ChemComm
www.rsc.org/chemcomm

NMR characterisation of unstable solvent and dihydride complexes generated at low temperature by *in-situ* UV irradiation†

Cyril Godard,[a] Philip Callaghan,[a] Jenny L. Cunningham,[a] Simon B. Duckett,*[a] Joost A. B. Lohman[b] and Robin N. Perutz[a]
[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: sbd3@york.ac.uk*
[b] *Bruker BioSpin, Banner Lane, Coventry, UK CV4 9GH*

Received (in Cambridge, UK) 15th August 2002, Accepted 8th October 2002
First published as an Advance Article on the web 28th October 2002

Low temperature *in-situ* UV irradiation of toluene solutions containing bis(alkene)rhodium complexes and parahydrogen in conjunction with NMR monitoring enables the characterisation of unstable η²-solvent complexes and dihydrogen activation products.

The characterisation of unstable complexes by NMR spectroscopy is normally limited by the warming effect of the air stream that is utilised to lower samples into the NMR probe. Ball, and others, have demonstrated how UV photolysis of samples within the NMR probe can be used to generate materials that can subsequently be characterised using conventional methods[1] while others have used photo-CIDNP to determine kinetic parameters.[2] Here we demonstrate a refinement of this approach where a 325 nm 25 mW He–Cd cw laser is employed as the radiation source.† UV irradiation through the side of the NMR tube results in product generation in the high sensitivity detection region of the probe, whereas the more common approach directs the light beam vertically. Our arrangement ensures that high-resolution spectra can be collected on pressurised samples at low temperature.

Previous studies have demonstrated that the stepwise photochemical displacement of ethene from (η^5-C_5H_5)Rh(C_2H_4)$_2$ **1a** occurs readily,[3–5] with (η^5-C_5H_5)Rh(C_2H_4)(H)($SiEt_3$) and (η^5-C_5H_5)Rh(H)$_2$($SiEt_3$)$_2$ being produced in the presence of Et_3SiH.[3] With our *in-situ* equipment, conversion of **1a** into these products is achieved in a comparable time to that for analogous bench-top reactions induced by an unfiltered 300 W Hg arc lamp. Laser alignment was achieved in real-time by optimising hydride signal intensities seen in single-scan *p*-H_2 enhanced NMR spectra of Ru(CO)$_2$(dppe)(H)$_2$ generated from Ru(CO)$_3$(dppe).[6]

A sample of **1a** (3 mg) was dissolved in toluene-d$_8$ and irradiated continuously, *in-situ*, at 203 K. The corresponding ^{1}H NMR spectrum recorded after 30 min contained evidence for a new cyclopentadienyl ligand resonance at δ 4.23 and free ethene at δ 5.36. When the level of conversion had reached 30%, additional signals at δ 3.15, 2.74, 1.35 and −0.27 due to coordinated ethene protons were also visible with the relative areas of 1 : 0.6 : 1 : 0.6 suggesting that two products were formed (Fig. 1a). When the ethene proton resonating at δ 1.35 was probed in a selective 1D nOe experiment, rapid exchange into the site resonating at δ −0.27 occurred. When the reverse selection was made, the corresponding exchange peak was significantly smaller, and when the two remaining signals at δ 3.15 and δ 2.75 were examined, directly analogous results were observed. These data suggested that two interconverting species were formed even though only one new cyclopentadienyl ligand resonance was evident. This hypothesis was confirmed when the cyclopentadienyl proton resonance at δ 4.23 was probed since a cross-peak was observed to a new ring proton resonance at δ 4.80 which had previously been screened by the cyclopentadienyl proton resonance of **1a**. Distinct ^{103}Rh chemical shifts were also observed for these species.‡

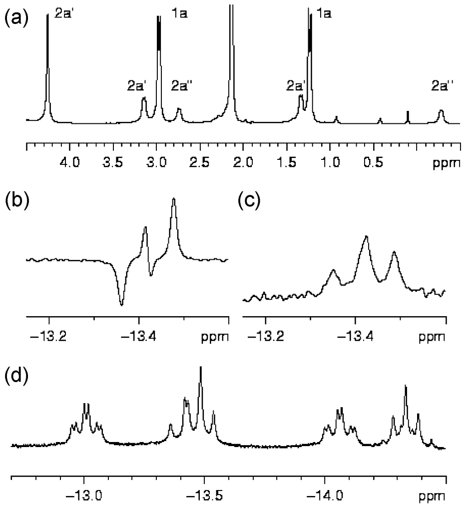
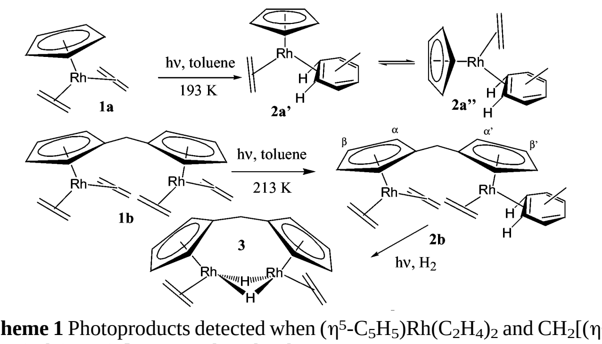


Fig. 1 (a) ^{1}H spectrum at 193 K showing key resonances for isomers **2a′** and **2a″** of CpRh(C_2H_4)(η^2-toluene) at 3 h irradiation; (b) 8 scan ^{1}H NMR spectrum of CpRh($C_2H_3SiMe_3$)(H)$_2$ **4** obtained during continuous laser irradiation of **1c** at 213 K with *p*-H_2; (c) 185 scan ^{1}H spectrum of **4** obtained after 1 h irradiation with laser blanked during acquisition; (d) ^{1}H NMR spectrum obtained after 6 h irradiation of **1c**.

The product resonances are assigned to the solvent complex (η^5-C_5H_5)Rh(C_2H_4)(toluene) **2**, as expected on the basis of previous low temperature UV and room temperature flash photolysis studies.[5] It should also be noted that the related species (η^5-C_5H_5)Ir(C_2H_4)(C_6F_6) exists in two isomeric forms where the metal binds to the π-face in an η^2-fashion and the C_6 plane points towards or away from the cyclopentadienyl ring.[7] Rotation about the Rh–arene bond interconverts isomers **2a′** and **2a″** and accounts for the observed exchange peaks (Scheme 1).‡ At 193 K, the equilibrium constant connecting the two isomers of **2** is 1.7 and the rate of exchange between the major and minor isomers is 26 s^{-1}. In this system, the presence of the arene's methyl substituent results in three potential η^2-arene–metal arrangements, for each of the two arene orientations. Since we see evidence for only one such isomer, rapid exchange between each of the three forms is required or one isomer dominates.

When the low temperature irradiation of **1a** in toluene-d$_8$ was monitored in the presence of H_2, **2** was the only organometallic product to be detected even though the formation of (η^5-



Scheme 1 Photoproducts detected when (η^5-C_5H_5)Rh(C_2H_4)$_2$ and CH_2[(η^5-C_5H_4)Rh(C_2H_4)$_2$]$_2$ are irradiated at low temperature.

DOI: 10.1039/b208007a

---

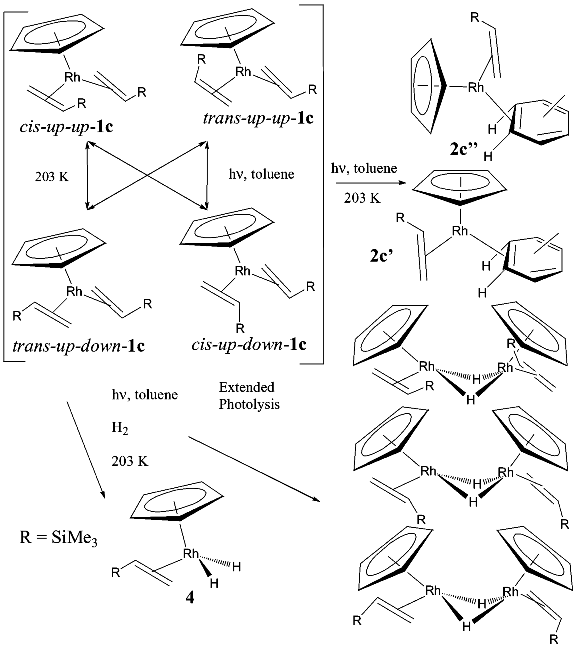
† Electronic supplementary information (ESI) available: description of experimental set-up and NMR data for **1c** and **5a–c**. See http://www.rsc.org/suppdata/cc/b2/b208007a/

$C_5H_5)Rh(C_2H_4)(H)_2$ was expected on the basis of previous work in liquid xenon.[2] However, upon warming this solution to above 240 K, the liberated ethene was rapidly consumed and both ethane and partially deuterated methyl-cyclohexane were observed. Thus although hydrogenation occurred, the detection of the key species $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)(H)_2$ was not achieved.

When the related complex $CH_2[(\eta^5\text{-}C_5H_4)Rh(C_2H_4)_2]_2$ **1b**, first reported by Werner,[8] was photolysed in toluene-d_8 at 213 K the analogous solvent complex $CH_2[(\eta^5\text{-}C_5H_4)Rh(C_2H_4)_2][(\eta^5\text{-}C_5H_4)Rh(C_2H_4)(\text{toluene})]$ **2b** was characterised. Whilst the proton resonances of the unsubstituted $[(\eta^5\text{-}C_5H_4)Rh(C_2H_4)_2]$ centre appear at very similar chemical shifts to those observed in **1b**, two inter-converting sets of four inequivalent resonances are observed for both the ring and the ethene protons of the $[(\eta^5\text{-}C_5H_4)Rh(C_2H_4)(\text{toluene})]$ moiety. We conclude that **2b** also exists as two exchanging rotamers.‡

NMR studies in conjunction with parahydrogen (p-H_2) offer opportunities to characterise very low concentrations of dihydride species that contain spin-coupled magnetically inequivalent hydride ligands.[9] When the irradiation of **1b** was repeated in the presence of p-H_2, a new species was observed in addition to **2b**. This product, **3** exhibited a single hydride resonance at δ −12.60 with triplet multiplicity due to coupling to two equivalent rhodium centres that did not show any signal enhancement. Upon warming this solution to 295 K, ethane and partially deuterated methylcyclohexane were formed and the signals for **3** found to disappear. Complex **3** is assigned as the symmetrical hydride species $CH_2[(\eta^5\text{-}C_5H_4)Rh(C_2H_4)(\mu\text{-}H)]_2$.

In order to explore these reactions further, a sample of $(\eta^5\text{-}C_5H_5)Rh(C_2H_3SiMe_3)_2$ **1c** was prepared. We reported in 1989 that this complex exists as two geometrical isomers, *cis-up-up*-**1c** and *trans-up-up*-**1c**, (where *up* signifies that a substituent points towards the C_5H_5 ring)[3] and were surprised to observe two additional rotameric forms, *cis-up-down*-**1c** and *trans-up-down*-**1c**, on a modern NMR spectrometer (Scheme 2, *cf.* $(\eta^5\text{-}C_5Me_5)Rh$ analogue).[10] When a sample of **1c** (3 mg) was dissolved in toluene-d_8 and photolysed at 203 K the proportion of the two minor isomers increased rapidly and two new cyclopentadienyl resonances corresponding to two isomers of $(\eta^5\text{-}C_5H_5)Rh(C_2H_3SiMe_3)(\text{toluene})$ **2c** were detected (Scheme 2). We deduce from these data that alkene rotation in **1c** is suppressed at 203 K and that **2c** also exists in two inter-converting forms.



Scheme 2 Photoproducts detected when $CpRh(C_2H_3SiMe_3)_2$ is irradiated at low temperature in toluene with H_2.

When **1c** was irradiated at 203 K in the presence of p-H_2, the resultant ^1H NMR spectra recorded during laser irradiation, contained a pair of p-H_2 enhanced hydride resonances. The new resonances arise from $(\eta^5\text{-}C_5H_5)Rh(C_2H_3SiMe_3)(H)_2$ **4** which contains magnetically, and chemically distinct hydride ligands by virtue of the alkene's $SiMe_3$ substituent. Figs. 1b and c illustrate the effects of laser irradiation and demonstrate that p-H_2 enhancement of the hydride resonances of **4** arises because they are observed immediately after **4** is formed and before the nuclear spin state has relaxed. In addition, the observed enhancement also allows us to conclude that intermediate $(\eta^5\text{-}C_5H_5)Rh(C_2H_3SiMe_3)$ is in a singlet electronic state.[6] Based on the photon flux and a conservative estimate of the quantum yield these spectra illustrate the detection of 1 nano-mole of material. Upon extended photolysis, the resonances due to **4** diminished in size and four new bridging hydride resonances appear (Figs. 1d). The formation of three stereo-isomers of $[(\eta^5\text{-}C_5H_5)Rh(C_2H_3SiMe_3)(\mu\text{-}H)]_2$ is indicated (Scheme 2).† We note that alkene and arene hydrogenation are again observed, with GC-MS revealing that the methylcyclohexane exists as the isotopomers $C_7H_{14-x}D_x$ with the most significant contributions from $x = 8$ to 14.

We have used this method to characterise arene solvent complexes in far more detail than previously and to observe the first NMR spectra of the elusive Rh(alkene)$(H)_2$ moiety. Of particular interest is the p-H_2 enhancement of $(\eta^5\text{-}C_5H_5)Rh(C_2H_3SiMe_3)(H)_2$ **4** that depends on capturing the NMR spectra before relaxation. This overcomes a major limitation of the technique, which normally requires rapid thermal H_2 cycling. Through use of alternative laser sources, the methods described here could be applied to a wide range of photochemical problems spanning organic, inorganic and biological areas.

We are grateful to Bruker, the EPSRC and York University for funding and R. Girling and D. Schott for experimental help. A loan of $RhCl_3$ from Johnson Matthey is also appreciated.

Notes and references

‡ Selected spectroscopic data for **2a**, **2b**, **3** and **4** in toluene-d_8 at 400.13 MHz (^1H) and 12.59 MHz (^{103}Rh): **2a′**: ^1H (193 K) δ 1.35 (br, 2H, C_2H_4), δ 3.15 (br, 2H, C_2H_4), δ 4.23 (s, 5H, Cp), ^{103}Rh −333.6 **2a″** ^1H (193 K) δ −0.27 (br, 2H, C_2H_4), δ 2.75 (br, 2H, C_2H_4), δ 4.80 (s, 5H, Cp), ^{103}Rh −373.6 **2b′** ^1H (203 K) δ 1.34 and δ 2.81 $(CH_2CH_2)_2$, δ 2.35 CH_2, δ 4.54 (β-CH), δ 5.12 (α-CH), −0.2 and 2.54 (CH_2CH_2), δ 4.08 (β′-CH), δ 4.16 (α′-CH) **2b″** ^1H (203 K) 1.34 and 2.81 $(CH_2CH_2)_2$, δ 2.35 CH_2, 4.54 (β-CH), 5.04 (α-CH), 2.87 and 1.43 (CH_2CH_2), 4.61 (β′-CH), 4.86 (α′-CH) **2c′**: ^1H (203 K) δ −0.17 (m, CH(d)), 0.31 Me, δ 2.58 (d 9.37 Hz, CH_2(d)), δ 3.17 (d 12.5 Hz, CH_2(u)), δ 4.32 (s, 5H, Cp); **2c″**: ^1H (193 K) δ 4.86 (s, 5H, Cp). **3** ^1H (203 K) −12.60 t ($J_{RhH} = 22.4$), δ 2.63 CH_2, 4.57 (β-CH), 5.39 (α-CH), ^{103}Rh (203 K) δ −1101. **4**. ^1H (203 K) −13.43 (m, J_{RhH} = 25.3 Hz, RhH), δ −13.37 (m, J_{RhH} = 25.3 Hz, RhH), 0.25 $SiMe_3$, 1.21(m, CH(u)), 1.97 (m, CH_2(u)), 2.67 (m, CH_2(d)), ^{103}Rh −1401. (d = down, u = up).

1 S. Geftakis and G. E. Ball, *J. Am. Chem. Soc.*, 1999, **121**, 6336; N. A. Knatochnil, J. A. Pachinson, P. J. Bedmaishi and P. J. Sadler, *Angew. Chem., Int. Ed.*, 1999, **38**, 1460.
2 C. E. Lyon, J. L. Lopez, B.-M. Cho and P. J. Hore, *Mol. Phys.*, 2002, **100**, 1261; T. Kühn and H. Schwalbe, *J. Am. Chem. Soc.*, 2002, **122**, 6169.
3 S. B. Duckett, D. M. Haddleton, R. N. Perutz, S. A. Jackson, R. K. Upmacis and M. Poliakoff, *Organometallics*, 1989, **7**, 1526–1532.
4 J. Müller, C. Hirsch, A. L. Guo and K. Qiao, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2069.
5 S. T. Belt, S. B. Duckett, D. M. Haddleton and R. N. Perutz, *Organometallics*, 1989, **8**, 748–759.
6 D. Schott, C. J. Sleigh, J. P. Lowe, S. B. Duckett, R. J. Mawby and M. G. Partridge, *Inorg. Chem.*, 2002, **41**, 2960–2970.
7 T. W. Bell, M. Helliwell, M. G. Partridge and R. N. Perutz, *Organometallics*, 1992, **11**, 1911.
8 H. Werner, *Inorg. Chim. Acta*, 1992, **198**, 715.
9 S. B. Duckett and C. J. Sleigh, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1999, **34**, 71.
10 C. P. Lenges, P. S. White and M. Brookhart, *J. Am. Chem. Soc.*, 1999, **121**, 4385.