ChemComm

New products in an old reaction: isomeric products from H_2 addition to Vaska's complex and its analogues

Sarah K. Hasnip,[a] Simon B. Duckett,*[a] Christopher J. Sleigh,[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 Amoco Chemicals, BP Chemicals Limited, Salt End, Hull, UK HU12 8DS*

Received (in Cambridge, UK) 12th July 1999, Accepted 29th July 1999

***para*-Hydrogen enhanced NMR signals aid detection of minor isomers of complexes $IrH_2(L)_2(CO)Cl$ (L = PPh_3, PMe_3, PPh_2Cl and $AsPh_3$) containing magnetically inequivalent hydride ligands that are produced *via* addition across the L–Ir–L axis of $Ir(L)_2(CO)Cl$: in the case of L = PPh_3, reaction with CO and H_2 is shown to yield the substitution product $IrH_2(CO)_2(PPh_3)Cl$ which reacts further *via* HCl transfer to form $IrH(CO)(PPh_3)_2Cl_2$ and thereby enables the detection of $IrH_3(CO)_2(PPh_3)$.**

It has been shown that the addition of H_2 enriched in the *para* spin state to a transition metal centre leads to greatly enhanced hydride signals in associated ^{1}H NMR spectra.[1] This phenomenon is a powerful tool available to characterise minor reaction products such as *all-cis* $Ru(H)_2(CO)_2(PMe_3)_2$[2] and investigate hydrogenation kinetics.[3] The addition of H_2 to Vaska's complex,[4] *trans*-$Ir(CO)(PPh_3)_2Cl$ **1a**, and its analogues has been the subject of much investigation and it is currently accepted that, in general, addition proceeds exclusively over the OC–Ir–Cl axis. However, calculations by Sargent and Hall[5] revealed that H_2 addition over the OC–Ir–Cl axis rather than the P–Ir–P axis is favoured by 9.5 kJ mol^{-1} in the case of $Ir(CO)(PMe_3)_2Cl$. Furthermore, calculations indicate that increasing the π-accepting nature of the phosphine will favour H_2 addition across the P–Ir–P axis. Here, we describe studies that test this prediction by monitoring reactions of $Ir(L)_2(CO)Cl$ (L = PPh_3, PMe_3, PPh_2Cl and $AsPh_3$) with *para*-hydrogen (p-H_2).

It has already been shown that when a solution containing *cis,trans*-$IrH_2(CO)(PPh_3)_2Cl$ **2a** is examined by ^{1}H NMR spectroscopy the corresponding hydride resonances are polarised (**2a**, 0.1 mmol dm^{-3}, toluene-d$_8$, 343 K and 3 atm p-H_2).[6] Under these conditions, H_2 addition is reversible, and exchange leads to hydride signal enhancements that are 11 fold. At 298 K the hydride resonances of **2a** are unaffected by the presence of p-H_2 because exchange is suppressed. However, when the reaction of **1a** with p-H_2 is monitored by NMR spectroscopy, *in-situ*, the dihydride products are detected as they form and prior to spin population relaxation. In the corresponding ^{1}H spectrum polarised hydride resonances are detected for **2a**, and a second previously unreported species, as shown in Fig. 1(a). The enhanced resonance of this minor product is only visible when **1a** is reacting with p-H_2 and the associated signals decay away rapidly. Furthermore, the extra hydride resonance arises from a second order spin system with magnetically distinct hydrides.[6,7] The ^{31}P and ^{13}C chemical shifts and the multiplicities of the hydride, phosphine and carbonyl resonances of this product, located *via* a series of 2D NMR experiments, are consistent with their origin in *cis,cis*-$IrH_2(CO)(PPh_3)_2Cl$ **3a**. This product is formed by H_2 addition over the P–Ir–P axis of **1a**, as shown in Scheme 1.† At 295 K, the difference in hydride signal intensities of **2a** and **3a** was determined by the application of a pulse sequence involving a 90° ^{1}H pulse, a pulsed field gradient, a 100 ms delay, and a 45° ^{1}H read pulse. This procedure enables the instantaneous observation of the ratio of **2a** : **3a** by suppressing signals from pre-formed materials and suggests the ratio of **2a** to **3a** is ≈ 100 if similar enhancements are assumed for each species. There is no evidence to suggest that these two species interconvert on the NMR time scale.

In order to test the generality of this reaction pathway we repeated this procedure with $Ir(CO)(L)_2Cl$ [L = PMe_3 **1b**, Fig. 1(*b*) and L = $AsPh_3$ **1c**]. In both these cases dihydride products corresponding to addition over the Cl–Ir–CO and L–Ir–L axes of *trans*-$IrCl(L)_2(CO)$ are detected. The spectral features of the PMe_3 products **2b** and **3b** are similar to those of their PPh_3 analogues.† However, hydride resonances for both these species are visible at 333 K for extended periods. The failure to observe **3b** with normal hydrogen suggests that while both **2b** and **3b** are accessible by H_2 addition to **1b**, both are able to reductively eliminate H_2 at 333 K, otherwise **3b** would become a significant reaction product.

When the reaction with L = $AsPh_3$ is monitored with normal hydrogen, two isomers, *cis,trans*-$IrH_2(CO)(AsPh_3)_2Cl$ **2c** (with hydride resonances at δ −7.11 and −18.91) and *cis,cis*-$IrH_2(CO)(AsPh_3)_2Cl$ **3c** (hydride δ −9.62) are detected in the ratio 1 : 2.85, respectively, at 295 K.† After five days the ratio became 1 : 0.1, this suggests that addition over the As–Ir–As

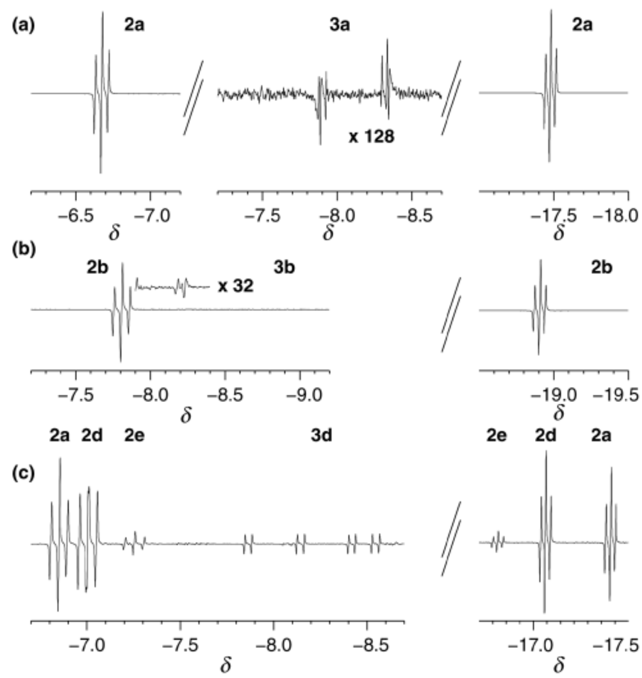
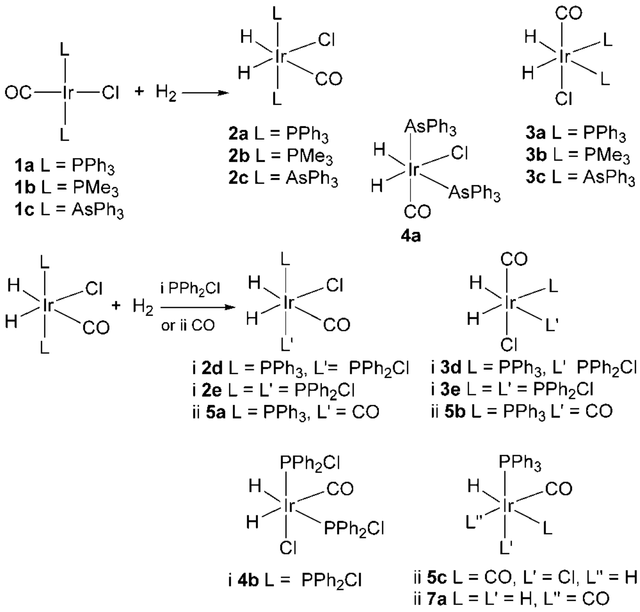


Fig. 1(a) ^{1}H NMR spectrum (400 MHz, 295 K) of a 0.1 mM solution of **1a** in benzene-d$_6$ under 3 atm of p-H_2. The weak second order resonance arises from *cis,cis*-$IrH_2(CO)(PPh_3)_2Cl$ **3a**. (b) ^{1}H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of **1b** in benzene-d$_6$ under 3 atm of p-H_2 with resonances due to **2b** and **3b** indicated. (c) ^{1}H NMR spectrum (400 MHz, 333 K) of a 0.1 mM solution of **2a** in benzene-d$_6$ in the presence of a four-fold excess of PPh_2Cl under 3 atm of p-H_2 showing resonances due to **2a**, **2d**, **2e** and **3d**.



Scheme 1 Species observed in the reactions of a series of chlorocarbonylbis(phosphine)iridium(I) and dihydridochlorocarbonylbis(phosphine)-iridium-(III) complexes under p-H_2.

axis is kinetically preferred while addition over the OC–Ir–Cl axis leads to the thermodynamic product. Product **2c** was characterised by 2D NMR methods at 333 K where the rate of H_2 exchange is fast and the p-H_2 signal enhancements are long-lived.† The structure of the *cis,cis* product **3c** was confirmed by ^{13}C labelling experiments, ^{1}H integral measurements, and the presence of two ν(IrH) modes at 2083 and 2115 cm^{-1} in the corresponding IR spectrum.

Interestingly, a third p-H_2 enhanced isomer, **4a**, was detected at 338 K in the ^{1}H NMR spectrum that was not previously visible [Fig. 1(c)]. The chemical shifts of the hydride resonances of this product, δ −11.70 and −18.50, suggest hydride locations *trans* to CO or arsine, and *trans* to chloride, respectively. NOE measurements revealed that the hydride ligand of **4a** which resonates at δ −11.70 is close in space to a single set of *ortho*-phenyl protons (δ 7.65) while that which is *trans* to chloride is adjacent to two different sets (δ 7.65 and 7.60). **4a** therefore contains two inequivalent arsine ligands. When a ^{13}CO labelled sample was examined, the δ −11.70 signal showed a small ^{1}H–^{13}CO coupling of 3.4 Hz indicating that the hydride is *trans* to arsine rather than CO. In the NOE experiment, no interconversion between **2c**, **3c** and **4a** was observed which suggests that the most probable route to formation of the minor isomer **4a** is H_2 addition over the OC–Ir–As axis of the *cis* isomer of Ir(CO)$(AsPh_3)_2$Cl (Scheme 1).

A sample containing a four-fold excess of PPh_2Cl relative to **2a** was examined to test the π-accepting role of the phosphine [Fig. 1(c)]. While this spectrum contains no resonances that can be assigned to trisphosphine species, signals corresponding to the hydride resonances of mono- and bis-phosphine exchange products (**2d**, **2e**, Scheme 1) containing *cis* hydrides and *trans* phosphines were readily assigned. Furthermore, resonances for the *cis,cis* isomers **3d** and **3e** were present in significantly higher proportions than those seen in the reaction with **1a** described above. Significantly, by virtue of the mixed phosphines, **3d** contains inequivalent hydride ligands which resonate at δ −8.13 and −8.34 with the resonances having doublet of doublet of doublet multiplicities consistent with *trans* and *cis* phosphine connections. This product is formed by H_2 addition across the P–Ir–P axis of Ir(CO)$(PPh_3)(PPh_2Cl)$Cl. Weak signals due to **4b** were also present.† Ultimately the signals of all these species disappear, and the major hydride resonances are associated with the bisphosphine carbonyl dichloride monohydride complexes **6a** and **6b**.[8] Complex **6a** is also observed in the reaction chemistry of **1a** when both CO and p-H_2 are present. Under these conditions, three isomers of $IrH_2(CO)_2(PPh_3)Cl$, **5a**, **5b** and **5c** and the *fac-trans* isomer of $IrH_3(CO)_2(PPh_3)$ **7a** are detected as p-H_2 enhanced products (Scheme 1).[9] These observations are consistent with HCl transfer from $IrH_2(CO)_2Cl(PPh_3)$ to **1a**, followed by H_2 addition to yield the dicarbonyl trihydride product.

Here we have demonstrated that H_2 addition to a series of iridium(I) carbonyl complexes based on Ir(CO)$(PPh_3)_2$Cl involves a minor reaction pathway where addition proceeds across the P–Ir–P axis. We also show that in the presence of mixtures of CO and H_2, $IrH_2(CO)(PPh_3)_2Cl$ and the phosphine substitution product $IrH_2(CO)_2Cl(L)$ are detected in addition to HCl transfer products and a series of trihydride complexes.

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

Notes and references

† *Selected spectroscopic data* at 400.13 MHz (^{1}H) and 161.45 MHz (^{31}P) and 100.2 MHz (^{13}C) in benzene-d_6 (couplings Hz): **2a**: ^{1}H, δ −6.64 {H, J(PH) 18.8, J(HH) −5.7}, −17.48 {H, J(PH) 13.7, J(HH) −5.7}; ^{31}P, δ 8.4. **2b**: ^{1}H, δ −7.80 {H, J(PH) 20.8, J(HH) −5.2}, −18.90 {H, J(PH) 14.7, J(HH) −5.2}, ^{31}P, δ −41.1; ^{13}C, δ 183.0 {CO}. **2c** (296 K): ^{1}H, δ −7.11 {H, J(COH) 44.5, J(HH) −5.0}, −18.91 {H, J(CH) 3.7, J(HH) −5.0}; ^{13}C, δ 177.2 {CO, s}. **2d** ^{1}H, δ −6.81 {H, J(PH) 14.4, J(PH) 14.7, J(HH) −4.7}, −16.99 {H, J(PH) 17.3, J(PH) 17.3, J(HH) −4.7}, ^{31}P, δ 9.0 {PPh_3, J(PP) 398.6}, 66.2 {PPh_2Cl, J(PP) 398.6}, ^{13}C, δ 176.3 {CO, J(PC) 7.9}. **2e** ^{1}H, δ −7.24 {H, J(PH) 20.3, J(COH) 44.0, J(HH) −5.0}, −16.73 {H, J(PH) 15.0, J (COH) 3.5, J(HH) −5.0}; ^{31}P, δ 65.1; ^{13}C, δ 174.8 {CO, J(PC) 7.9}. **3a** (295 K): ^{1}H, δ −8.10 {m, second order}; ^{31}P, δ −5.9; ^{13}C, δ 167.1 {CO}. **3b** (333 K): ^{1}H δ −8.15 {m, second order}; ^{31}P δ −7.98, ^{13}C, δ 173.37 {CO}. **3c** (296 K): ^{1}H, δ −9.62 {H, J(COH) 6.4}; ^{13}C δ 165.7 {CO, s}. **3d**: ^{1}H, δ −8.13 {H, J(PH) 222.4, J(PH) 15.0, J(HH) −1.8}, −8.34 {H, J(PH) 160.8, J(PH) 15.9, J(HH) −1.8}; ^{31}P, δ −4.0 {PPh_3, J(PP) 28.5}, 65.2 {PPh_2Cl, J(PP) 28.5}; ^{13}C, δ 165.3 {CO, J(PC) 6}. **3e**: ^{1}H, δ −8.37 {m, second order}; ^{31}P, δ 62.9. **4a** (338 K): ^{1}H, δ −11.70 {H, J(COH) 3.4, J(HH) −5.9}, −18.50 {H, J(CH) 4.7, J(HH) −5.9}; ^{13}C, δ 170.3 {CO, s}. **4b**: ^{1}H, δ −7.52 {H, J(PH) 16, J(PH) 23, J(CH) 48, J(HH) −2.9}, −9.50 {H, J(PH) 202.2, J(PH) 23.0, J(CH) 4.4, J(HH) −2.9}; ^{31}P, δ 65.3 {PPh_2Cl, br}; ^{13}C, δ 174 {CO}. **5a**: ^{1}H, δ −7.42 {H, J(PH) 14.5, J(COH) 56.9 and 7, J(HH) −7}, −8.37 {H, J(PH) 162.0, J(COH) 5, J(HH) −7}; ^{31}P, δ −5.7; ^{13}C, δ 169.8 {CO, J(PC) 8}, 161.7 {CO, J(PC) 123}. **5b**: ^{1}H, δ −7.97 {H, J(PH) 17.4, J(COH) 45.5 and 6, J(HH) −5}, −16.51 {H, J(PH) 16.0, J(COH) 2.8, J(HH) −5}; ^{31}P, δ 5.2 {J(PC) 123.4}; ^{13}C, δ 170.8 {CO, J(PC) 8}, 166.1 {CO, J(PC) 123}. **5c**: ^{1}H, δ −8.09 {H, J(PH) 18.8, J(COH) 57.2 and 6}. **6a** (333 K): ^{1}H, δ −14.60 {H, J(PH) 11.6, J(COH) 5.2}; ^{31}P, δ −2.9 {J(PC) 7.9}; ^{13}C, δ 163.2 {CO}. **6b**: ^{1}H, δ −14.22 {H, td, J(PH) 12.3, J(COH) 5.0}, ^{31}P, δ −3.0 {P, PPh_3, J(PP) 456}, 55.7 {P, PPh_2Cl, J(PP) 456}, ^{13}C, δ 162.3 {CO}. **7a**: ^{1}H, δ −8.8 {H, J(PH) 136.9, J(HH) 2.7}, −9.7 {H, J(PH) 121.6, J(HH) −2.4}: δ_p 43.2.

1 C. R. Bowers and D. P. Weitekamp, *J. Am. Chem. Soc.*, 1987, **109**, 5541; R. Eisenberg, *Acc. Chem. Res.*, 1991, **24**, 110; J. Natterer and J. Bargon, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1997, **31**, 293; C. J. Sleigh and S. B. Duckett. *Prog. Nucl. Magn. Reson. Spectrosc.*, 1999, **34**, 71.

2 S. B. Duckett, C. L. Newell and R. Eisenberg, *J. Am. Chem. Soc*., 1994, **116**, 10 548; S. B. Duckett and R. Eisenberg, *ibid*., 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.

3 P. Hubler, R. Giernoth, G. Kummerle and J. Bargon, *J. Am. Chem. Soc*., 1999, **121**, 5311.

4 L. Vaska and M. F. Wernke, *Trans. N. Y. Acad. Sci*., 1971, **33**, 80; P. B. Chock and J. Halpern, *J. Am. Chem. Soc*., 1966, **88**, 3511; R. Ugo, A. Pasini and S. Cenini, *ibid*., 1972, **94**, 7364.

5 A. L. Sargent and M. B. Hall, *Inorg. Chem*., 1992, **31**, 317.

6 B. A. Messerle, C. J. Sleigh, M. G. Partridge and S. B. Duckett, *J. Chem. Soc., Dalton Trans.*, 1999, 1429. C. J. Sleigh, S. B. Duckett, and B. A. Messerle, *Chem. Commun.*, 1996, 2395; S. B. Duckett, C. L. Newell and R. Eisenberg, *J. Am. Chem. Soc*., 1993, **115**, 1156.

7 S. B. Duckett, G. K. Barlow, M. G. Partridge and B. A. Messerle, *J. Chem. Soc., Dalton Trans*., 1995, 3427.

8 R. A. Vanderpool and H. B. Abrahamson, *Inorg. Chem*., 1985, **24**, 2985.

9 S. K. Hasnip, S. B. Duckett, D. R. Taylor and M. J. Taylor, *Chem. Commun*., 1998, 923.

Communication 9/05590H