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Rapid Characterisation of Rhodium Dihydrides by Nuclear Magnetic Resonance Spectroscopy using Indirect Two-dimensional Methods and *para*-Hydrogen†

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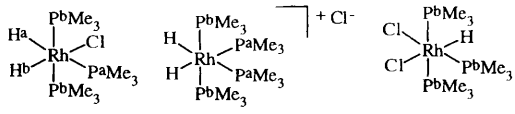
When $[RhH_2(PMe_3)_3Cl]$, incorporating chemically inequivalent hydrides, and $[RhH_2(PMe_3)_4]Cl$, containing magnetically inequivalent hydrides, were generated using *para*-enriched hydrogen, their ^1H–^{103}Rh and ^1H–^{31}P two-dimensional NMR spectra were quickly obtained from < 1 mg of complex with and without the aid of pulsed field gradients.

Enhanced absorption and emission signals have been observed in NMR spectra of nuclei which arise from those of *para*-hydrogen (p-H_2), or possess a direct scalar coupling to these nuclei.[1] The enhancement, termed *para*-hydrogen-induced polarisation (PHIP) by Eisenberg,[2] is a direct result of the destruction of the antisymmetric p-H_2 spin state, a nuclear singlet, in a spin-correlated chemical process. Such processes occur in catalytic hydrogenation reactions, resulting in large enhancements of NMR signal intensity for hydrogenation products and metal dihydrides.[3] Here we show for the first time that indirect measurements, in conjunction with the use of p-H_2, allow the measurement of ^{31}P and ^{103}Rh NMR spectra for species present in concentrations of $\ll 1$ mmol dm^{-3}. In addition, we demonstrate that chemically equivalent, but magnetically inequivalent, hydride nuclei in metal dihydrides can be detected by their PHIP signature.

The reaction chemistry concerns the addition of H_2 to $[Rh(PMe_3)_3Cl]$[4] **1** and $[Rh(PMe_3)_4]Cl$[5] **2**. A 1 mg sample of $[Rh(PMe_3)_3Cl]$ in CD_2Cl_2 under 3 atm p-H_2 was examined at 312 K using a modified heteronuclear multiple quantum correlation (HMQC) experiment.[6] The maximum initial transverse magnetisation obtainable from the two-spin order $I_{z1}I_{z2}$ product state formed in the p-H_2 derived product $[RhH_2(PMe_3)_3Cl]$ **3** arises when the first $\frac{\pi}{2}(^1H)$ pulse in the HMQC sequence is replaced by a $\frac{\pi}{4}$ pulse.[1,7] The rest of the sequence, $-\tau-\frac{\pi}{2}(X)-t_1-\pi(^1H)-t_1-\frac{\pi}{2}(X)-\tau-\frac{\pi}{2}(X)$–detect ($^1H$) is identical to that in a standard HMQC experiment in which the magnetisation created by the initial pulse evolves during the fixed delay, τ, with respect to heteronuclear couplings, thereby enabling the generation of heteronuclear multiple quantum coherence. The duration of t_1, the evolution period, is incremented for each slice to build up the two-dimensional data matrix. Phase-sensitive acquisition was achieved using time proportional phase incrementation[8] by incrementing the phase of the first pulse to the heteronucleus (X) by $\frac{\pi}{2}$ for each slice of the two-dimensional data set. The sequence is completed with a purge pulse. Using this indirect approach we are able to detect the ^{31}P and ^{103}Rh nuclei of the H_2 addition products *via* their most sensitive ^1H signature (Fig. 1). The hydride resonances at δ −9.79 and −19.5 are assigned to the ligands, H_a and H_b of complex **3**.‡ In the ^1H–^{31}P correlation spectrum four cross-peaks are observed connecting each phosphorus centre, P_a and P_b, to its proton coupling partners, the hydrides H_a and H_b. The relative intensities of the four cross-peaks depend on the value of τ; when $\tau = \frac{1}{2}J(P_aH_a)$ the strongest cross-peak connects the hydride at $\delta(^1H)$ −9.79 (H_a) to the phosphorus centre at $\delta(^{31}P)$ −21.3 [P_a, dt, $J(RhP_a)$ = 88, $J(PP)$ = 28 Hz] and confirms their *trans* arrangement [Fig. 1(*a*) and 1(*c*)].§ The short data-storage time of 25 ms used in this HMQC



3 **4** **5**

† *Non-SI unit employed:* atm ≈ 101 325 Pa.

‡ Selected NMR data (in CD_2Cl_2, 500.13 MHz ^1H, 202.45 MHz ^{31}P and 15.77 MHz ^{103}Rh; ^{103}Rh spectra, recorded on 5 mm samples in a 10 mm inverse-geometry probe, were referenced relative to 3.16 MHz, δ 0): **3**, ^1H (312 K) δ −9.79 [H_a, $J(P_aH)$ = 176, $J(P_bH)$ = −19, $J(RhH)$ = 15, $J(HH)$ = −8] and −19.5 [H_b, $J(RhH)$ = 27, $J(P_aH)$ = 13, $J(P_bH)$ = 20, $J(HH)$ = −8]; ^{31}P (312 K) δ −7.4 [P_b, dd, $J(RhP_b)$ = 103, $J(PP)$ = 28] and −21.3 [P_a, dt, $J(RhP_a)$ = 88, $J(PP)$ = 28]; ^{103}Rh (312 K) δ −319 [dt, $J(RhP)$ = 88, 103]; **4**, ^1H (300 K) δ −10.72 [2 H, m, $J(PH_{trans})$ = 149, $J(PH_{cis})$ = 32.7, $J(RhH)$ = 14.5, $J(P_bH)$ = 20.3]; ^{31}P (300 K) δ −12.6 [P_b, dt, $J(RhP_b)$ = 96, $J(P_bP_a)$ = 28] and −23.6 [P_a, dt, $J(RhP_a)$ = 86, $J(P_bP_a)$ = 28]; ^{103}Rh (300 K) δ −1007 [tt, $J(RhP_a)$ = 86, $J(RhP_b)$ = 96]; **5**, ^1H (300 K, CD_2Cl_2) δ −17.74 [H, $J(P_bH)$ = 15, $J(P_aH)$ = 18.6, $J(RhH)$ = 21.7]; ^{31}P (300 K) δ 8.71 [P_a, dt, $J(PP)$ = 32, $J(RhP)$ = 131] and −6.90 [P_b, dd, $J(RhP)$ = 93, $J(PP)$ = 32 Hz]; ^{103}Rh (300 K) δ 892.

§ In all cases one-dimensional ^1H NMR spectra were first recorded in order to measure the value of $J(XH)$ used for muiltiplet selection in the two-dimensional sequence and to optimise the temperature for a given experiment time. For example, at 343 K in C_6D_6 the hydrides of complex **3** briefly showed 200-fold enhancement. However, at 312 K, in CD_2Cl_2 the initial hydride signal enhancement fell to 30 fold but remained appreciable for up to 20 min. In addition, we independently optimised the recycle time to yield the maximum refreshed signal for each sample/temperature (typically this lies between 20 and 100 ms) and between 1024 and 256 increments were recorded. Only increments stored before the p-H_2 enhancement drops to zero (no signal) were used in the transformed data. In the two-dimensional spectra passive phosphorus–and rhodium–phosphorus couplings were observed in the second dimension.

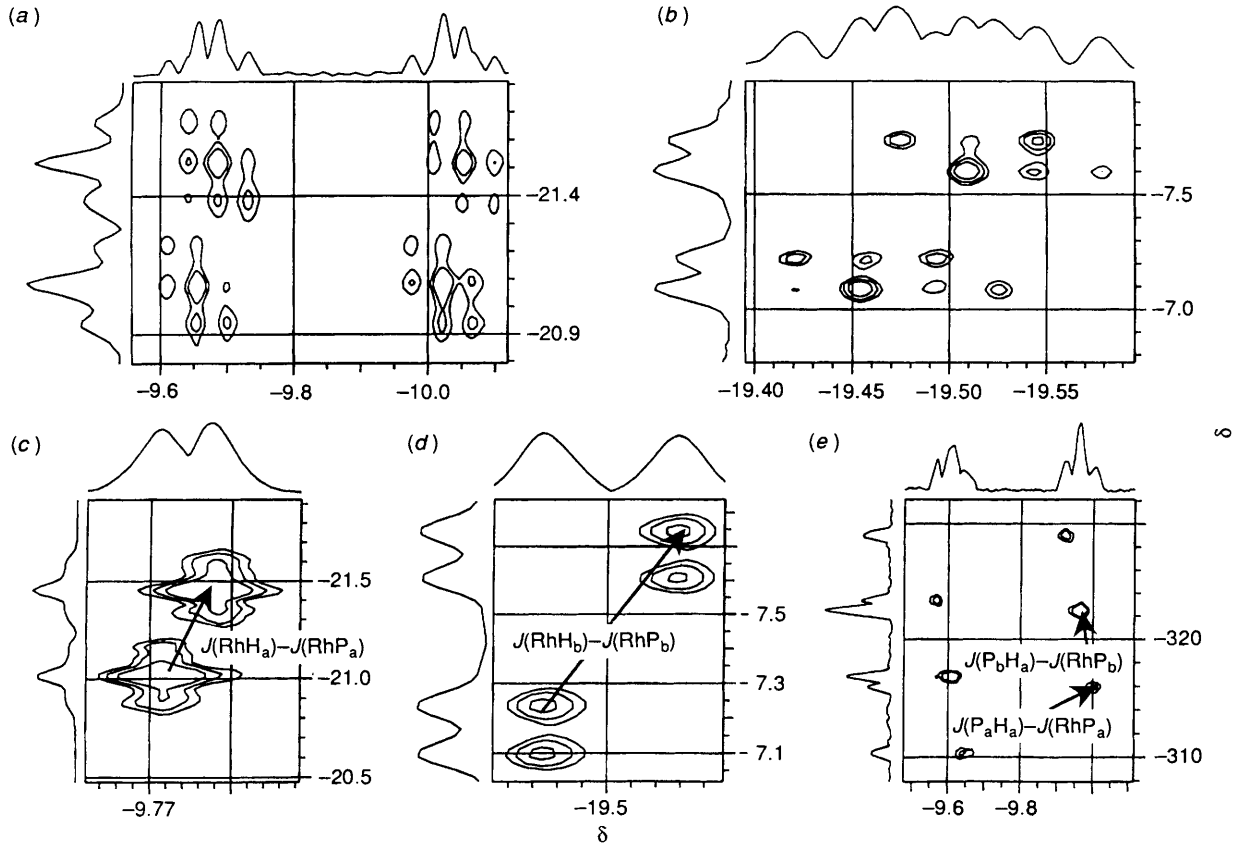


Fig. 1 Selected cross-peaks (positive contours) and projections from ^1H–^{31}P and ^1H–^{103}Rh correlation spectra of $[RhH_2(PMe_3)_3Cl]$ **3**, obtained with *p*-H_2 in CD_2Cl_2 at 312 K. The slopes of the solid lines reveal the sign of the product of the indicated couplings. (*a*) The ^1H–^{31}P correlation spectrum acquired using $\tau = \frac{1}{2}J(P_aH_a)$, showing the cross-peak connecting H_a to P_a; (*b*) the ^1H–^{31}P correlation spectrum acquired using $\tau = \frac{1}{2}J(P_bH_b)$, showing the cross-peak connecting H_b and P_b; (*c*) the ^1H–^{31}P correlation spectrum, ^{31}P decoupled, acquired using $\tau = \frac{1}{2}J(P_aH_a)$, showing the cross-peak connecting H_a and P_a; (*d*) the ^1H–^{31}P spectrum, ^{31}P decoupled, using $\tau = \frac{1}{2}J(P_bH_b)$, showing the cross-peak for H_b and P_b; (*e*) the ^1H–^{103}Rh correlation spectrum, ^{103}Rh decoupled, acquired using $\tau = \frac{1}{2}J(RhH_a)$ for multiplet selection, showing correlated transitions between H_a and ^{103}Rh in **3**

experiment precludes the observation of the H_a–H_b coupling [J(HH) = −7.5 Hz] but is sufficient to allow the observation of the rhodium–hydrogen coupling. On acquiring the ^1H–^{31}P correlation with the delay $\tau = \frac{1}{2}J(P_bH_b)$, the observed cross-peak connects H_b at $\delta(^1H)$ −19.5 to P_b at $\delta(^{31}P)$ −7.4 [dd, $J(RhP_b)$ = 103, J(PP) = 28 Hz] [Fig. 1(*b*) and 1(*d*)]. In the corresponding ^1H–^{103}Rh NMR spectrum of compound **3**, acquired with rhodium decoupling during acquisition [Fig. 1(*e*)], the hydride at $\delta(^1H)$ −9.79 [dt, $J(P_aH_a)$ = 176, $J(P_bH_a)$ = −19 Hz] is connected to the rhodium centre at $\delta(^{103}Rh)$ −319 [dt, $J(RhP_a)$ = 88, $J(RhP_b)$ = 103 Hz].*

The magnitude of the heteronuclear coupling constants can be measured directly from these spectra; in Fig. 1(*a*) and 1(*b*) the peaks are separated by J(PH) and J(RhH) in the ^1H dimension and J(PP) and J(RhP) in the ^{31}P dimension, while in Fig. 1(*c*) and 1(*d*) J(PH) is removed because the spectra are acquired with ^{31}P decoupling. In the ^1H–^{103}Rh spectrum [Fig. 1(*e*)] the hydride resonances are separated by $J(P_aH_a)$ and $J(P_bH_a)$ in the ^1H dimension while in the rhodium dimension $J(RhP_a)$ and $J(RhP_b)$ operate. In addition to this information, the sign of the slope between connected transitions within each cross-peak in the decoupled experiments determines the relative sign of the product of their couplings. It follows that while $J(RhH_a)$, $J(RhH_b)$, $J(RhP_a)$ and $J(RhP_b)$ all have the same sign, the sign of $J(P_bH_a)$ is opposite to this. Spectral analysis therefore reveals that $J(P_bH_a)$ is negative while the remaining coupling constants are positive [the sign of J(PP) is unknown].

When a *z*-field gradient is used to reduce the phase-cycling requirements of the NMR experiment the new ^1H–^{31}P spectrum requires only one scan per increment because these experiments are not signal-limited. Using this simple procedure we are able to quadruple the spectral resolution obtained in the second dimension without increasing the duration of the experiment whilst also reducing the size of spectral artefacts. This result is of critical importance because it allows measurement before relaxation leads to significant depletion of the *p*-H_2 spin-state population. Data measurement using all these methods is extremely rapid because the optimum scan–scan repetition time is determined solely by the hydrogen-exchange rate; all these experiments can be completed in less than 3 min of spectrometer time.

The related complex $[Rh(PMe_3)_4]Cl$ **2** reacts with H_2 to form $[RhH_2(PMe_3)_4]Cl$ **4**.[5] When a CD_2Cl_2 solution of **2**, under 3 atm of *p*-H_2, is monitored by NMR spectroscopy at 300 K the ^1H NMR spectrum shown in Fig. 2(*a*) is obtained immediately. This figure illustrates the *para*-hydrogen-enhanced resonance of the two chemically equivalent, but magnetically inequivalent, hydride ligands of **4**. The anti-phase character seen in these signals is a consequence of the *para*-hydrogen-induced population difference between connected transitions in the $[AX]_2$ spin system. In the fully coupled ^1H–^{31}P experiment the ^{31}P resonance for nucleus P_b shows passive couplings to rhodium and phosphorus (multiplet selection causes the loss of the central triplet feature) with $J(RhP)$ = 96 and J(PP) = 28

* Both hydrides were observed and show similar doublet of triplet multiplicity in the ^{103}Rh dimension.

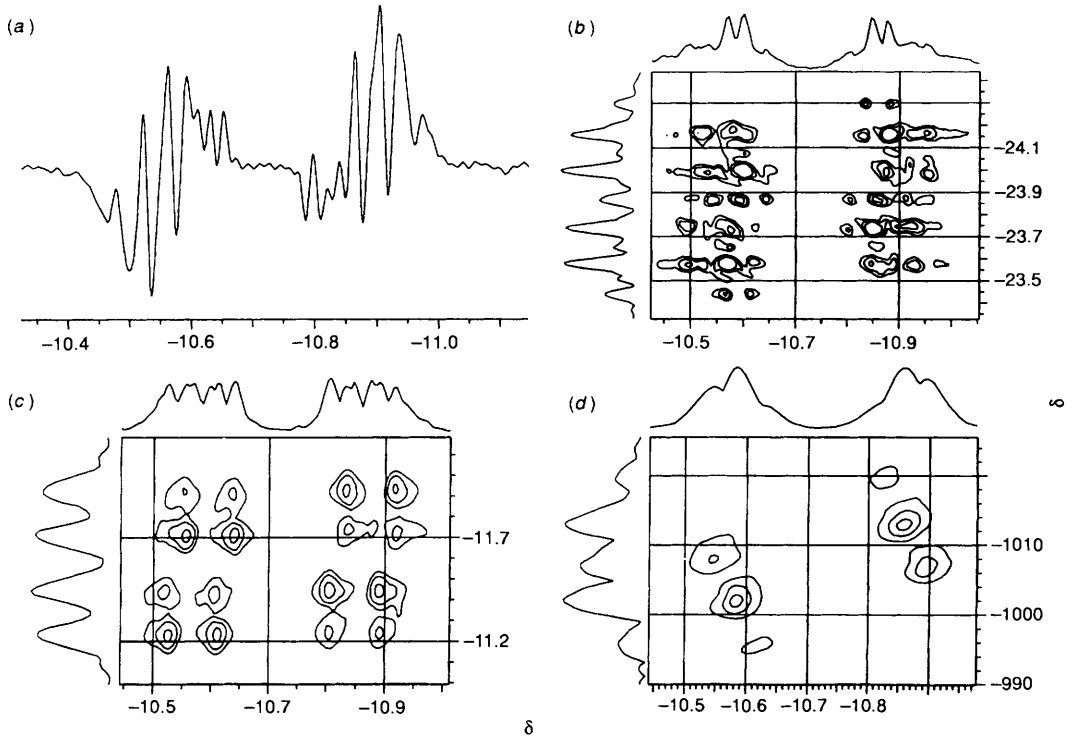


Fig. 2 The NMR spectra of $[RhH_2(PMe_3)_4]Cl$ **4** obtained with p-H_2 in CD_2Cl_2 at 300 K: (*a*) ^1H (the enhanced anti-phase components arise from transitions within the $[AX]_2$ spin system); (*b*) ^1H–^{31}P correlation acquired using $J(P_aH_a)$ for multiplet selection, showing correlated transitions between H_a and P_a (positive contours); (*c*) ^1H–^{31}P correlation acquired with $\tau = \frac{1}{2}J(P_bH_a)$, showing correlated transitions between H_a and P_b (absolute value display); (*d*) ^1H–^{103}Rh correlation, ^{103}Rh decoupled, using J(RhH) for multiplet selection, showing correlated transitions between H_a and ^{103}Rh (positive contours)

Hz [Fig. 2(*b*)]. The higher-field phosphine signal, P_a [Fig. 2(*c*)], appears as a complex multiplet from which J(RhP) = 86 Hz can be extracted. (These resonances have been simulated using WIN-DAISY.[9]) The corresponding ^1H–^{103}Rh spectrum of compound **4** acquired with rhodium decoupling shows that the hydride at $\delta(^1H)$ −10.72 connects to the rhodium centre at $\delta(^{103}Rh)$ −1007 [Fig. 2(*d*)].

When the sample of complex **2** and p-H_2 was warmed to 325 K additional polarised hydride resonances corresponding to those of **3** were observed, as were signals for the monohydride complex $[RhH(PMe_3)_3Cl_2]$ **5**, which eventually became the dominant species in solution.[10] Similar results were obtained when samples of **1** and p-H_2 were warmed to 325 K. In view of the report that **1** and **2** react directly with CD_2Cl_2 to yield either $[Rh(CD_2Cl)(PMe_3)_3Cl_2]$ or $[Rh(CD_2PMe_3)(PMe_3)_2Cl_3]$ complexes,[11] **3** and **4** must be in equilibrium in CD_2Cl_2 under 3 atm H_2. We are therefore not able to say whether **3** or **4** is the source of **5** but clearly **1** and **2** must react much faster with H_2 than with CD_2Cl_2.

These experiments reveal for the first time that p-H_2 facilitates the acquisition of inverse spectra for highly insensitive nuclei such as ^{103}Rh. In addition, metal dihydride complexes containing magnetically inequivalent hydride ligands can be detected and identified using this technique. We have also shown that simple field-gradient methods offer dramatic rewards; we are currently using them as spectroscopic filters in the examination of catalytic hydrogenation reactions with p-H_2.

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References

1 C. R. Bowers and D. P. Weitekamp, *J. Am. Chem. Soc.*, 1987, **109**, 5541.
2 R. Eisenberg, *Acc. Chem. Res.*, 1991, **24**, 110.
3 S. B. Duckett, C. L. Newell and R. Eisenberg, *J. Am. Chem. Soc.*, 1993, **115**, 1156; 1994, **116**, 10548; S. B. Duckett, R. Eisenberg and A. S. Goldman, *J. Chem. Soc., Chem. Commun.*, 1993, 1185; J. Barkemeyer, M. Haake and J. Bargon, *J. Am. Chem. Soc.*, 1995, **117**, 2927.
4 R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 511.
5 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1971, **93**, 2397.
6 A. Bax, R. H. Griffey and B. L. Hawkins, *J. Magn. Reson.*, 1983, 301; M. H. Frey, G. Wagner, M. Vasak, O. W. Sorensen, D. Neuhaus, E. Worgotter, J. H. R. Kagi, R. R. Ernst and K. Wuthrich, *J. Am. Chem. Soc.*, 1985, **107**, 6847.
7 O. W. Sorensen, G. W. Eich, M. H. Levitt, G. Bodenhausen and R. R. Ernst, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1983, **16**, 163; G. Wagner, G. Bodenhausen, N. Muller, M. Rance, O. W. Sorensen, R. R. Ernst and K. Wuthrich, *J. Am. Chem. Soc.*, 1985, **107**, 6440.
8 G. Drobny, A. Pines, S. Sinton, D. Weitekamp and D. Wemmer, *Faraday Symp. Chem. Soc.*, 1979, **13**, 49; G. Bodenhausen, R. L. Vold and R. R. Vold, *J. Magn. Reson.*, 1980, **37**, 93.
9 WIN-DAISY, Brüker–Franzen Analytik, GmbH.
10 G. M. Intille, *Inorg. Chem.*, 1972, **11**, 695.
11 T. B. Marder, W. C. Fultz, J. C. Calabrese, R. L. Harlow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1543.

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