Equilibria between isomers of ruthenium dihydride complexes: detection of minor isomers by parahydrogen induced polarisation

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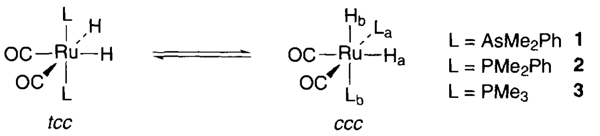
Enhancements of NMR signals by parahydrogen induced polarisation aids detection of a minor isomer of complexes $[RuL_2(CO)_2(H)_2]$ (L = $AsMe_2Ph$, PMe_2Ph, PMe_3) containing inequivalent hydride ligands: some enhancement is also observed for the major isomer in which the hydrides are equivalent, and this is increased by use of $[RuL_2(^{13}CO)(^{12}CO)(H)_2]$.

We have recently shown that the enhanced absorption and emission signals observed in NMR spectra of nuclei arising from para-enriched-hydrogen (p-H_2) can be used to detect and characterise materials present in concentrations too low for detection by normal methods.[1,2] In this communication, we describe how the complexes $[RuL_2(CO)_2(H)_2]$ (L = $AsMe_2Ph$, PMe_2Ph, PMe_3) behave with p-H_2. We show that, using this approach, we are able to identify minor isomers of **2** and **3** that were previously undetected and that the major isomers can be made p-H_2 active. The synthesis and reactions of **1**, **2** and **3** have already been reported, and importantly for this work they have been shown to undergo thermal exchange of the hydride ligands with H_2.[3]

Complex **1** has already been shown to exist as two isomers *trans,cis,cis*-$[Ru(AsMe_2Ph)_2(CO)_2(H)_2]$, *tcc*-**1**, and *all-cis*-$[Ru(AsMe_2Ph)_2(CO)_2(H)_2]$, *ccc*-**1**, (where L = $AsMe_2Ph$) in the ratio 4 : 3 at 298 K. When a C_6D_6 solution containing **1** (< 1 mg) is placed under 3 atm of p-H_2 at 343 K, the ^1H NMR spectrum shown in Fig. 1(*a*) is obtained. This single-scan spectrum, collected with a $\pi/4$ excitation pulse, shows for the first time that substantial p-H_2 enhancements are possible at ruthenium and confirms that a concerted addition of p-H_2 to $[Ru(AsMe_2Ph)_2(CO)_2]$, formed by initial elimination of H_2, operates. The two polarised hydride resonances at δ −6.89 and −8.82 are assigned to the hydride ligands H_a and H_b of *ccc*-**1** respectively.† The coupling, J(HH) is measured directly from the separation between the antiphase peaks, and the emission absorption profile reveals that J(HH) is negative. The enhanced antiphase character shown by each of these signals arises from an over-population of the αβ and βα spin states in the coupled dihydride spin system, and corresponds to a 1035-fold increase in signal strength over that expected from reaction with normal H_2. This enhancement, five times larger than the greatest previously reported for a transition-metal complex, is still substantially smaller than the theoretical maximum of 17 000.[1] It is now accepted that concerted H_2 addition proceeds through a transition state, or intermediate, which involves substantial σ bonding between the two hydrogen centres.[4] Stable non-classical dihydrogen complexes of this type are known to have short relaxation times (T_1) that are dominated by dipole–dipole interactions.[4] The observed enhancement will therefore be a function of the rate of addition and the efficiency of relaxation. The latter will be minimised in the spin-dilute arsine complex used in this study, and this explains the large enhancement observed.



L = $AsMe_2Ph$ **1**
L = PMe_2Ph **2**
L = PMe_3 **3**

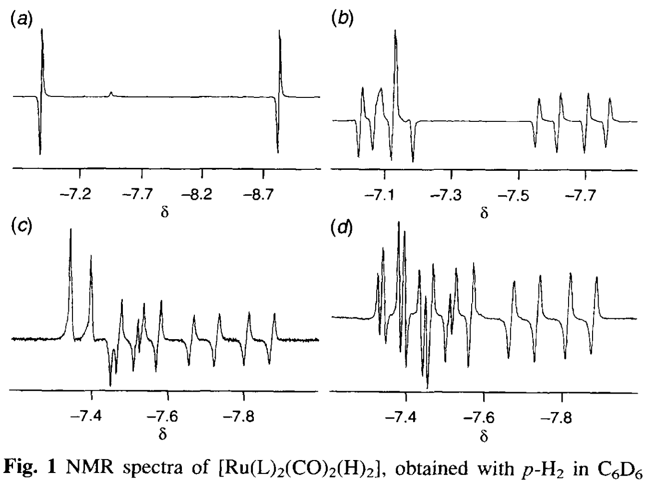


Fig. 1 NMR spectra of $[Ru(L)_2(CO)_2(H)_2]$, obtained with p-H_2 in C_6D_6 showing the hydride region only. The antiphase components arise in transitions involving protons that originate from p-H_2. (*a*) ^1H spectrum of **1** at 343 K; (*b*) ^1H spectrum of **2** at 333 K; (*c*) ^1H spectrum of **3** at 333 K; (*d*) ^1H spectrum of **3**-^{13}CO at 333 K.

Surprisingly, the hydride resonance due to *tcc*-**1**, observed at δ −7.45, is itself 60-fold enhanced, even though the two hydride ligands of this isomer are in magnetically equivalent environments. This represents the first time that substantial enhancements have been observed at a metal centre with both chemically and magnetically equivalent hydrides. A conventional two-dimensional nuclear Overhauser experiment with normal H_2 shows that the two isomers interconvert *via* a process in which the hydrides remain on the metal. The origin of the unprecedented enhancement in the *tcc*-**1** isomer may originate in the inequivalence of the hydride ligands in *ccc*-**1**. Intramolecular isomerisation of *ccc*-**1** to *tcc*-**1** may lead to a loss of phase correlation, and hence enhancement, for the hydride signal of *tcc*-**1**. Similar effects have been seen in the spectra of organic hydrogenation products formed by hydrogen transfer from metal dihydride species that contain inequivalent hydride ligands.[5]

The complex $[Ru(PMe_2Ph)_2(CO)_2(H)_2]$ **2**, was originally reported[3] to exist in C_6D_6 solution solely as the *trans,cis,cis* isomer *tcc*-**2**. Even without the use of p-H_2, careful observation reveals the presence of the *cis,cis,cis* isomer *ccc*-**2**, but the *tcc*-**2** isomer is in large excess (*ca.* 96 : 4). The presence of *ccc*-**2** becomes obvious, however, when a ^1H NMR spectrum of a C_6D_6 solution of **2** (< 1 mg) which has been treated with p-H_2 is run at 333 K. The four-scan spectrum shown in Fig. 1(*b*), obtained at 333 K, shows two sets of antiphase multiplets at δ −7.08 and δ −7.66, assigned to the hydride ligands H_a and H_b of *ccc*-**2** respectively.† Each of these hydride resonances exhibits two phosphorus splittings in addition to the H_a–H_b coupling [J(HH) = −6 Hz] that separates the antiphase signals. The H_b resonance of *ccc*-**2** appears in an otherwise clear spectral region and shows one large phosphorus splitting [$J(P_bH)$ = 73.6 Hz] and one smaller splitting [$J(P_aH)$ = 32.2 Hz].

Unfortunately, the resonance due to $\mathrm{H_a}$, at δ −7.08, overlaps with the triplet signal, δ −7.13 [J(PH) = 28.6 Hz], due to the hydride ligands of the major isomer *tcc*-**2**, and values for $J(\mathrm{P_aH_a})$ and $J(\mathrm{P_bH_a})$ cannot be accurately determined. However, the ratio of the hydride signal intensities for *tcc*-**2** and *ccc*-**2**, determined from a ^{1}H{^{31}P} spectrum, is 1 : 3.4 at 333 K. This corresponds to an 85-fold increase in signal intensity for the hydride resonances of isomer *ccc*-**2** relative to those for *tcc*-**2**.

We used a modified heteronuclear multiple quantum correlation experiment (HMQC)[6] to measure the chemical shifts for the two inequivalent phosphorus nuclei of *ccc*-**2** [Fig. 2(*a*) and (*b*)].[7] This approach makes optimal use of the p-$\mathrm{H_2}$ enhancement seen in the hydride signature of the complex and employs the most receptive nucleus, ^{1}H, to obtain ^{31}P chemical shift information. In addition, the ^{1}H–^{31}P correlation separates the hydride resonances of the two isomers by virtue of the improved chemical shift dispersion seen in the ^{31}P dimension. Four cross-peaks connecting the phosphorus nuclei, $\mathrm{P_a}$, $\delta(^{31}\mathrm{P})$ 8.8, and $\mathrm{P_b}$, $\delta(^{31}\mathrm{P})$ 0.19, to their proton coupling partners, $\mathrm{H_a}$ and $\mathrm{H_b}$, are observed for *ccc*-**2**. Appropriate rows in the ^{1}H dimension reveal that the cross-peak at $\delta(^{1}\mathrm{H})$ −7.08, $\delta(^{31}\mathrm{P})$ 8.8, connecting $\mathrm{H_a}$ to $\mathrm{P_a}$, is made up of signals with triplet multiplicity [$J(\mathrm{P_aH}) = J(\mathrm{P_bH})$ = 23 Hz]. Examination of the columns at the point of intersection, or mapping the ^{31}P dimension, reveals that each cross-peak is split into a doublet with $J(\mathrm{P_aP_b})$ = 28 Hz. These data confirm that while $\mathrm{H_b}$ is *trans* to $\mathrm{P_b}$ and *cis* to $\mathrm{P_a}$, $\mathrm{H_a}$ is *cis* to both $\mathrm{P_a}$ and $\mathrm{P_b}$ and therefore *trans* to CO. The additional cross-peak connects the hydride and phosphorus resonances of *tcc*-**2**.

When a $\mathrm{C_6D_6}$ solution containing < 1 mg of $[\mathrm{Ru(PMe_3)_2(CO)_2(H)_2}]$ **3**, is observed under normal $\mathrm{H_2}$, only the *tcc*-**3** isomer can be detected even after 10 000 scans. However, with p-$\mathrm{H_2}$, the *ccc*-**3** isomer can be clearly identified. The four-scan ^{1}H NMR spectrum recorded with p-$\mathrm{H_2}$ at 333 K is shown in Fig. 1(*c*) and contains two polarised resonances at δ −7.50 and −7.74, due to $\mathrm{H_a}$ and $\mathrm{H_b}$ of *ccc*-**3**. Once again, the resonance due to $\mathrm{H_a}$ overlaps with that for the *tcc* isomer at δ −7.38, while that due to $\mathrm{H_b}$ shows one large *trans* phosphorus splitting [$J(\mathrm{P_bH})$ = 73.6 Hz], a smaller *cis* splitting [$J(\mathrm{P_aH})$ = 34.0 Hz] and an antiphase component [J(HH) = −6.2 Hz]. The corresponding ^{1}H–^{31}P correlation spectrum shown in Fig. 2(*c*) and (*d*) illustrates the cross-peaks that connect the resonances due to the phosphorus nuclei, $\mathrm{P_a}$, $\delta(^{31}\mathrm{P})$ −6.85 and $\mathrm{P_b}$, $\delta(^{31}\mathrm{P})$ −16.45 [$J(\mathrm{P_aP_b})$ = 20 Hz] to those of their hydride coupling partners, $\mathrm{H_a}$ and $\mathrm{H_b}$ and reveals that $J(\mathrm{P_aH}) = J(\mathrm{P_bH})$ = 26 Hz.[†] The ratio of the hydride signal intensity *tcc*-**3** to *ccc*-**3** was determined to be 1 : 2 at 333 K from the corresponding ^{1}H{^{31}P} experiment.

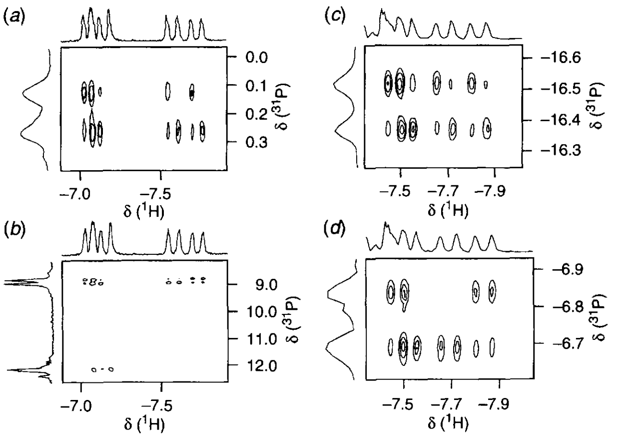


Fig. 2 Selected cross-peaks (absolute value display) and projections from ^{1}H–^{31}P correlation spectra of $[\mathrm{Ru(L)_2(CO)_2(H)_2}]$, obtained with p-$\mathrm{H_2}$ in $\mathrm{C_6D_6}$ at 333 K. ^{1}H–^{31}P correlation spectra showing the cross-peaks connecting $\mathrm{H_a}$ and $\mathrm{H_b}$ to $\mathrm{P_b}$ in *ccc*-**2** (*a*), and $\mathrm{H_a}$ and $\mathrm{H_b}$ to $\mathrm{P_a}$ in *ccc*-**2** and $\mathrm{H_c}$ to $\mathrm{P_c}$ in *tcc*-**2** (*b*); ^{1}H–^{31}P correlation spectra acquired showing the cross-peaks for *ccc*-**3** connecting $\mathrm{H_a}$ and $\mathrm{H_b}$ to $\mathrm{P_b}$ (*c*), and to $\mathrm{P_a}$ (*d*).

One of the major limitations of p-$\mathrm{H_2}$ is that it only readily enhances signals that result from transportation of the p-$\mathrm{H_2}$ nuclei into different magnetic environments. If p-$\mathrm{H_2}$ is to be used to study the involvement of spin-dilute transition-metal carbonyl complexes in hydroformylation, or the water-gas-shift reaction, then the problem of chemical equivalence within a planar $\mathrm{(H)_2M(CO)_2}$ metal core must be overcome. Magnetic inequivalence has been shown to result in p-$\mathrm{H_2}$ activity in complexes with a planar $\mathrm{(H)_2M(PR_3)_2}$ core[6] and symmetrical hydrogenation products when they contain ^{13}C.[8]

The major *trans,cis,cis* isomer of these ruthenium complexes thus represents an ideal system with which to examine whether similar effects result from ^{13}CO incorporation. We therefore exposed a $\mathrm{C_6D_6}$ solution of $[\mathrm{Ru(PMe_3)_2(CO)_3}]$ **4**, containing 36% ^{13}CO to 3 atm of p-$\mathrm{H_2}$. After *ca.* 100 s at 333 K, the ^{1}H NMR spectrum shown in Fig. 1(*d*) was recorded. The spectrum shows a complex polarised multiplet centred at δ −7.38 and two additional hydride resonances at δ −7.50 and −7.74. The two high-field signals correspond to those already seen for $\mathrm{H_a}$ and $\mathrm{H_b}$ in *ccc*-**3**, and possess weak ^{13}C satellites from the $[\mathrm{Ru(PMe_3)_2(^{13}CO)(^{12}CO)(H)_2}]$ *ccc*-**3** isotopomer; the satellites are most clearly seen in the corresponding ^{1}H{^{31}P} spectrum. The appearance of the complex multiplet at δ −7.38 can also be easily explained: clearly, the p-$\mathrm{H_2}$ activity of the *tcc* isomer of $[\mathrm{Ru(PMe_3)_2(^{13}CO)(^{12}CO)(H)_2}]$ is enhanced as a result of the inequivalence generated by the ^{13}CO. Attempts to utilise this isotopic perturbation are currently underway.

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Footnote

[†] *Selected spectroscopic data* for **1**, **2** and **3** in $\mathrm{C_6D_6}$ at 500.13 MHz (^{1}H) and 202.45 MHz (^{31}P) recorded on 5 mm samples in a 5 mm inverse geometry probe. *ccc*-**1**: ^{1}H (343 K) δ −6.89 [$\mathrm{H_a}$, J(HH) = −7 Hz], −8.82 [$\mathrm{H_b}$, J(HH) = −7 Hz]. *ccc*-**2**: ^{1}H (333 K) δ −7.08 [$\mathrm{H_a}$, $J(\mathrm{P_aH}) = J(\mathrm{P_bH})$ = 23 Hz, J(HH) = −6 Hz], −7.66 [$\mathrm{H_b}$, $J(\mathrm{P_bH})$ = 73.6 Hz, $J(\mathrm{P_aH})$ = 32.2 Hz, J(HH) = −6 Hz]. ^{31}P (333 K); δ 8.8 [$\mathrm{P_a}$, d, J(PP) = 28 Hz], 0.19 [$\mathrm{P_b}$, d, J(PP) = 28 Hz]. *ccc*-**3**: ^{1}H (333 K) δ −7.50 [$\mathrm{H_a}$, $J(\mathrm{P_aH}) = J(\mathrm{P_bH})$ = 26 Hz, J(HH) = −6.2 Hz], −7.74 [$\mathrm{H_b}$, $J(\mathrm{P_bH})$ = 73.6 Hz, $J(\mathrm{P_aH})$ = 34 Hz, J(HH) = −6.2 Hz]. ^{31}P (333 K); δ −6.85 [$\mathrm{P_a}$, d, J(PP) = 26 Hz], −16.45 [$\mathrm{P_b}$, d, J(PP) = 26 Hz].

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