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

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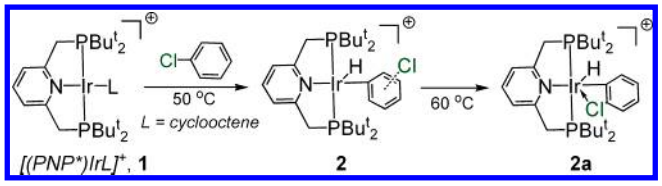
Haloarenes are among the most commonly used organic substrates. Their involvement in transition-metal-catalyzed processes often entails oxidative addition (OA) reactions.[1] In this context, the metal has a choice of one or more different C−H bonds and a C−Hal bond (Hal = halide). An important question 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 d^8 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]

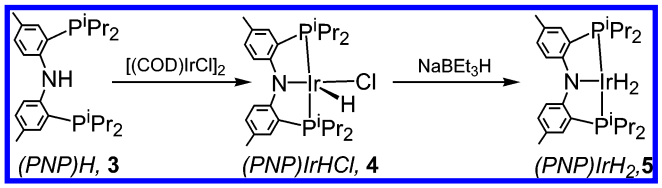
Recent work by Milstein et al. described the activation of only C−H bonds in halobenzenes via OA to the cationic (PNP*)Ir[I] fragment (Scheme 1).[6d] Mild thermolysis of the mixture of isomers of **2** (and their Br analogues) gave isomerization to the thermodynamically most stable haloaryl/hydride product **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



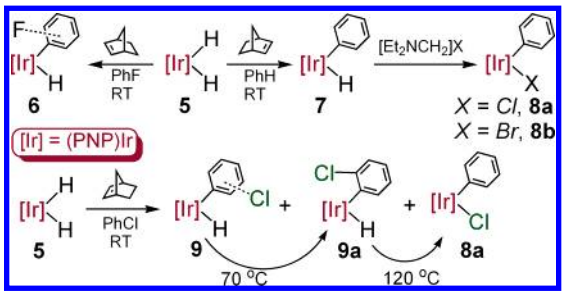
We recently reported the preparation of **4** and other work exploring the group 9 chemistry of the anionic PNP pincer ligands.[7] The dihydride **5** can be easily synthesized from **4** (Scheme 2). We were generally interested in the OA reactivity of the (PNP)Ir[I] fragment, especially in the context of the (PCP)Ir chemistry[8] 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 C_6H_6 cleanly produced **7** (Scheme 3). When PhF was used as solvent, a mixture of four isomers of **6** was produced (four new ^{19}F NMR resonances and four hydridic ^{1}H 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)(C_6H_4Br) (**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 C_6D_6. **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

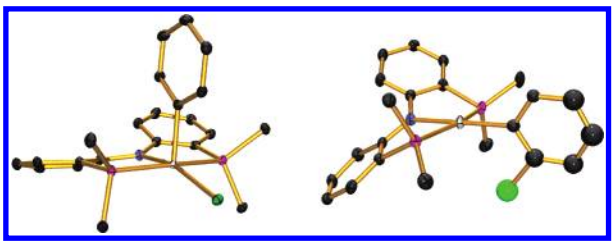


Figure 1. POV−Ray rendered ORTEP plots of **8b** (left) and **9a** (right), 50% thermal ellipsoids.[13] H atoms and CH_3 groups are omitted for clarity.

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 d^6 compounds with

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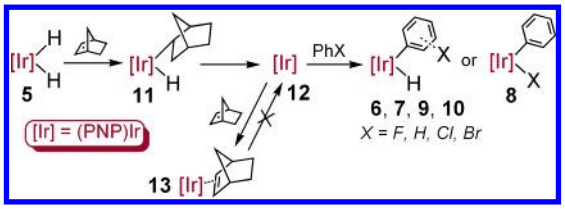
only one distinctly strong trans-influence ligand (Ph here).[10] The C_6H_5 ring is "sandwiched" between the two PPr^i_2 groups. The rotation about the Ir−C axis in solution is inhibited as evidenced by the observation of five inequivalent ^{1}H NMR resonances for the C_6H_5 group in **8a** or **8b**.

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 C_6H_6 or C_6H_5Cl 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 ^{1}H 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*-ClC_6H_4 simply forms the strongest σ-Ir−C bond among the isomeric ClC_6H_4 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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