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

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Received 18th May 2000, Accepted 16th June 2000
Published on the Web 30th June 2000

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 ^{1}H 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-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–^{1}H couplings were observed suggests that they are too small to be easily detected.[8]

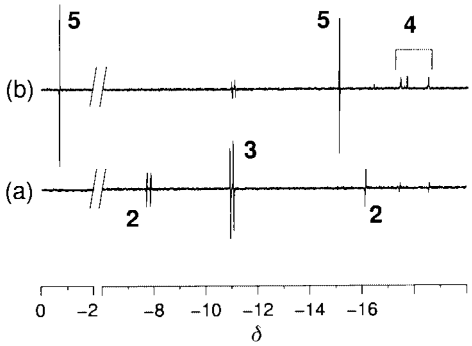
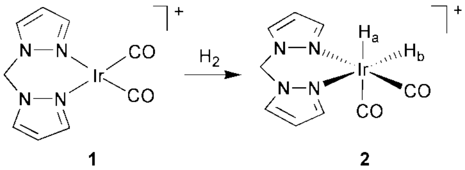


Fig. 1 ^{1}H NMR spectra collected with a $\pi/4$ pulse, showing parahydrogen enhanced hydride resonances for [Ir(BPM)(^{13}CO)$_2$]$^+$, **1-^{13}C**: (a) 2 min after addition of p-H_2, and (b) 30 min after addition of p-H_2. Typically, 1 mg samples were prepared in tetrahydrofuran-d$_8$ in a sealed NMR tube, which was filled with 3 atm parahydrogen.[7]

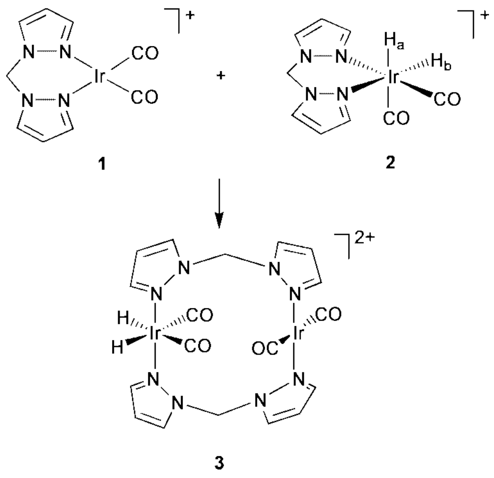


Scheme 1

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-^{1}H 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 ^{1}H 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.

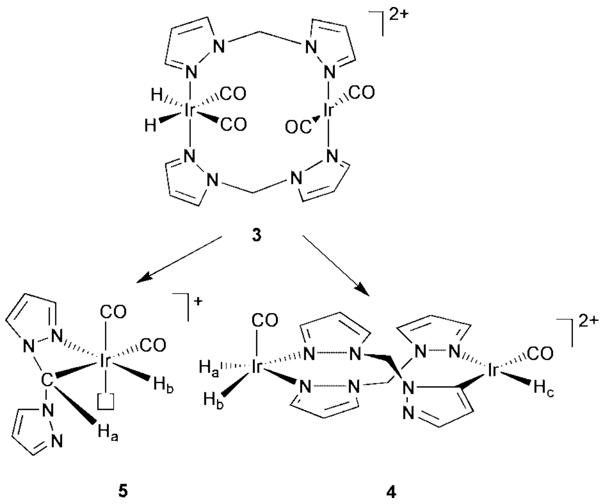
DOI: 10.1039/b003987j



Scheme 2

Species **3** could therefore be formed by direct H_2 addition to $[Ir_2(CO)_4(\kappa^1N\text{-}BPM)_2]^+$ 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

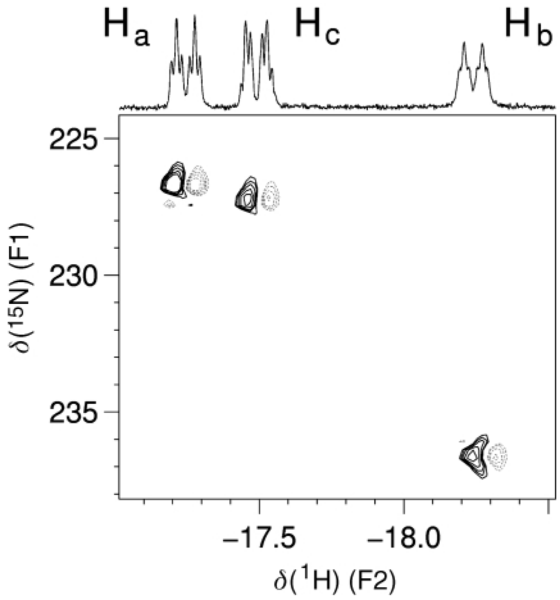


Fig. 2 Heteronuclear correlation ^{15}N–^{1}H HSQC[13] for complex **4-^{15}N,^{13}C** (fixed delay set for J_{NH} = 25 Hz, 12,830 Hz and 6000 Hz spectral widths in ω_2 and ω_1 respectively, and 4.5 h acquisition). ^{15}N was externally referenced to liquid ammonia.[14]

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

Financial support from the Australian Research Council (ARC), Australian Commonwealth Government (Australian Postgraduate Award for W. J. S.), and the University of Sydney (Gritton Award for L. P. S.) are gratefully acknowledged.

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