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Addition of H_2 to a cationic iridium(I) complex: a study using parahydrogen NMR

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Parahydrogen enhanced NMR signals are used to monitor the reaction between the cationic iridium(I) complex $[Ir(BPM)(CO)_2][BPh_4]$ (BPM = bis(pyrazol-1-yl)methane) and dihydrogen: four major products are formed in a cascade of reactions.

While the nuclear magnetic resonance (NMR) experiment is intrinsically insensitive, the sensitivity of the experiment can be significantly enhanced by creating a non-Boltzman population state. Parahydrogen (p-H_2) provides a viable route to achieve this aim in hydrogen addition reactions where the addition step occurs in a concerted fashion.[1,2] Consequently, large enhancements of NMR signal intensity have been observed in both hydrogenation products and transition metal dihydrides.[1,3] Notable successes of this approach include the detection of intermediates in catalytic hydrogenation reactions, such as $RhH_2Cl(PPh_3)_2(alkene)$, species in minor reaction pathways, such as $RhH_2(PPh_3)_2(\mu\text{-}Cl)_2Rh(PPh_3)(CO)$, and minor constituents in equilibria, such as all-*cis*-$[RuH_2(PMe_3)_2(CO)_2]$.[4] It is now well established that sp^2 N-donor ligands can be useful alternatives to phosphines in a number of catalytic systems.[5] We have observed the reaction of H_2 with iridium(I) complexes containing N-donor ligands, and the hydrogenation of alkene substrates.[6] Here we describe the reaction between the cationic iridium(I) complex $[Ir(BPM)(CO)_2][BPh_4]$[6] and p-H_2, where BPM is the bidentate sp^2 N-donor ligand bis(pyrazol-1-yl)methane.

When a solution containing $[Ir(BPM)(CO)_2][BPh_4]$ **1** (0.1 mM, tetrahydrofuran-d_8) was charged with 3 atm p-H_2 in a sealable 5 mm NMR tube, and examined by ^1H NMR spectroscopy at 323 K over a period of 2 h, a series of products containing metal–hydride ligands were observed as a consequence of the signal enhancement available through p-H_2 (Fig. 1). Isotopic labelling and two-dimensional NMR methods were used to identify these species.

The first formed, kinetically preferred, reaction product was the iridium(III) product formed by direct H_2 addition over one of the CO–Ir–N axes: all-*cis*-$[Ir(H)_2(BPM)(CO)_2]^+$ **2** (Scheme 1). The two inequivalent metal–hydrides, H_a and H_b, of **2** are mutually coupled ($J = 4$ Hz) and resonate at δ −7.80 and δ −16.13, which indicates that H_a is *trans* to a CO and H_b is *trans* to the N-donor. These assignments were confirmed using the ^{15}N- and ^{13}C-labelled analogues of **1**, $[Ir(^{15}N\text{-}BPM)(^{13}CO)_2][BPh_4]$, **1-^{15}N,^{13}C**, and $[Ir(BPM)(^{13}CO)_2][BPh_4]$, **1-^{13}C**.[6] Thus, in the case of **2-^{13}CO**, the resonance for H_a contains additional large and small couplings to ^{13}C of 61 and 8 Hz corresponding to *trans* and *cis* CO orientations. The signal for H_b shows two additional small couplings of 6 and 8 Hz due to *cis* CO's. On using **1-^{15}N,^{13}C** an additional 24 Hz coupling was observed to H_b, indicating an ^{15}N nucleus *trans* to H_b. The fact that no resolved *cis* ^{15}N–^1H couplings were observed suggests that they are too small to be easily detected.[8]

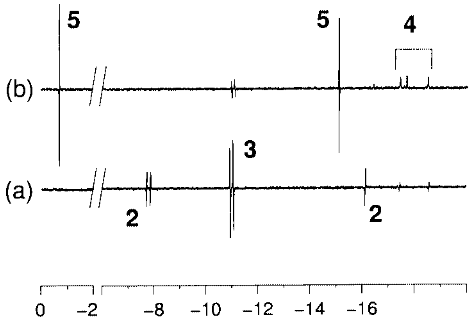
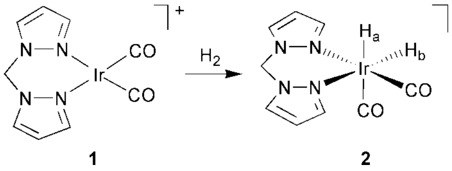


Fig. 1 ^1H NMR spectra collected with a $\pi/4$ pulse, showing parahydrogen enhanced hydride resonances for $[Ir(BPM)(^{13}CO)_2]^+$, **1-^{13}C**: (a) 2 min after addition of p-H_2, and (b) 30 min after addition of p-H_2. Typically, 1 mg samples were prepared in tetrahydrofuran-d_8 in a sealed NMR tube, which was filled with 3 atm parahydrogen.[7]



Scheme 1

When using **1-^{13}C** or **1-^{15}N,^{13}C** as the starting material a new, previously unobserved, reaction product (**3**) was detected in addition to **2** (Fig. 1). The new product **3** exhibits a single resonance due to two metal-bound hydrides at δ −11.01, which appears as an antiphase multiplet (J_{HH} of 3 Hz, and J_{CH} of 48 Hz and 8 Hz). Although the hydrides of **3** are chemically equivalent, magnetic inequivalence in the form of an AA′XX′ spin system allowed their observation,[4,9] and consequently the 2D heteronuclear correlation NMR experiment (^{13}C-^1H HMQC[7]) reveals a single ^{13}C resonance at δ 182.0. No significant hydride coupling to ^{15}N was observed with **1-^{13}C,^{15}N** as the starting material, indicating that the ^{15}N nuclei are *cis* to the metal bound hydrides in **3**.[8] There are two *trans* positions to be filled, which cannot be occupied by a single pyrazolyl ligand, so **3** is most likely to be binuclear with bridging pyrazolyl ligands. In view of the fact that these reaction products represent minor species in solution, **3** is most consistently formulated as the binuclear complex shown in Scheme 2.

The lability of the BPM ligand in species such as **3** was confirmed by ^1H NMR observations of free exchange between **1** and free ligand (in the absence of H_2). In addition, when a solution of **1-^{13}C,** and free BPM, was placed under an atmosphere of p-H_2, an additional product was observed with a hydride resonance centred on δ –9.83 which was similar in profile to that of **3**. The logical identity of this species is a mononuclear complex, with *cis* hydrides, *cis* carbonyls, and two mutually *trans* η^1 BPM ligands.

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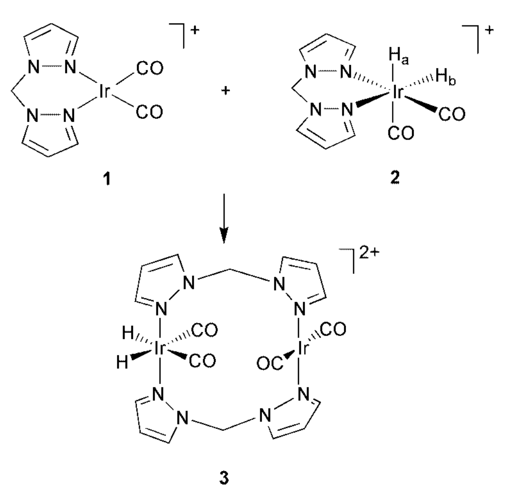
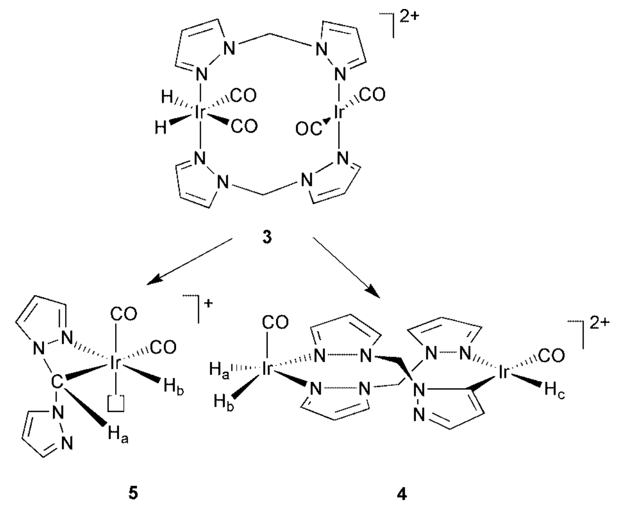


Scheme 2

Species **3** could therefore be formed by direct H_2 addition to $[Ir_2(CO)_4(\kappa^1 N\text{-BPM})_2]^+$ or *via* a more complex process that relies on labilisation of the N-donor that is *trans* to the hydride in **2** and subsequent attack on unreacted **1**.[10]

After 30 min at 323 K, the p-H_2 enhanced signals for **2** and **3** were dramatically reduced in size and two new products, **4** and **5** were observed (Fig. 1(b), Scheme 3). Significantly, when this reaction was repeated with normal hydrogen the only detectable product was **4**. Complex **4** contains three hydride ligands with resonances at δ −17.40 (H_a), −17.66 (H_c) and −18.48 (H_b) respectively. H_a and H_b are coupled to each other (J_{HH} of 7 Hz) and show p-H_2 enhancement for only a short time indicating limited exchange with free H_2. NOESY and COSY experiments confirm that H_a and H_b are bound to the same metal centre and their high field shift suggests that they are *trans* to hard ligands. With normal hydrogen, the resonances due to H_a and H_b grow at the same rate as that of H_c, which indicates that all three hydrides arise from the same product. When **1-^{13}C,^{15}N** was employed, the resonances due to H_a and H_b both showed additional splittings due to one *cis*-carbonyl ligand (J_{CH} of 8 Hz). The hydride resonances also showed scalar coupling to two *trans*-^{15}N donors (J_{NH} of 25 Hz). This is consistent with the observation of two ^{15}N resonances, coupled to H_a and H_b, at δ 226.8 and δ 236.8 (Fig. 2). Under these conditions, the resonance due to H_c detected with normal hydrogen showed additional splittings due to ^{13}C (J_{CH} of 8 Hz, single *cis* carbonyl resonating at δ 160.0) and ^{15}N (J_{NH} of 23 Hz, *trans* donor resonating at δ 227.2 (Fig. 2)). Two additional long range ^{15}N couplings ($J_{NH} \approx 2$ Hz) account for the complex multiplicity of the H_c resonance shown in Fig. 2 (1D projection). These data are consistent with the structure for **4** shown in Scheme 3, where the monohydride H_c is formed by loss of CO from each of the Ir centres and rearrangement of the iridium(I) centre of **3** by insertion into a pyrazolyl C–H bond of a bridging BPM ligand. The reactivity of C–H bonds of this type has previously been studied by Heinekey *et al.* through studies of the cyclometallation of iridium tris(pyrazol-1-yl)methane and tris(pyrazol-1-yl)borate complexes.[11]



Scheme 3

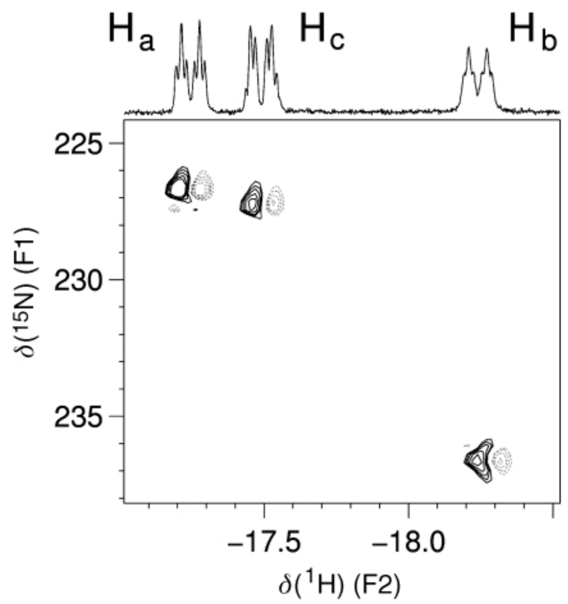


Fig. 2 Heteronuclear correlation ^{15}N–^{1}H HSQC[13] for complex **4-^{15}N,^{13}C** (fixed delay set for J_{NH} = 25 Hz, 12,830 Hz and 6000 Hz spectral widths in ω_2 and ω_1 respectively, and 4.5 h acquisition). ^{15}N was externally referenced to liquid ammonia.[14]

The second set of coupled hydride resonances (J_{HH} of 3 Hz) due to complex **5** (Scheme 3), appear at unusual chemical shifts at δ −0.68 (H_a) and −15.05 (H_b). The hydrides of **5** must exchange freely with free p-H_2, in contrast to those of **4**, since these signals remain visible for up to 2 h at 323 K. The resonance due to H_b showed additional small couplings to ^{13}C nuclei when **1-^{13}C,^{15}N** was used as the starting material, however, neither were large enough to be due to a *trans* arrangement of carbonyl and hydride. Surprisingly, H_a also showed no resolvable couplings to labelled donor atoms. The chemical shift of H_a (δ −0.68) indicates it is most probably bound to a metal-bound carbon, while H_b is a metal-bound hydride in a geometry *trans* to a hard ligand. The mononuclear structure of **5** shown in Scheme 3 most readily tallies with our experimental observations. Compound **5** could be derived from either **1** or **3** by the oxidative insertion of an iridium(I) centre into a C–H bond of the BPM ligand's methylene backbone with subsequent elimination/rearrangement. The extended period of enhancement of H_a and H_b NMR signals under p-H_2 can only come about by concerted exchange of these protons with free p-H_2. This exchange could occur by elimination of H_2 from **5** to form an iridium carbene intermediate which then adds free p-H_2 in a concerted fashion. Such a process has its precedent in the exchange between a hydride and proton attached to a metal-bound carbon, *via* a carbene intermediate, in cyclometallated rhodium(III) complexes studied by Crocker *et al.*[12]

Acknowledgements

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References

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

2 J. Natterer and J. Bargon, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1997, **31**, 293.
3 S. B. Duckett, C. L. Newell and R. Eisenberg, *J. Am. Chem. Soc.*, 1993, **115**, 1156; S. B. Duckett, R. Eisenberg and A. S. Goldman, *J. Chem. Soc., Chem. Commun.*, 1990, 511; J. Barkemeyer, M. Haake and J. Bargon, *J. Am. Chem. Soc.*, 1995, **117**, 2927.
4 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.
5 A. Togni and C. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 497 and references therein.
6 L. P. Soler, PhD Thesis, University of Sydney, 1999.
7 B. A. Messerle, C. J. Sleigh, M. G. Partridge and S. B. Duckett, *J. Chem. Soc., Dalton Trans.*, 1999, 1429.
8 G. Otting, L. P. Soler and B. A. Messerle, *J. Magn. Reson.*, 1999, **137**, 413; G. Otting, B. A. Messerle and L. P. Soler, *J. Am. Chem. Soc.*, 1997, **119**, 5425.
9 J. Barkemeyer, M. Haake and J. Bargon, *J. Am. Chem. Soc.*, 1995, **117**, 2927.
10 P. D. Morran, S. B. Duckett, P. R. Howe, J. E. McGrady, S. A. Colebrooke, R. Eisenberg, M. G. Partridge and J. A. B. Lohman, *J. Chem. Soc., Dalton Trans.*, 1999, 3949.
11 D. M. Heinekey, W. J. Oldham, Jr. and J. S. Wiley, *J. Am. Chem. Soc.*, 1996, **118**, 12842.
12 C. Crocker, R. J. Errington, W. S. McDonald, K. J. Odell, B. L. Shaw and R. J. Goodfellow, *J. Chem. Soc., Chem. Commun.*, 1979, 498.
13 G. Bodenhausen and D. J. Ruben, *Chem. Phys. Lett.*, 1980, **69**, 185; G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, 1979, **101**, 760.
14 D. S. Wishart, C. G. Bigam, J. Yao, F. Abildgaard, H. J. Dyson, E. Oldfield, J. L. Markley and B. D. Sykes, *J. Biomol. NMR*, 1995, **6**, 135.