

Metal–Ligand Cooperation in C–H and H₂ Activation by an Electron-Rich PNP Ir(I) System: Facile Ligand Dearomatization–Aromatization as Key Steps

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Bond activation by metal complexes, in which both the metal center and the ligand play active, synergistic roles, can provide new opportunities in organometallic chemistry and catalysis.¹ An example is the Ru(II)-catalyzed hydrogenation of unsaturated polar bonds, in which H₂ activation involves both the metal center and a polar (N- or O-based) ligand, followed by a concerted transfer of acidic and hydridic hydrogens to an unsaturated substrate.¹ Here we report on a (PNP)Ir(I) (PNP = 2,6-bis-(di-*tert*-butylphosphino)methyl)pyridine) system in which the PNP ligand and the metal act in concert in H₂ and C–H activation via dearomatization/aromatization processes of the ligand. Moreover, our work raises the question whether a seemingly simple H₂ oxidative addition to Ir(I) might actually involve H₂ activation by an Ir(III) intermediate.

Upon reaction of our previously reported electron-rich cationic Ir(I) complex **1**² with ^tBuOK in THF at room temperature, a rapid color change from pink-red to violet-red was observed with formation of the novel dearomatized complex **2** (Scheme 1).

The ³¹P NMR spectrum of **2** exhibits an AB quartet centered at 33 ppm, indicating nonequivalent phosphorus atoms. Signals at 5.4, 6.35, and 6.43 ppm in the ¹H NMR spectrum, corresponding to three protons, indicate dearomatization of the pyridine ring. An X-ray crystallographic study of complex **2** shows unambiguously that the pyridine ring underwent dearomatization. Thus, the C(1)–C(2) bond (1.35 Å) is much shorter than C(6)–C(7) (1.505 Å) (Scheme 1). Such dearomatization following deprotonation of the benzylic protons is known³ and was shown by us to be involved in Ru-catalyzed dehydrogenation of alcohols to form esters^{3a} and in hydrogenation of esters.^{3b}

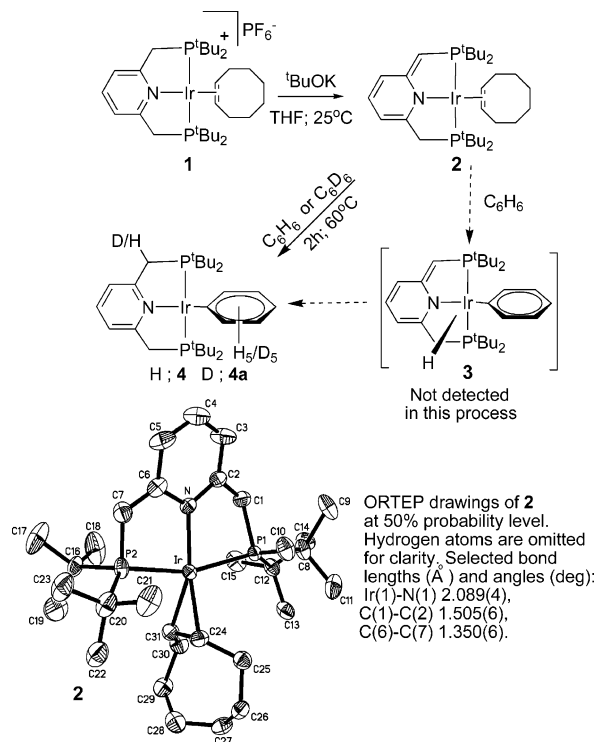
When a benzene solution of complex (PNP*)Ir(I) **2** (PNP* = dearomatized PNP) was mildly heated at 60 °C for 2 h, quantitative C–H activation to form the complex (PNP)Ir(I)(C₆H₆), **4** (with no overall change in oxidation state), took place (Scheme 1).

The ³¹P NMR spectrum of **4** exhibits a singlet at 55 ppm, indicating C_{2v} symmetry. The benzylic protons give rise to one signal at 2.8 ppm in the ¹H NMR spectrum, implying rearomatization of the PNP ligand. The X-ray structure of **4** (Figure 1) reveals that the iridium atom is located in the center of a slightly distorted square-planar geometry, with the phenyl group located *trans* to the pyridine ring, perpendicular to the PNP plane.

Upon reaction of complex **2** with C₆D₆, deuterium incorporation into a benzylic group of complex **4a** was observed (Scheme 1), the ¹H NMR spectrum revealing only three benzylic protons.⁴ While no intermediates were directly observed in the C–H activation process, indirect evidence suggests that intermediacy of the Ir(III) complex **3** is a viable possibility.

Thus, deprotonation of the cationic complex [(PNP)Ir(H)(C₆H₅)]-PF₆, **5**,² in THF at –78 °C with ^tBuOK resulted in formation of the neutral Ir(III) complex **3**.⁵ Reaction follow-up at –50 °C by

Scheme 1



NMR showed that **3** was quantitatively converted to **4** after 10 h (Scheme 2). No intermediates were observed. When the isotopomer complex **5a** was reacted with ^tBuOK at –78 °C, an Ir–D signal was observed at –47 ppm in the ²H NMR spectrum, and no hydride was observed, indicating that no direct Ir–D deprotonation took place. Moreover, upon warming **3a** to room temperature, complex **4** incorporating a D-labeled benzyl “arm” was formed, as a result

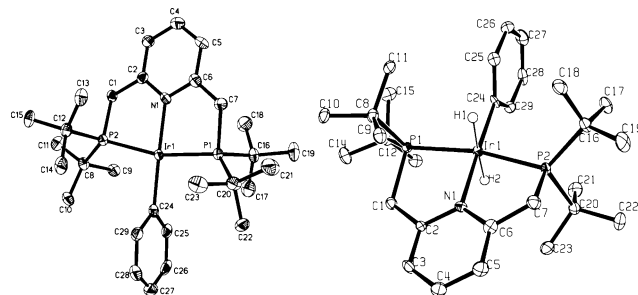
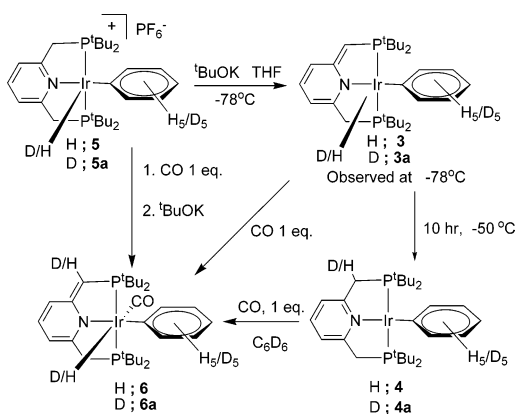


Figure 1. ORTEP drawings of **4** (left) and **7** at 50% probability level. Hydrogen atoms (except hydrides) are omitted for clarity. Selected bond lengths (Å): **4**: Ir(1)–N(1) 2.087(4), Ir(1)–C(24) 2.057(5), Ir(1)–P(1) 2.272(2), Ir(1)–P(2) 2.267(2). **7**: Ir(1)–N(1) 2.119(4), Ir(1)–C(24) 2.075(4), Ir(1)–H(1) 1.64(5), Ir(1)–H(2) 1.73(6), Ir(1)–P(1) 2.287(1), Ir(1)–P(2) 2.287(1).

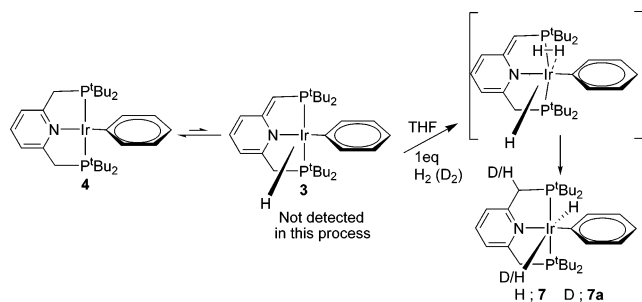
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Scheme 2



Scheme 3



of migration of the deuteride ligand from the metal to the “arm”. These observations support the intermediacy of **3** in the C–H activation of benzene by the neutral Ir(I) complex **2**.⁶

Surprisingly, when the Ir(I) phenyl complex **4** was reacted with one equivalent of CO in benzene at 25°C , oxidation of the metal center took place, quantitatively forming the Ir(III) phenyl hydride complex **6**. Complex **6** was synthesized independently by deprotonation of [(PNP)Ir(C_6H_6)(H)(CO)]PF₆² (Scheme 2). This process might take place by reversible proton migration from the benzylic position to the metal center, followed by trapping of the neutral phenyl hydride complex **3** by CO.⁷ Indeed, complex **6** was formed upon reaction of **3** with CO at -78°C . Complex **6** was thermally stable (up to 80°C) in solution and did not eliminate benzene, similar to its cationic aromatic analogue.²

Remarkably, upon reaction of complex **4** with 1 equiv of H_2 at 25°C in benzene (Scheme 3), only the *trans*-dihydride complex (PNP)Ir(H)₂(C_6H_5), **7**, was observed. The two equivalent hydride ligands give rise to a triplet at -8.3 ppm in the ¹H NMR spectrum, indicative of a *trans*-dihydride arrangement. There is no evidence for the formation of the *cis*-dihydride complex.⁸ While *cis*-to-*trans* isomerizations of octahedral Ir dihydrides are known,⁹ the barrier is high,^{9b} and the process requires heating.^{9a} Thus, **7** is likely to be the kinetic product. X-ray structure analysis of **7** (Figure 1) shows a slightly distorted octahedral geometry with the *trans*-dihydride ligands perpendicular to the PNP plane.

Significantly, reaction of the Ir(I) complex **4** with D_2 under the same conditions did not yield the Ir dideuteride. Rather, the Ir(H)(D) complex **7a** was obtained, with incorporation of one deuterium atom into the benzylic “arm”. This indicates the involvement of the benzylic carbons in the activation of H_2 . It might be suggested that complex **3** is present in solution in low concentration in equilibrium with **4** and is responsible for the unusual reactivity with H_2 .¹⁰ Indeed, complex **3** reacts with H_2 even at low temperature

(-78°C) to give complex **7**. Coordination of H_2 to complex **3** followed by its deprotonation by the amide nitrogen¹¹ or directly by the ligand “arm” may lead to formation of complex **7** (Scheme 3). Intriguingly, regardless of the exact mechanism, our evidence raises the possibility of activation of H_2 by Ir(III) in an overall apparent oxidative addition of H_2 to Ir(I).

In conclusion, a number of unusual reactions are reported, in which the PNP ligand takes an active role in the activation of H_2 and benzene, via facile aromatization/dearomatization processes of the ligand. The new, dearomatized electron-rich PNP-based Ir(I) complex **2** activates benzene to form an Ir(I)–Ph complex, which upon treatment with CO undergoes a surprising oxidation process to form the Ir(III) complex **6**, involving proton migration from the ligand “arm” to the metal, with concomitant dearomatization. Another interesting transformation of **4** is the stereoselective activation of molecular hydrogen to exclusively form the *trans*-dihydride **7**. Our evidence, including D-labeling, suggests that the 16e Ir(I) complex **4** may be transformed to the (independently prepared) 16e Ir(III) **3** which could be the actual complex undergoing H_2 activation. Further experimental and theoretical investigations on this system are in progress.

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Supporting Information Available: Experimental procedures and characterization of complexes **1–7**, and X-ray data for **2**, **4** and **7** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The protons were integrated with a time delay of 20 s, calibrated to the pyridinic aromatic protons.
- The dearomatized pyridine protons of **3** give rise to three signals in the ¹H NMR spectrum: one characteristic signal at 5.67 ppm as a broad doublet and two multiplets at 6.45–6.85 ppm. The Ir–H appears at -47 ppm. For detailed assignments see Supporting Information.
- Migration of the hydride ligand might be either intra- or intermolecular. Experimental and theoretical studies of the mechanism are in progress.
- While CO coordination to Ir(I) followed by proton migration to the metal cannot be excluded at this stage, we think that it is less likely because of the lower electron density at the Ir(CO) center. The mechanism of this process is being studied.
- Preliminary DFT calculations showed that the *cis*-isomer is more stable than the *trans*-isomer and should have been observed had it been formed.
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- However, no NMR evidence for an equilibrium involving **3** was obtained upon cooling solutions of **4** to -80°C .
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