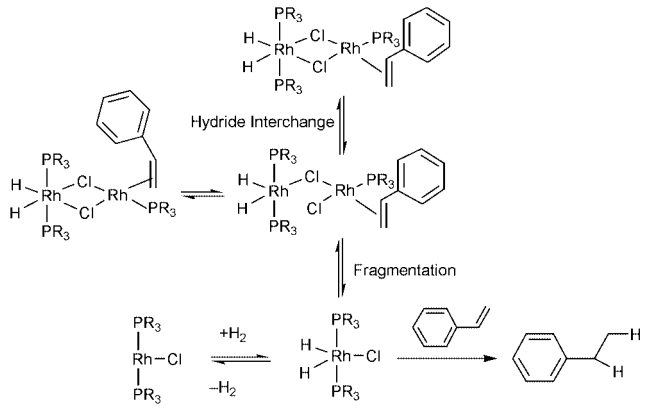
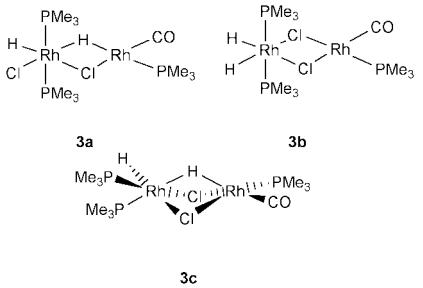
ligands of **2**: (i) intramolecular hydride interchange (ii) exchange with free hydrogen and (iii) transfer into the alkene (bound or free).

When the hydride resonances of **2a** at δ −18.72 or −19.51 were probed in separate experiments, NOE connections were visible, with both selections, to two *ortho* phenyl resonances at δ 8.20 and 7.85, supporting the conclusion that the two phosphines of the Rh(III) centre are inequivalent. The spectrum shown in Fig. 1(b) illustrates the result for the δ −19.51 hydride resonance of **2a**. The presence of the second peak, at δ −18.72, indicates that hydride interchange occurs during the mixing time. The magnitude of this exchange peak, for a given mixing time, proved to be independent of the concentration of styrene, and catalyst, which suggests that the hydride interchange process is intramolecular. Eyring analysis of the resulting rate data yielded activation parameters for hydride interchange, $\Delta H^{\ddagger}$ = 42 ± 4 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −100 ± 12 J K^{-1} mol^{-1}. A process involving halide bridge rupture, followed by rotation about the remaining Rh–Cl bridge, and bridge re-establishment is consistent with this information (Scheme 1).[7]



Scheme 1 (R = Ph).

The overall situation is complicated by the fact that the hydride resonances of **2** also connect to the resonance of free H_2. Surprisingly, as the concentration of alkene in solution falls both the proportion (rate) of reductive elimination of H_2 from **2** and the relative signal intensities of the two hydride resonances increase. For example, when the alkene concentration was reduced by a factor of 16, the associated hydride signals of **2a** increased by over 100 times. Significantly, at even lower alkene concentrations magnetisation transfer from the hydrides of **2a** to the alkyl protons of the hydrogenation product ethylbenzene is observed [Fig. 1(c)]. This corresponds to direct evidence for the binuclear metal dihydride complexes themselves being linked to alkene hydrogenation. In order to account for this 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 $RhClH_2(PR_3)_2$ fragment by alkene, rather than halide of a mononuclear rhodium centre, being productive in this regard. We therefore examined the hydrogenation activity of $RhCl(CO)(PMe_3)_2$. As a control, a benzene solution of $RhCl(CO)(PMe_3)_2$ was first reacted with p-H_2 at 295 K. The corresponding 1024 scan ^{1}H spectrum, shown in Fig. 1(d), contained polarised signals due to $(H)(Cl)Rh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)Rh(CO)(PMe_3)$ **3a**.[7] When an identical sample was prepared and monitored in the presence of a 1.5 fold excess of styrene relative to $RhCl(CO)(PMe_3)_2$, the spectrum shown in Fig. 1(e) was obtained. Now the new species $(H)_2Rh(PMe_3)_2(\mu\text{-}Cl)_2Rh(CO)(PMe_3)$ **3b** and $HRh(PMe_3)_2(\mu\text{-}H)(\mu\text{-}Cl)_2Rh(CO)(PMe_3)$ **3c** are clearly visible, and there is a dramatic 16 fold increase in size of the associated hydride signal intensities of **3a**; the spectral features of these species are



similar to those of their iodide derivatives.[7] These additional complexes are visible because p-H_2 cycling in **3** is enhanced by the hydrogenation pathway (in addition to simple reversible H_2 exchange).

In summary, these studies have demonstrated that there is a role for binuclear dihydride species as a 'hydrogen store' during hydrogenation catalysis. For **2**, this corresponds to direct evidence for H_2 transfer from the binuclear complex to the substrate *via* initial fragmentation to $RhH_2Cl(PPh_3)_2$. Significantly, we have shown that (metal–dihydride)–p-H_2 exchange reactions can be promoted by the addition of a sacrificial alkene with the result that previously unseen species become observable with this technique.

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Notes and references

† *Selected spectroscopic data* at 400.13 MHz (^{1}H) and 161.45 MHz (^{31}P) and 100.2 MHz (^{13}C) in benzene-d_6 (couplings Hz): **2a**: ^{1}H, δ −18.72 (ddt, $^2J_{HH}$ −10.9, $^1J_{RhH}$ 22.1, $^2J_{PH}$ 17), −19.51 (ddt, $^2J_{HH}$ −10.9, $^1J_{RhH}$ 22.7, $^2J_{PH}$ 17), 8.20 (m, *o*-Ph), 7.85 (m, *o*-Ph); ^{31}P, δ 42.73 ($^1J_{RhP}$ 127, $^2J_{PP}$ 417); 35.23 ($^1J_{RhP}$ 127, $^2J_{PP}$ 417); ^{103}Rh, δ 900. **2b**: ^{1}H, δ −18.66 (ddt, $^2J_{HH}$ −11.0, $^1J_{RhH}$ 22.6, $^2J_{PH}$ 17), −19.46 (ddt, $^2J_{HH}$ −11.0, $^1J_{RhH}$ 22.4, $^2J_{PH}$ 17), 8.24 (m, *o*-Ph), 8.09 (m, *o*-Ph); ^{31}P, δ 40.42 ($^1J_{RhP}$ 127, $^2J_{PP}$ 417), 36.78 ($^1J_{RhP}$ 127, $^2J_{PP}$ 417). **2c**; ^{1}H, δ −18.73 (ddt, $^2J_{HH}$ −10.8, $^1J_{RhH}$ 23.4, $^2J_{PH}$ 17), −19.46 (ddt, $^2J_{HH}$ −10.8, $^1J_{RhH}$ 23.0, $^2J_{PH}$ 17); ^{31}P, δ 39.6 ($^1J_{RhP}$ 126.6). **2d**: ^{1}H, δ −19.12 (ddt, $^2J_{HH}$ −10.5, $^1J_{RhH}$ 23.7, $^2J_{PH}$ 16), −19.43 (ddt, $^2J_{HH}$ −10.5, $^1J_{RhH}$ 23.8, $^2J_{PH}$ 16); ^{31}P, δ 41.2 ($^1J_{RhP}$ 132.9). **3a**: ^{1}H, δ −17.09 (ddddt, $^2J_{HH}$ −3.2, $^1J_{RhH}$ 29, $^1J_{RhH}$ 19, $^2J_{PH}$ 15.5, $^2J_{PH}$ 30), −17.57 (ddt, $^2J_{HH}$ −3.2, $^1J_{RhH}$ 24.8, $^2J_{PH}$ 15.5). **3b**: ^{1}H, δ −20.75 (ddt, $^2J_{HH}$ −11, $^1J_{RhH}$ 30.9, $^2J_{PH}$ 19), −21.3 (ddt, $^2J_{HH}$ −11, $^1J_{RhH}$ 30.0, $^2J_{PH}$ 22). **3c**: ^{1}H δ −10.1 (ddddt, $^2J_{HH}$ −7, 2 × $^1J_{RhH}$ 20.2, $^2J_{PH}$ 115, $^2J_{PH}$ 20, 17), −17.95 (ddt, $^2J_{HH}$ −7, $^1J_{RhH}$ 18.5, $^2J_{PH}$ 19, 11).

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