

Halobenzenes and Ir(I): Kinetic C–H Oxidative Addition and Thermodynamic C–Hal Oxidative Addition

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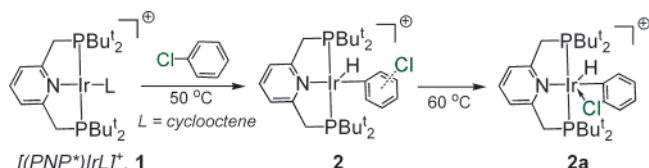
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Haloarenes are among the most commonly used organic substrates. Their involvement in transition-metal-catalyzed processes often entails oxidative addition (OA) reactions.¹ In this context, the metal has a choice of one or more different C–H bonds and a C–Hal bond (Hal = halide). An important question is why some metal centers prefer C–Hal bonds while others prefer C–H bonds. OA of aromatic C–Cl, C–Br, and C–I bonds has been studied almost exclusively in the context of the chemistry of zero-valent group 10 metals (especially Pd).^{2,3} OA of aromatic C–F received more attention for group 9 metals.⁴ Aromatic C–H OA reactions are much more common across the periodic table, particularly for d⁸ metal centers.^{1,5} Selective C–H activation in the presence of aromatic C–Cl or C–Br bonds has been reported in some Pd, Ir, and Au systems.⁶

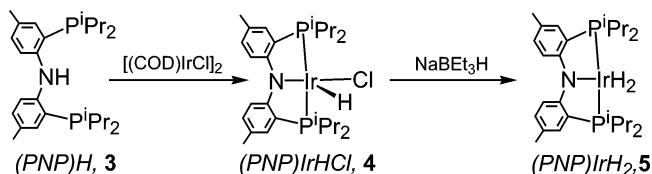
Recent work by Milstein et al. described the activation of only C–H bonds in halobenzenes via OA to the cationic (PNP*)Ir^I fragment (Scheme 1).^{6d} Mild thermolysis of the mixture of isomers of **2** (and their Br analogues) gave isomerization to the thermodynamically most stable haloaryl/hydride product **2a**.^{6d} In the present work, we show that, in a closely related Ir system, all C–H OA products are kinetic, and the global minimum for an OA reaction is the product of the C–Hal OA.

Scheme 1



We recently reported the preparation of **4** and other work exploring the group 9 chemistry of the anionic PNP pincer ligands.⁷ The dihydride **5** can be easily synthesized from **4** (Scheme 2). We were generally interested in the OA reactivity of the (PNP)Ir^I fragment, especially in the context of the (PCP)Ir chemistry⁸ and the work with (PNP*)Ir^I.^{6d}

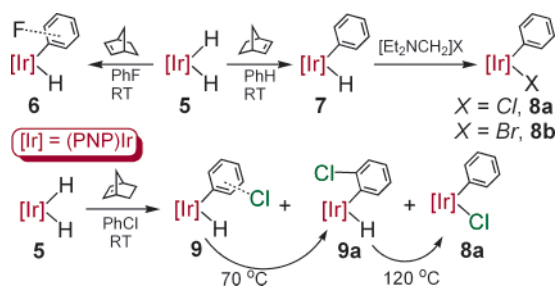
Scheme 2



On the basis of the (PCP)Ir methodology by Goldman et al.,^{8b} we opted to use norbornene (NBE) to strip the hydrides from the Ir center in **5**. The reaction of **5** with NBE in C₆H₆ cleanly produced

7 (Scheme 3). When PhF was used as solvent, a mixture of four isomers of **6** was produced (four new ¹⁹F NMR resonances and four hydridic ¹H NMR resonances observed).⁹ Upon thermolysis (100 °C, 20 h), this mixture evolves into a mixture of only two isomers. No products arising from OA of C–F were observed.

Scheme 3



The reaction between **5** and NBE in PhCl produced a mixture of four C–H OA products (**9**)⁹ along with a small (5%) fraction of the C–Cl OA product **8a** (Scheme 3). Thermolysis of this mixture at 70 °C led to slow isomerization of the other isomers of **9** into **9a** (71% after 72 h) without change in the fraction of **8a** present. **9a** was isolated in 44% yield by recrystallization. Thermolysis of **9a** (or of the mixture in Scheme 3) at >100 °C for 24–48 h led to the >80% isomerization to the C–Cl OA product **8a**. Thermolysis of isolated, pure **9a** does not lead to the formation of other isomers of **9**, consistent with **9a** being the lowest energy C–H OA isomer. The reaction of **5** with NBE in PhBr at 22 °C produced a mixture of two isomers of (PNP)Ir(H)(C₆H₄Br) (**10**) and (PNP)Ir(Ph)(Br) (**8b**). Upon thermolysis at 100 °C, the isomers of **10** slowly evolved into **8b** (80% after 48 h). **8a** and **8b** were synthesized independently from **7** (Scheme 3). No isomerization of **8a** or **8b** was detected after thermolysis of pure samples at 120 °C in C₆D₆. **8a** and **8b** are thus global OA minima in the [(PNP)Ir + PhHal] systems.

The structure of **8b** was elucidated by an X-ray diffraction study (Figure 1). The geometry about Ir in **8b** is approximately square

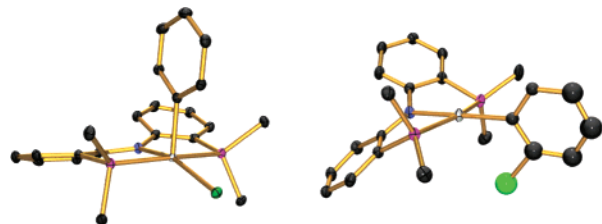


Figure 1. POV-Ray rendered ORTEP plots of **8b** (left) and **9a** (right), 50% thermal ellipsoids.¹³ H atoms and CH₃ groups are omitted for clarity.

pyramidal. The P–Ir–P angle is 167.14(3)°, typical for PNP complexes,⁷ and the N–Ir–Br angle is 162.57(7)°. Square pyramidal geometry is expected for five-coordinate d⁶ compounds with

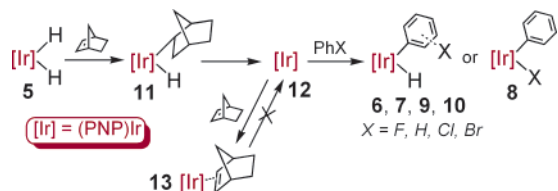
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only one distinctly strong trans-influence ligand (Ph here).¹⁰ The C₆H₅ ring is “sandwiched” between the two PPr₂ groups. The rotation about the Ir–C axis in solution is inhibited as evidenced by the observation of five inequivalent ¹H NMR resonances for the C₆H₅ group in **8a** or **8b**.

We propose, by analogy with the (PCP)Ir systems, that the OA reactions proceed via a 14-electron (PNP)Ir species **12** (Scheme 4).¹¹ It is thought to arise from **11** via C–H reductive elimination. Notably, **13** is not an intermediate in these reactions. **13** can be prepared independently and does not react with halobenzenes at 22 °C. Neither does **5** react with haloarenes. **12** can also be accessed by dehydrohalogenation of **4**.^{8a} Treatment of **4** with KOBu^t in C₆H₆ or C₆H₅Cl leads to the same products as from **5** and NBE.¹²

Scheme 4



The structure of **9a** (Figure 1) can be described as square pyramidal with the hydride ligand occupying the apical site. The orientation of the aryl ligand in the crystal of **9a** is disordered by a 180° rotation of the chlorophenyl ring (Cl above or below the PNP–Ir plane) and the presumed concomitant disorder of the hydride. The hydride ligand was not located in the XRD study. Its presence is unambiguously inferred from the characteristic ¹H NMR resonance in solution (δ –40.3 ppm). The *ortho*-Cl is oriented appropriately for additional Cl → Ir donation, but the Ir–Cl distance is quite long (2.96 or 3.00 Å). This is ca. 0.2 Å longer than the Ir–Cl distance in **2a**. It is likely that the positive charge and the inability of the PNP* ligand to stabilize unsaturation via π -donation in **2a** translate into higher Lewis acidity for the Ir center in **2a** compared with **9a**. In solution NMR spectra, the hydrides of **2a** and **6a** resonate at δ –33 and –40.3 ppm, respectively. In square pyramidal five-coordinate Ir^{III} compounds, hydrides trans to an empty site resonate at ca. –45 ppm.^{6d,7,8} A downfield shift is reflective of coordination of a sixth ligand trans to H as is the case in **2a** but much more weakly (if at all) in **6a**. It is tempting to stipulate that the preference for **9a** (or **2a**) among the C–H OA products arises from the stabilizing Ir–Cl interaction. However, given that this interaction is at best very weak in **9a**, it is also possible that *o*-ClC₆H₄ simply forms the strongest σ -Ir–C bond among the isomeric ClC₆H₄ ligands.^{8b}

In summary, we report that, for PhCl/PhBr and (PNP)Ir^I, the product of C–Hal OA is thermodynamically preferred over the products of C–H OA but is separated by a high activation barrier and is only kinetically accessible at >100 °C. The intramolecular isomerization among the C–H OA isomers proceeds at 60–70 °C, well below the temperature required for detectable isomerization to the C–Hal OA product. Among the C–H OA isomers, the one with the *ortho*-halophenyl ligand is of the lowest energy. We anticipate that a similar energetic picture may apply to a number of other transition metal systems capable of OA reactions. Although related findings have been reported for fluoroarenes,¹⁴ this is the first such demonstration for the more synthetically relevant heavier haloarenes.

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Supporting Information Available: Experimental details, crystallographic information in the form of the CIF files, characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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