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NMR detection of thermal and photochemical dihydrogen addition products of mono- and tri-nuclear ruthenium complexes containing carbonyl and triphenylphosphine ligands through *para*-hydrogen induced polarisation

Christopher J. Sleigh, Simon B. Duckett,* Roger J. Mawby and John P. Lowe

Department of Chemistry, University of York, York, UK YO10 5DD. E-mail: sbd3@york.ac.uk

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Enhancement of NMR signals by *para*-hydrogen induced polarisation is shown to facilitate the detection of isomers of $Ru(CO)_2(H)_2(PPh_3)_2$ and $Ru(CO)_3(H)_2(PPh_3)$ which contain inequivalent hydride ligands, and to demonstrate that $Ru_3(CO)_9(PPh_3)_3$ adds H_2 to form $Ru_3(CO)_8(H)(\mu\text{-}H)(PPh_3)_3$, as well as undergoing fragmentation to form $Ru(CO)_3(H)_2(PPh_3)$.

We have shown that the enhanced absorption and emission signals observed in NMR spectra of complexes incorporating hydrogen nuclei derived from *para*-enriched hydrogen[1] (p-H_2) can be used to detect and characterise materials present at concentrations too low for detection by normal NMR methods.[2] In particular, using this approach we have been able to identify minor all-*cis* isomers of $Ru(CO)_2(H)_2L_2$ (L = PMe_2Ph or PMe_3) that were previously unknown.[3] Here we extend this approach by demonstrating how both $Ru(CO)_3(H)_2(PPh_3)$ **1** and $Ru(CO)_2(H)_2(PPh_3)_2$ **2** behave with p-H_2. We show that two isomers of both **1** and **2** are detectable, and demonstrate that $Ru_3(CO)_9(PPh_3)_3$ reacts with hydrogen to yield new clusters containing bridging and terminal hydride ligands and also fragments to $Ru(CO)_3(H)_2(PPh_3)$. The precursors required for these studies, $Ru(CO)_3(PPh_3)_2$, $Ru_3(CO)_9(PPh_3)_3$ and *trans*-*cis*–*cis*-$Ru(CO)_2(H)_2(PPh_3)_2$ **2a**, were prepared by standard methods.[4] These complexes were selected for study because, despite the fact that ruthenium/carbonyl/triphenylphosphine species have been implicated in catalytic cycles involving H_2, their reactivity towards H_2 is only poorly understood.[5–7]

When a benzene-d_6 solution of $Ru(CO)_3(PPh_3)_2$ under 3 atm of p-H_2 was warmed to 353 K, no change in the ^1H NMR spectrum of the solution was detected. However, when a similar solution, also under p-H_2 was photolysed for 2 min, an NMR spectrum recorded at 308 K contained enhanced resonances at δ -6.67 (H_a, dd, J_{PH} 15.9, J_{HH} -5.4 Hz) and δ -7.34 (H_b, dd, J_{PH} 61.6, J_{HH} -5.4 Hz) [Fig 1(a)]. The values for J_{PH} suggested that the species responsible for these resonances, **1a**, contained a single PPh_3 ligand lying *cis* to H_a and *trans* to H_b. The p-H_2 enhanced complex **1a** was further characterised by 2D NMR,[8] allowing the ^{31}P resonance to be located at δ 20.3. In order to obtain ^{13}C data, ^{13}CO-labelled $Ru(CO)_3(PPh_3)_2$ was photolysed with p-H_2. In the resulting ^1H NMR spectrum of ^{13}CO-labelled **1a**, the H_a resonance showed an additional doublet splitting (J_{CH} 27.8 Hz) indicative of a *trans* H–Ru–CO arrangement. Two ^{13}CO resonances were detected at δ 197.6 and 199.5 by a ^1H–^{13}C HMQC experiment. The data indicated that **1a** was the *mer* isomer of $Ru(CO)_3(H)_2(PPh_3)$. This complex has not previously been observed by NMR, although high pressure IR studies have indicated its existence.[6] Surprisingly, in the corresponding ^1H–^{31}P correlation, additional resonances corresponding to the *fac* isomer of $Ru(CO)_3(H)_2(PPh_3)$ **1b** were detected which were missed in the original ^1H NMR spectrum owing to coincidental overlap with the resonance due to H_a of **1a**.

A very weak hydride resonance could also be seen in the ^1H NMR spectra of the photolysed solutions at δ -6.35 (t, J_{PH} 23.2 Hz). This was shown to be due to the *trans*–*cis*–*cis* isomer of $Ru(CO)_2(H)_2(PPh_3)_2$ **2a** by comparison with the spectrum of an authentic sample (see above). Under normal H_2, and after prolonged photolysis, **2a** was the only detectable product.

When the solution containing $Ru(CO)_3(PPh_3)_2$ and **1a** enhanced with p-H_2 was warmed to 328 K, the hydride resonances for **1a** broadened substantially, and a second pair of polarised hydride resonances appeared at δ -6.27 (ddd, J_{PH} 26.4, 19.1, J_{HH} = -7.1 Hz) and -7.52 (ddd, J_{PH} 75.1, 33.0, J_{HH} -7.1 Hz). Resonances for two inequivalent ^{31}P nuclei, both doublets with J_{PP} 32.0 Hz, were located in the ^1H–^{31}P spectrum at δ 50.2 and 41.6. It was concluded that the species responsible for the new resonances was the previously undetected all-*cis* isomer of $Ru(CO)_2(H)_2(PPh_3)_2$ **2b**.

A ^1H–^1H PHIP–EXSY experiment, recorded at 308 K, contained exchange peaks that indicated that the hydride ligands of *mer*-$Ru(CO)_3(H)_2(PPh_3)$ **1a** were interchanging positions with a rate constant of 40 s^{-1}. Even at higher temperatures, however, no peaks connected the resonances of **1a** to those of **2b**, suggesting that the interchange may be intramolecular,

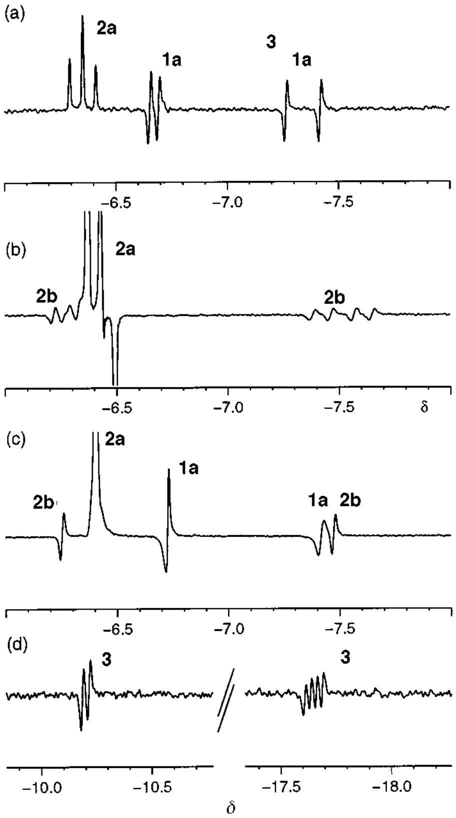
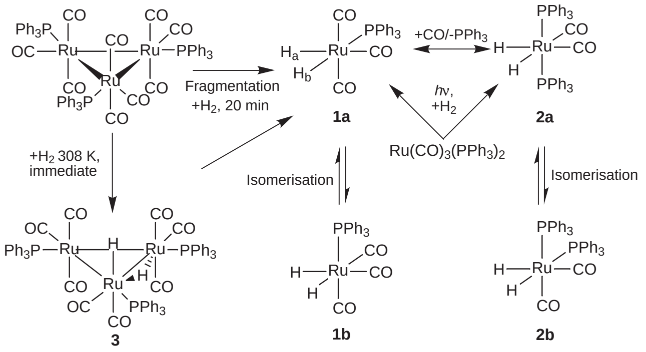


Fig 1 NMR spectra of reaction products obtained with p-H_2 in C_6D_6 showing the hydride region only. The antiphase components arise in transitions involving protons that originate from p-H_2. (a) ^1H spectrum of **1a** generated after UV irradiation of a sample of $Ru(CO)_3(PPh_3)_2$ at 308 K; (b) ^1H spectrum of **2b** at 328 K; (c) ^1H spectrum of a sample of **2a** warmed with p-H_2 in the presence of CO at 318 K; (d) ^1H spectrum of **3** generated from a sample of $Ru_3(CO)_9(PPh_3)_3$ at 308 K.



Scheme 1

perhaps a trigonal twist process similar to that reported for $Ru(CO)(H)_2(PPh_3)_3$.[9]

The interconversions between **2a**, **2b** and **1a** were further investigated using an authentic sample of **2a**. When a benzene-d_6 solution of **2a** was heated under 3 atm of p-H_2 to 328 K, no signals for **1a** were visible in the ^1H NMR spectrum, but the hydride resonances for **2b** were again observed [Fig. (1b)]. An NMR tube containing a fresh solution of **2a** was then placed under 1 atm of CO, frozen and then filled with 3 atm of p-H_2. When the solution was warmed to 318 K, the enhanced hydride resonances of **1a** and **2b** were observed [Fig. 1(c)]. Evidently **2a** readily undergoes replacement of PPh_3 by CO. We have recently adapted an NMR probe to allow a sample to be irradiated by UV light from a HgXe arc while NMR spectra are recorded.[10] ^1H NMR spectra recorded during photolysis of a benzene-d_6 solution $Ru(CO)_3(PPh_3)_2$ under 3 atm of p-H_2 at 292 K showed large enhanced hydride signals due to **1a** and a small non-enhanced signal due to **2a**. The signals for **1a** were not observed in the absence of UV radiation, confirming that, in this case, hydrogen exchange between **1a** and free H_2 is photochemical rather than thermal.

Many phosphine-substituted derivatives of $Ru_3(CO)_{12}$ have been characterised and studied, but the reactions of these complexes with hydrogen are less well understood.[11] We have therefore used p-H_2 to monitor the reaction of $Ru_3(CO)_9(PPh_3)_3$ with hydrogen. Nevinger *et al*. used a complex synthetic procedure to obtain a species believed to be $Ru_3(CO)_{11}H(\mu\text{-}H)$, whose ^1H NMR spectrum contained hydride resonances at δ −11.79 and 18.55.[12] We recorded the ^1H NMR spectrum of a benzene-d_6 solution of $Ru_3(CO)_9(PPh_3)_3$ under p-H_2 at 308 K, and detected enhanced resonances at δ −10.20 (dd, J_{PH} 11.2, J_{HH} −6.0 Hz) and −17.64 (ddd, J_{PH} 21.2,10.4, J_{HH} −6.0 Hz) for two mutually coupled hydrides in a species **3** [Fig. 1(d)]. The chemical shifts and couplings to phosphorus suggested that the former resonance represented a terminal hydride *cis* to a phosphine and the latter a hydride bridging two ruthenium atoms and *cis* to a phosphine ligand on each ruthenium. A 2D experiment located the resonances for the corresponding ^{31}P nuclei at δ 44.4 (coupled to both hydrides) and −17.6 (coupled only to the terminal hydride). From this evidence it appeared that **3** was the 48-electron cluster $Ru_3(CO)_8H(\mu\text{-}H)(PPh_3)_3$, with the structure shown in Scheme 1. The third ^{31}P nucleus was not detected by the 2D experiment because it is not coupled to either hydride. Complex **3**, which is comparable to both $Ru_3(CO)_{11}H(\mu\text{-}H)$ and $Os_3(CO)_{10}H(\mu\text{-}H)L$ (L = PPh_3 or CD_3CN),[13] is presumably formed by a simple substitution of CO by H_2.

After 20 min at 308 K, resonances for isomer **1a** of $Ru(CO)_3H_2(PPh_3)$ had appeared in the ^1H NMR spectrum of the solution. Consequently, either unreacted $Ru_3(CO)_9(PPh_3)_3$ or $Ru_3(CO)_8H(\mu\text{-}H)(PPh_3)_3$ fragment under hydrogen to yield mononuclear ruthenium complexes under relatively mild conditions. This observation is interesting, given that mixtures of $Ru_3(CO)_{12}$ and PPh_3 have been used in hydroformylation catalysis and $Ru(CO)_3(H)_2(PPh_3)$ has been implicated as an intermediate in hydroformylation.[5,7] No *para*-hydrogen enhanced products, either tri- or mono-nuclear, were detected on treating $Ru_3(CO)_{12}$ with p-H_2 either in the presence or the absence of UV irradiation.

Here, we have established some features of the ruthenium carbonyl/triplenylphosphine/hydrogen system, which shows some important differences from those with PMe_2Ph and PMe_3. Furthermore, we have established the feasibility of using p-H_2 to probe photochemical reactions, H_2 addition to clusters, and cluster fragmentations.

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Notes and references

† *Selected spectroscopic data* for **1a**, **1b**, **2a**, **2b** and **3**: NMR spectra in C_6D_6 at 400.13 MHz (^1H) and 202.45 MHz (^{31}P) recorded on 5 mm samples in a 5 mm inverse geometry probe. **1a**: ^1H δ_H(328 K) −6.67 [H_a, J(PH) 15.9, J(COH) 27.8, J(HH) −5.4 Hz], −7.34 [H_b, J(PH) 61.6, J(HH) −5.4 Hz]. δ_P(328 K) 20.3 (s). δ_C(328 K); 199.5 d [J(PC) 8.4 Hz], 197.6 [d J(PC) 4.6 Hz]. **1b**: δ_H(308 K) −6.68 [J(PH) 23 Hz], δ_P(328 K) 55.1 (s). **2a**: δ_H(295 K) −6.35 [H, J(PH) 23.2 Hz]. δ_P(295 K) 57.7 (s). δ_C(295 K) 202.0 [t, J(PC) 8.3 Hz]. **2b**: δ_H(328 K) −6.27 [H_c, J(PH) 26.4, 19.1, J(HH) −7.1 Hz], −7.52 [H, J(PH) 75.1, 33.0, J(HH) −7.1 Hz]. δ_P(328 K) 50.2 d [J(PP) 32 Hz], 41.6 [d, J(PP) 32 Hz]. **3**: δ_H(300 K) −10.20 [H, J(PH) 11.2, J(HH −6.0 Hz], −17.64 [H, J(PH) 21.2, 10.4, J(HH) −6.0 Hz]. δ_P (308 K) 44.4 (s) and 31.2 (s).

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