Parahydrogen enhanced NMR studies on thermally and photochemically generated products from $[IrH_3(CO)(PPh_3)_2]$

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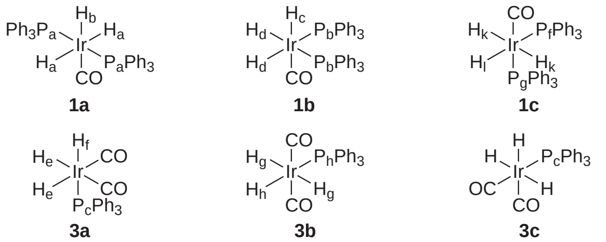
Parahydrogen induced polarisation is used to enable the rapid NMR characterisation of thermally and photochemically generated complexes of general formula $[IrH_3(CO)_{3-x}(PPh_3)_x]$ (x = 1–3).

It has been shown that parahydrogen (p-H_2) increases the size of detectable signals in NMR spectroscopy by enabling access to non-Boltzmann spin populations.[1,2] This phenomenon has facilitated the observation of materials found in low concentrations, such as intermediates in catalytic hydrogenation reactions, species in minor reaction pathways such as $[RhH_2(PPh_3)_2Cl_2Rh(PPh_3)(CO)]$ and minor constituents in equilibria, for example *all-cis*-$[Ru(PMe_3)_2(CO)_2(H)_2]$.[3]

The reaction chemistry presented here relates primarily to hydrogen exchange reactions of $[IrH_3(CO)(PPh_3)_2]$. This complex has been shown by Harrod and Yorke[4] to exist in solution in two isomeric forms, **1a** with *trans* phosphines and *mer*-hydrides and **1b** with *cis* phosphines and *fac*-hydrides (Scheme 1). We describe how the sensitivity gain provided by p-H_2 allows the rapid characterisation of these, and related trihydride complexes of iridium, and enables the examination of their thermal and photochemical reactivity. We use pulsed field gradient-assisted 2D homo- and hetero-nuclear NMR methods to monitor these reactions.



Scheme 1 Structural isomers of the trihydrides $[IrH_3(CO)(PPh_3)_2]$ and $[IrH_3(CO)_2(PPh_3)]$

When a 0.1 mM solution containing equal amounts of **1a** and **1b**, in $[^2H_6]$benzene under 3 atm of p-H_2, is monitored between 303 K and 343 K by ^1H NMR spectroscopy, enhanced resonances are detected in the hydride region of the spectrum. The $^1H\{^{31}P\}$ NMR spectrum shown in Fig. 1(a) was recorded at 343 K and shows two pairs of anti-phase multiplets that can be assigned to the hydride ligands of **1a** and **1b**.‡ These results confirm that the hydride ligands in **1a** and **1b** undergo exchange with free H_2. We note that under these conditions, even with the p-H_2 derived signal amplification, no resonances are detected that can be attributed to isomer **1c** (Scheme 1). The spectral features of the p-H_2 enhanced trihydrides, illustrated in Fig. 1, are surprising.[5] The two polarised hydride resonances at δ −9.29 and −10.02 are assigned to the hydride ligands H_a and H_b of **1a**, respectively.[4] In a regular $^1H\{^{31}P\}$ spectrum these signals would appear as doublets and triplets respectively with peak separation J_{HH}. The observed signals have relative intensities of 2 : 1 and their anti-phase line separation (4.4 and 8.8 Hz) indicates that the central feature of the triplet is no longer visible. This can be understood by examining the p-H_2 controlled populations of the eight spin wavefunctions of the trihydride (AX_2). While four wavefunctions are simple products of the form $\alpha\alpha\alpha$, $\boldsymbol{\alpha\beta\beta}$, $\boldsymbol{\beta\alpha\alpha}$ and $\beta\beta\beta$, four belong to combinations of the form $\boldsymbol{\alpha(\alpha\beta - \beta\alpha)}$, $\boldsymbol{\alpha(\alpha\beta + \beta\alpha)}$, $\boldsymbol{\beta(\alpha\beta - \beta\alpha)}$ and $\boldsymbol{\beta(\alpha\beta + \beta\alpha)}$. Exchange with p-H_2 ($\alpha\beta - \beta\alpha$ spin state) at **1a** involves the A and one X nucleus, with the result that the six product states indicated, **in bold**, become equally populated while the $\alpha\alpha\alpha$ and $\beta\beta\beta$ states are unpopulated. Consequently, the only visible transitions for nucleus A, spin flips $\alpha\alpha\alpha\leftrightarrow\boldsymbol{\beta\alpha\alpha}$ and $\boldsymbol{\alpha\beta\beta}\leftrightarrow\beta\beta\beta$, correspond to the outer lines of the triplet and are seen in emission and absorption. The emission–absorption phase profile reveals that J_{HH} is negative.[2] The central line, corresponding to spin flips $\boldsymbol{\alpha(\alpha\beta - \beta\alpha)}\leftrightarrow\boldsymbol{\beta(\alpha\beta - \beta\alpha)}$ and $\boldsymbol{\alpha(\alpha\beta + \beta\alpha)}\leftrightarrow\boldsymbol{\beta(\alpha\beta + \beta\alpha)}$, vanishes because the associated levels have identical populations. In a similar way, examination of the symmetry allowed transitions for H_a (X_2) reveals that observable spin flips connect $\alpha\alpha\alpha\leftrightarrow\alpha(\alpha\beta + \beta\alpha)$, and $\beta(\alpha\beta + \beta\alpha)\leftrightarrow\beta\beta\beta$. These transitions are separated by J_{AX} (J_{HH}) and are

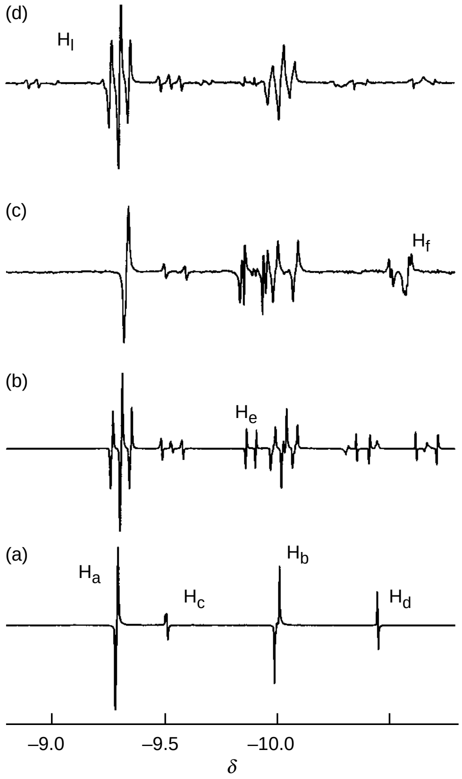


Fig. 1 NMR spectra (400 MHz) of $[IrH_3(CO)_{3-x}(PPh_3)_x]$ (x = 1–3) obtained with p-H_2 in C_6D_6 showing the hydride region only. The anti-phase components arise in transitions involving protons that originate from p-H_2. (a) $^1H\{^{31}P\}$ spectrum of **1a** and **1b** at 343 K; (b) ^1H spectrum of **1a 1b** and **3a** generated *in situ* from $[IrH(CO)_2(PPh_3)_2]$; (c) $^1H\{^{31}P\}$ spectrum of a ^{13}CO labeled sample of **1a**, **1b** and **3a**; (d) $^1H\{^{31}P\}$ spectrum recorded at 313 K immediately after UV photolysis of a sample of **1a** and **1b**.

visible as emission and absorption signals, with twice the overall intensity seen for signal A (H_b).

Interestingly, isomer **1b** reveals a different pattern; the two hydride resonances at $\delta - 9.53$ and -10.48, assigned to H_c and H_d respectively, appear as absorption and emission signals because J_{HH} is now positive. Because both hydride resonances are enhanced we can confirm that the dominant dihydrogen exchange pathway involves reductive elimination of H_cH_d rather than H_dH_d in **1b**. At 333 K the hydride resonance enhancements, 30-fold for **1a** and 5-fold for **1b**, are consistent with faster dihydrogen exchange at **1a**.

A modified heteronuclear multiple quantum correlation experiment (HMQC) using gradients and ^{31}P decoupling was used to measure the chemical shifts of the phosphorus nuclei of **1a** and **1b**.[6] In the two-dimensional map cross-peaks connect the hydrides to the corresponding phosphorus nuclei; P_a [δ(^{31}P) 18.0] connects to H_a and H_b whilst P_b [δ(^{31}P) 8.8] connects to H_c and H_d. Spectra recorded on this sample at 333 K using a ^{31}P decoupled gradient-assisted EXSY sequence (mixing time of 300 ms) contain cross-peaks that connect the two hydride resonances of **1a**. This indicates that the hydride ligands of **1a** are able to interchange identities *via* a process which is intramolecular with respect to the hydrides. This spectrum also contains nOe-derived cross-peaks that connect the hydrides to the *ortho*-phenyl protons of the phosphine ligand.[7] Under these conditions no cross-peaks connect the hydride resonances of **1a** to those of **1b**. However, with a mixing time of 500 ms cross-peaks connect the hydrides resonances of **1a** to free H_2.

When a frozen C_6D_6 solution of [IrH(CO)$_2$(PPh$_3$)$_2$] **2**, under an atmosphere of *p*-H_2, is thawed and rapidly introduced into the NMR spectrometer for monitoring by ^1H spectroscopy at between 313 and 333 K, three hydride containing species are detectable [Fig. 1(*b*)]. Two of these species can be assigned to the previously described **1a** and **1b**, produced by CO loss from **2** and subsequent H_2 addition. The two new sets of anti-phase multiplets at δ -9.86 and -10.54, are assigned to the hydride ligands H_e and H_f of the new product **3a** (Scheme 1) with $J_{HH} = -1.8$ Hz.‡ The H_e resonance of **3a** shows one additional *cis* phosphorus splitting [$J(P_cH)$ 17.24 Hz] while the resonance due to H_f shows a larger *trans* phosphorus splitting [$J(P_cH)$ 121.6 Hz]. Interestingly, if the sample is monitored after degassing and refilling with fresh *p*-H_2 then the observed resonances for **3a** are weaker than those seen initially. Repeating this process reduces their signal intensity still further, until eventually they are no longer visible.[8] The ^1H NMR spectrum of this sample, collected 48 h after filling the NMR tube with 50 Torr of ^{13}CO, revealed that [IrH(^{13}CO)$_2$(PPh$_3$)$_2$] was formed, as evidence by the ^{13}C coupled hydride resonance at δ -10.3 (J_{CH} 6.4 Hz). This sample was then refilled with *p*-H_2 and monitored by NMR spectroscopy as before. The fully carbon decoupled ^1H–^{13}C HMQC spectrum of this sample located a single carbonyl resonance for **3a**, while the corresponding ^1H–^{31}P spectrum reveals that the hydride resonance for H_e possesses additional ^{13}C couplings which are indicative of a planar (H)$_2$Ir(^{13}CO)$_2$ core [Fig. 1(*c*)]. These additional data indicate that **3a** has *fac*-hydrogen atoms (Scheme 1).[9] When a sample of the related complex [IrH(CO)(PPh$_3$)$_3$] was examined with *p*-H_2 only **1a** and **1b** were detectable as *p*-H_2 enhanced products. These reactions are illustrated in Scheme 2.

$^1H\{^{31}P\}$ NMR spectra were obtained for C_6D_6 solutions under 3 atm of *p*-H_2 containing < 1 mg of [IrH$_3$(CO)(PPh$_3$)$_2$], with normal and enriched levels of ^{13}CO, after 5 min UV irradiation.[10] These spectra contain enhanced hydride resonances for several new species in addition to those already described for **1a**, **1b** and **3a**. In order to characterise these new species gradient-assisted COSY{^{31}P} and HMQC experiments were recorded. Signals due to the remaining isomer of the bisphosphine trihydride **1c** were assigned. Additional resonances assigned to the mono-triphenylphosphine complex **3b** are also present. For example, the hydride H_h at δ -9.08 [J(HH) -4.6, J(PH) 136.4, J(PH) 17.6 Hz] seen in Fig. 1(*d*) connects with a hydride resonance at δ -10.10 in the COSY spectrum and to two phosphorus nuclei [δ(^{31}P) 5.1 and 20.5] in the HMQC. These new isomers have short lifetimes with the result that after several minutes at 313 K the only species seen are **1a** and **1b**. They can be regenerated by repeating the photolysis step, however, when the sample is irradiated in the presence of benzaldehyde, a good CO source, resonances for **3a** are visible for much longer.

$$[\mathrm{IrH(CO)(PPh_3)_3}] \xrightarrow[\mathrm{H_2}]{\text{heat}} \mathbf{1a} + \mathbf{1b}$$

$$[\mathrm{IrH(CO)_2(PPh_3)_2}] \xrightarrow[\mathrm{H_2}]{\text{heat}} \mathbf{3a} + \mathbf{1a} + \mathbf{1b}$$

$$\mathbf{1a} + \mathbf{1b} \xrightarrow[\mathrm{H_2}]{hv} \mathbf{1c} + \mathbf{3a} + \mathbf{3b}$$

Scheme 2 *p*-H_2 enhanced trihydride products

Here, we have shown that *p*-H_2 derived spectral amplification can be used to examine trihydride systems, and view species that are normally only readily visible under high pressures of H_2.[11] *In situ* ^{13}CO labelling of 1 mg samples proved to be a viable and cost-effective way of fully characterising the ligand sphere of these species. In addition, we have demonstrated that UV irradiation may be employed to generate normally unstable structural isomers for characterisation with *p*-H_2.[12]

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Notes and References

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‡ *Selected spectroscopic data* at 333 K in C_6D_6 at 400.13 MHz (^1H), 161.45 MHz (^{31}P) and 100.2 MHz (^{13}C). **1a**: ^1H δ, 7.91 (*o*-phenyl H of P_a), -9.29 [H_a, J(HH) -4.4, $J(P_aH)$ 16.9 Hz], -10.02 [H_b, $J(P_aH)$ 19.7, J(HH) -4.4, $J(H^{13}CO)$ -36 Hz], ^{31}P, δ 18.0 (P_a, s), ^{13}C δ 179.6 [CO, t, J(PC) 10.3 Hz]. **1b**: ^1H, δ 7.9 (*o*-phenyl H of P_b), -9.51 [H_c, $J(P_bH)$ 17.1, $J(^{13}COH)$ 37.7, J(HH) + 2.4 Hz], -10.47 [H_d, $J(P_bH) + J(P_{b'}H)$ 122, J(HH) + 2.4 Hz], ^{31}P, δ 8.8 (P_b, s), ^{13}C, δ 179.3 [CO, t J(PC) 10.8]. **1c**: ^1H, δ -9.08 [H_l, $J(P_fH)$ 136.4, $J(P_gH)$ 17.6, J(HH) -4.6 Hz], -10.10 [H_k, $J(P_fH) = J(P_gH) = J$(HH) -4.4, Hz], ^{31}P, δ 20.5 (P_f), 5.1 (P_g). **3a**: ^1H, δ 7.9 (*o*-phenyl H or P_c), -9.86 [H_e, $J(P_cH)$ 17.2, $J(H^{13}CO_{trans}) + J(H^{13}CO_{cis})$ 40.6, J(HH) -2.4 Hz], -10.54 [H_f, $J(P_bH)$ 121.6, $J(^{13}COH)$ 4.7, J(HH) -2 Hz]. ^{31}P, δ 3.29 (P_c, s). ^{13}C, δ 172.15 [CO, d, J(PC) 6 Hz]. **3b**: ^1H, δ -8.8 [H_h, $J(P_hH)$ 136.9, J(HH) -2.7 Hz], -9.7 [H_g, $J(P_hH)$ 121.6, J(HH) -2.4 Hz], ^{31}P, δ 43.2 (P_h, s).

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7 The starting anti-phase magnetisation must be refocussed; this requires two delays, $\frac{1}{2}J_{HH}$ for H_a and $\frac{1}{4}J_{HH}$ for H_b.

8 When a sapphire NMR tube filled with a toluene solution of **1** was warmed to 80 °C, first under 40 atm of CO and then under 40 atm of normal H_2, the resonances of **3a** are visible in the ^1H spectrum.

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12 When [IrH$_2$(Cl)(CO)(PPh$_3$)$_2$] is photolysed with *p*-H_2 the trihydrides **1a** and **1b** are detected.

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