Kinetic and mechanistic examination of $NBu_4[IrH_2(CO)_2I_2]$ and $NBu_4[RhH_2(CO)_2I_2]$ *via para*-hydrogen enhanced NMR spectroscopy

Sarah K. Hasnip,[a] **Simon B. Duckett,***[a] **Diana R. Taylor,**[b] **Graham K. Barlow**[b] **and Mike J. Taylor**[b]

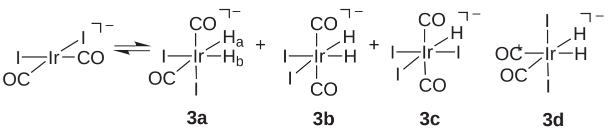
[a] *Department of Chemistry,University of York, Heslington, York, UK YO10 5DD. E-mail: sbd3@york.ac.uk*
[b] *BP Chemicals, BP Chemicals Limited, Salt End, Hull, UK HU12 8DS*

Received (in Cambridge, UK) 4th February 1999, Accepted 12th April 1999

***para*-Hydrogen enhanced NMR signals are used to show that $NBu_4[M(CO)_2I_2]$ (M = Rh, Ir) add hydrogen to form NBu_4-{*all-cis*-$[M(H)_2(CO)_2I_2]$} which for M = Ir undergoes H_2 elimination in a step where $\Delta H^{\ddagger}$ 106 ± 10 kJ mol^{-1} and $\Delta S^{\ddagger}$ 60 ± 6 J K^{-1} mol^{-1} while showing a rich substitution chemistry with PPh_3 that leads to both charged and neutral products *via* square pyramidal $Ir(H)_2(CO)_2I$.**

When transition metal complexes are reacted with *para*-hydrogen (p-H_2) the size of the detectable NMR signatures of many hydride reaction products are dramatically enhanced owing to the generation of non-Boltzmann spin populations.[1–4] This phenomenon provides sufficient sensitivity to facilitate the observation of intermediates in catalytic reactions, species in minor reaction pathways such as $RhH_2(PMe_3)_2I_2Rh(PMe_3)(CO)$ and minor constituents in equilibria, for example *all-cis*-$[Ru(PMe_3)_2(CO)_2(H)_2]$.[5] Here we examine the reactivity of $NBu_4[M(CO)_2I_2]$ (M = Ir, Rh) towards hydrogen. While these complexes are known to react with MeI to form $NBu_4[MI_3Me(CO)_2]$, and play a substantial role in acetic acid generation, their reactivity towards hydrogen, a substrate also present in this process, is far less well understood.[6] We show that two isomers of $NBu_4[IrH_2(CO)_2I_2]$ are formed upon H_2 addition to $NBu_4[Ir(CO)_2I_2]$, and report for the first time kinetic and thermodynamic parameters for H_2 elimination from a p-H_2 enhanced dihydride. The lability of the ligand sphere of the *all-cis* isomer is further explored by employing PPh_3 as a vacant coordination site scavenger.

When a 0.1 mM solution of $NBu_4[Ir(CO)_2I_2]$ **1** in benzene-d_6 is monitored by ^1H NMR spectroscopy at 295 K while under 3 atm of p-H_2 substantial signals arise from a previously undetected complex at δ −9.13 and −13.30 [Fig. 1(a)].† These resonances are assigned to the hydride ligands H_a and H_b of **3a**, and their chemical shifts indicate they are *trans* to carbonyl and iodide respectively.† The two carbonyl resonances of **3a** were detected at δ 167.2 and 160.9 by a ^1H–^{13}C HMQC experiment, and when a sample containing **1** and p-H_2 was monitored with an excess of NBu_4I present the product signal intensities were unchanged. This information suggests that **3a** corresponds to the *all-cis* isomer of $NBu_4[Ir(H)_2(CO)_2I_2]$ **3a** as shown in eqn. (1).



(1)

Weak hydride resonances attributable to species **3b** and **3c** of eqn. (1) were also observed in the ^1H NMR spectra.[7] Resonances attributable to **3a** are also observable in methanol-d_4 and acetic acid-d_4. We further note, that **3a** is only visible with p-H_2, and that isomer **3d** is not seen even when ^{13}CO labelled **1** is employed. Additionally, when the sample is left under H_2 at room temperature, the resonance for **3c** disappears leaving **3b** as the only detectable hydride containing species.

The mechanism of generation of these species requires further comment since concerted H_2 addition to NBu_4{*cis*-$[Ir(CO)_2I_2]$} should only yield **3a**. We therefore investigated the dynamic behaviour of **3a** using gradient-assisted EXSY spectroscopy. This revealed that at 323 K **3a** undergoes simple reductive elimination to form free H_2, which at temperatures beyond 350 K is complicated by both *intermolecular* hydride interchange and *intramolecular* exchange into **3b**. Under these conditions, addition of an excess of free NBu_4I, such that the solution is saturated, results in a 5% increase in the rate of H_2 loss and suppression of the intermolecular and intramolecular exchange peaks. In view of this we can state that H_2 loss occurs from **3a** rather than the 16-electron complex $[Ir(H)_2(CO)_2I]$. Analysis of the exchange peak intensity as a function of mixing time allowed the rate of H_2 elimination from **3a** to be determined; at 325 K this corresponds to 0.17 s^{-1}. Monitoring this process as a function of reaction temperature enabled the activation parameters $\Delta H^{\ddagger}$ 106 ± 10 kJ mol^{-1} and $\Delta S^{\ddagger}$ 60 ± 6 J $K^{-1}mol^{-1}$ to be calculated.

Importantly, when a 0.1 mM solution of the rhodium analogue **2** is warmed with p-H_2 to 350 K and monitored by ^1H NMR spectroscopy [Fig 1(b)] two rhodium coupled hydride resonances are observed at δ −9.75 (J_{RhH} 17.3, J_{HH} −4 Hz) and −14.15 (J_{RhH} 16.5 Hz) which are consistent with the formation of the previously unseen species NBu_4{*all-cis*-$[RhH_2(CO)_2(I)_2]$}. Clearly the extent to which NBu_4{*all-*

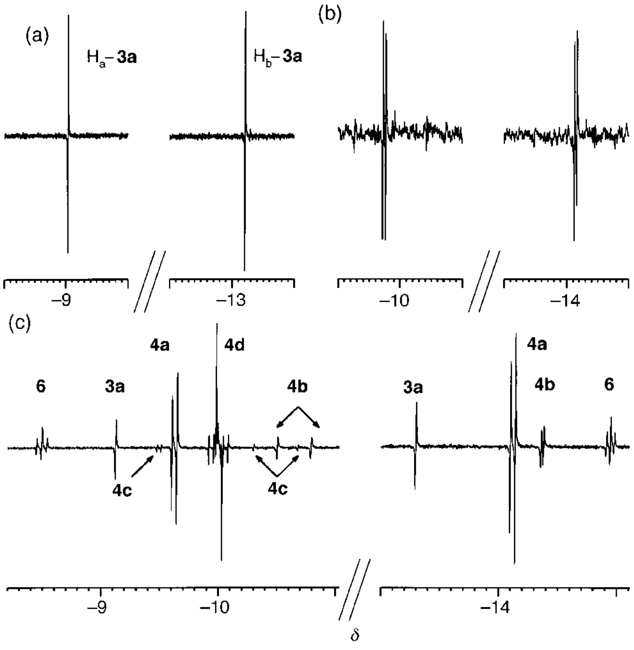
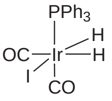
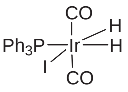


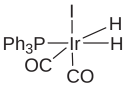
Fig. 1 (a) ^1H NMR spectrum (400 MHz, 295 K) of a 0.1 mM solution of **1** in benzene-d_6 under 3 atm of p-H_2. The antiphase resonances arise from the parahydrogen enhanced hydride resonances in the *all-cis* isomer of $NBu_4[Ir(H)_2(CO)_2I_2]$, **3a**. (b) ^1H NMR spectrum (400 MHz, 350 K) of a 0.1 mM solution of **2** in benzene-d_6 under 3 atm of p-H_2 showing resonances due to the *all-cis* isomer of $[Rh(H)_2I_2(CO)_2]$. (c) ^1H NMR spectrum (400 MHz, 295 K) of a 0.1 mM solution of **1** in benzene-d_6 under 3 atm of p-H_2, in the presence of 0.1 mM of PPh_3 with resonance assignments indicated.

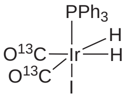
cis[$RhH_2(CO)_2(I)_2$]} forms is much lower than that of **3a**, and the temperatures required to observe it are at least 60 K higher.

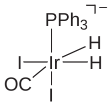
The observation of intramolecular and intermolecular exchange pathways indicated that the substitution reactivity of **3a** was worthy of examination. We therefore monitored benzene-d_6 solutions containing **1**, *p*-H_2 and PPh_3 (< 2 equivalents). A typical ^1H spectrum is shown in [Fig. 1(c)]. The new mononuclear products, identified by ^1H–^1H COSY, ^1H–^{31}P and ^1H–^{13}C HMQC techniques, correspond to four isomeric forms of $IrH_2(CO)_2(PPh_3)I$, three isomers of $NBu_4[IrH_2(CO)(PPh_3)I_2]$, and $IrH_2(CO)(PPh_3)_2I$ with *trans* phosphines are shown below.† Surprisingly, when $NBu_4[Rh(CO)_2I_2]$ **2**, *p*-H_2 and PPh_3 were examined at 350 K no new dihydride products were detected.

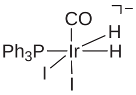

4a

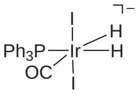

4b

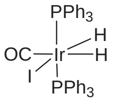

4c


4d


5a

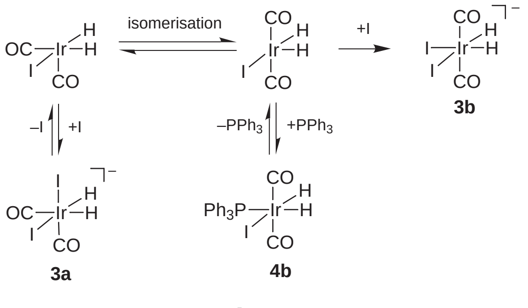

5b


5c


6

When samples containing **1**, PPh_3 and H_2 were monitored by EXSY spectroscopy at 295 K the signals observed for each hydride of **3a** connected to both hydride resonances of **4b** *via* cross peaks arising from chemical exchange. Examination of the intensity of these peaks indicated that interconversion of **3a** to **4b** places **3a**-H_a *trans* to phosphine in **4b** more often than *trans* to iodide; this process is suppressed upon addition of NBu_4I. As expected, the reverse situation is true when cross peaks from H_b-**3a** are considered and the difference in intensity between the corresponding hydride cross peaks falls as the temperature rises. This information suggests that **4b** forms from **3a** *via* a process involving iodide loss to yield an intermediate with inequivalent hydrides which undergoes rearrangement to form the square pyramidal intermediate $IrH_2(I)(CO)_2$ with *trans* carbonyls. Coordination of phosphine then generates **4b**, or iodide **3b**, as shown in Scheme 1. Furthermore, while the two hydride ligands of $IrH_2(I)(CO)_2$ are inequivalent they must be able to interchange their positions on the same time scale as phosphine coordination. Significantly, weaker cross peaks, connect the hydride resonances of **4b** to **3a** which indicates that they are in equilibrium.

The only other exchange peaks visible in the hydride region of the spectrum at 350 K connect the hydride resonances of **4c** to those of **4b**. This interconversion process occurs with a twofold preference for placing the hydride ligand of **4c** that was *trans* to phosphine *trans* to iodide in the product, **4b**. While both phosphine and CO loss from **4c** are possible in the first step, the data suggests CO loss is more likely since different intermediates to those shown in Scheme 1 are required to account for the dramatically different hydride exchange preferences seen in the two interconversion processes. This second reaction therefore most likely involves square pyramidal $Ir(H)_2(I)(CO)(PPh_3)$.



Scheme 1

Here, we have shown that *p*-H_2 derived spectral amplification can be used to examine the hydrogen addition chemistry of both $NBu_4[IrI_2(CO)_2]$ and $NBu_4[RhI_2(CO)_2]$. Products not previously observed have been characterised, and for the first time activation parameters have been determined for H_2 elimination from a *p*-H_2 enhanced product. Additionally, a new series of iridium dihydrides containing phosphine and carbonyl ligands have been characterised, and the intermediates, $IrH_2(I)(CO)_2$ and $Ir(H)_2(I)(CO)(PPh_3)$, involved in their formation shown to be square pyramidal.

Financial support from the EPSRC (Spectrometer and S.K.H.), BP Chemicals (CASE award S.K.H.), the Royal Society, NATO and Bruker UK, and discussions with Dr C. Sleigh, Professor R. Eisenberg, Profesor R. N. Perutz, Dr P. Dyson and Dr R. J. Mawby are gratefully acknowledged.

Notes and references

† *Selected spectroscopic data* in C_6D_6 at 295 K unless otherwise indicated with 400.13 MHz (^1H), 161.45 MHz (^{31}P) and 100.2 MHz (^{13}C). **3a**: ^1H δ −9.13 [H_a, *J*(HH) −4.4, *J*($H^{13}CO$) 58.4, 6.5 Hz], δ −13.30 [H_b, *J*(HH) −4.5, *J*($H^{13}CO$) 4.5 Hz], ^{13}C δ 167.2 (CO_a), 160.9 [CO_b, *J*(CC) 11.8 Hz]. **3b**: ^1H δ −15.40 [*J*($H^{13}CO$) 5.6 Hz}], ^{13}C δ 171.6 (CO). **3c**: ^1H δ −10.94 [*J*($H^{13}CO$) 2.9 Hz], ^{13}C δ 155.1 (CO). **4a**: ^1H δ 7.73 (*o*-phenyl H of P), −9.63 [H, *J*(PH) 17.0, *J*(^{13}COH) 44.9, 5.6, *J*(HH) −4.3 Hz], −14.12 [H, *J*(PH) 16.4, *J*(^{13}COH) 4.5, *J*(HH) −4.3 Hz], ^{31}P δ 0.2 (P, s), ^{13}C δ 164.3 [CO_a, *J*(PC) 118 Hz], 167.5 (CO_b). **4b**: ^1H δ −10.65 [H, *J*(PH) 115.6, *J*(^{13}COH) 4.0, *J*(HH) −4.7 Hz], −14.37 [H, *J*(PH) 8.8, *J*(^{13}COH) 4.0, *J*(HH) −4.7 Hz], ^{31}P δ −10.9 (P, s), ^{13}C δ 168.4 [CO, *J*(PC) 9 Hz]. **4c**: (T = 350 K) ^1H δ −9.62 [H, *J*(PH) 14.7, *J*(^{13}COH) 50.7, 3, *J*(HH) −3.5 Hz], −10.65 [H, *J*(PH) 151.1, *J*(HH) −3.5 Hz}, ^{31}P δ −16.3 (P, s), ^{13}C δ 164.3 [CO, *J*(PC) 118 Hz]. **4d**: (T = 350 K) ^1H δ −10.00 [H, *J*(PH) 17.1, *J*(^{13}COH) 45, 12 *J*(HH) −5.3 Hz], ^{31}P δ 3.7 (P, s), ^{13}C δ 166.1 [CO, *J*(PC) 18.8 Hz]. **5a** ^1H δ −8.13 [H, *J*(PH) 20.9, *J*(HH) −4.6 Hz], −16.45 [H, *J*(PH) 12.6, *J*(HH) −4.6 Hz], ^{31}P δ −18.1 (P, s). **5b** ^1H δ −10.20 [H, *J*(PH) 170.5, *J*(HH) −5.6 Hz], −14.80 [H, *J*(PH) 8.5, *J*(HH) −5.6 Hz], ^{31}P −14.5 (P, s). **5c** ^1H δ −9.89 [H, *J*(PH) 17.3, *J*(HH) −1.8 Hz], −10.60 [H, *J*(PH) 122.1, *J*(HH) −2.6 Hz], ^{31}P δ 3.00 (P, s). **6**: ^1H δ 8.02 (*o*-phenyl H of P), −8.49 {H, *J*(PH) 17.0, *J*(^{13}COH) 42.6, *J*(HH) −4.4 Hz], δ −14.95 [H, *J*(PH) 13.8, *J*(^{13}COH) 4, *J*(HH) −4.4 Hz], ^{31}P δ 6.1 (P, s), ^{13}C δ 175.4 [CO, *J*(PC) 8 Hz].

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 J. N. Atterer and J. Bargon. *Prog. Nucl. Magn. Reson. Spectrosc.*, 1997, **31**, 293.
4 C. J. Sleigh and S. B. Duckett. *Prog. Nucl. Magn. Reson. Spectrosc.*, 1999, **34**, 71.
5 S. B. Duckett, C. L. Newell and R. Eisenberg. *J. Am. Chem. Soc.*, 1994, **116**, 10548; S. B. Duckett and R. Eisenberg. *J. Am. Chem. Soc.*, 1993, **115**, 5292; S. B. Duckett, R. J. Mawby and M. G. Partridge. *Chem. Commun.*, 1996, 383; P. D. Morran, S. A. Colebrooke, S. B. Duckett, J. A. B. Lohmann and R. Eisenberg. *J. Chem. Soc., Dalton. Trans.*, 1998, 3363.
6 P. M. Maitlis, A. Haynes, G. J. Sunley and M. J. Howard, *J. Chem. Soc., Dalton Trans.*, 1996, 2187.
7 When ^{13}CO labelled **1** is used both these resonances are split into a triplet. The hydride resonance attributable to **3c** is observed when HI is added to **1**.

Communication 9/00961B