

Carbon–Halide Oxidative Addition and Carbon–Carbon Reductive Elimination at a (PNP)Rh Center

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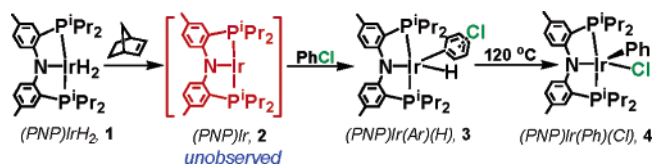
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Involvement of haloarenes in transition-metal-catalyzed processes often entails oxidative addition (OA) reactions.¹ In this context, it is of interest to discern the tendencies of transition metals to activate either a C–halogen or a C–H bond of haloarene. Oxidative addition of aromatic carbon–halogen bonds has been studied almost exclusively in the context of the chemistry of group 10 metals (especially Pd).^{2,3} Recently, several examples appeared where Rh catalysts enable C–C coupling of aryl halides, the reactivity that is typically achieved with Pd⁰ catalysts.⁴ These new Rh-catalyzed processes probably involve aromatic carbon–halide OA and C–C reductive elimination (RE). In the context of group 9 metals, the requisite aromatic carbon–halide OA reactions (for heavier halides)⁵ and C–C RE reactions remain largely unexplored.^{6–8} Here we present a system where the reactions of OA of unactivated aryl halides (including Ar–Cl) to Rh^I and of C–C RE from Rh^{III} are well-defined, easily studied, and occur at ambient conditions.

We have recently reported on the reactions of the (PNP)Ir^I fragment with haloarenes.⁹ In that case, C–H OA was favored kinetically, whereas the C–Cl (or C–Br) OA was preferred thermodynamically (Scheme 1). Both types of products were observed, and the C–H activation products were stable at ≤70 °C.

Scheme 1

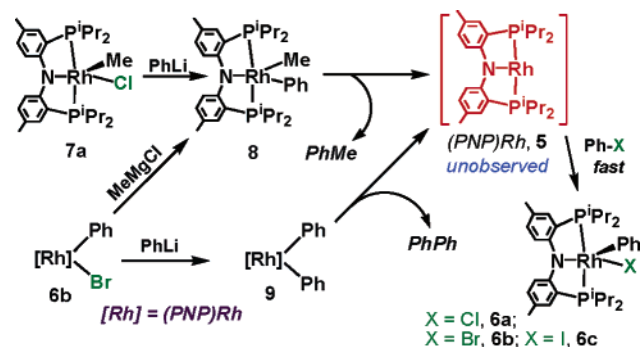


Here we disclose that an analogous rhodium fragment (PNP)Rh^I (**5**) reacts with haloarenes to produce exclusively C–X (in this paper, X = Cl, Br, I) OA products.

The (PNP)Ir^I fragment was accessed in situ via C–H RE. We reasoned that the Rh analogue **5** can be accessed via RE, as well. C–C reductive elimination¹⁰ serves well in this regard.

Addition of PhLi or PhMgBr to (PNP)Rh(Me)(Cl) (**7a**) in the presence of Ph–X (Scheme 2) cleanly produces (PNP)Rh(Ph)(X) (**6a–c**) in <24 h at 22 °C (Scheme 2).¹¹ Compound **8** is observed as an intermediate, formed upon mixing. Addition of MeMgCl to **6b** in the presence of PhX also results in the formation of **8** and subsequently, in the presence of PhX, **6a–c**. Addition of PhLi to **6b** rapidly produces (PNP)Rh(Ph)₂ (**9**) which evolves biphenyl and, in the presence of PhX, into **6a–c**. Owing to the instability of **8** and **9**, they were only characterized in situ. The resonances arising from the Rh–CH₃ moiety in **8** are particularly characteristic (¹³C NMR: δ 3.3 (dt, J_{C–Rh} = 33 Hz, J_{C–P} = 6 Hz); ¹H NMR: δ 1.95 (ddt, J_{H–C} = 160 Hz, J_{H–Rh} = 6 Hz, J_{H–P} = 3 Hz)). **9** is C_{2v}-symmetric (¹H NMR); the chemical shift of its ³¹P NMR resonance (δ 36.8 ppm) and the J_{Rh–P} (116 Hz) are near identical to those of **8**.

Scheme 2



Addition of MeMgCl to **7a** in the presence of PhX cleanly and rapidly produces **6a–c**, as well (Scheme 2). Although concomitant ethane formation was observed, (PNP)Rh(Me)₂ was not detected.

The kinetics of the C–C elimination from **8** and **9** in the presence of PhBr was investigated by ³¹P NMR.^{12–14} Both reactions followed clean first-order kinetics. The rate of elimination of Ph–Ph (*t*_{1/2} = 7 min at 40 °C) was greater than that of the elimination of Ph–Me (*t*_{1/2} = 17 min at 40 °C) (Figure 1). The rate of both reactions was independent of the concentration of PhBr (0.06–0.63 M). These results are consistent with rate-limiting C–C elimination that generates **5** (or its kinetic equivalent) followed by rapid C–X oxidative addition to **5**.

Both **8** and **9** are presumably five-coordinate d⁶ complexes. C–C RE from d⁶ Pt^{IV} complexes has been studied in detail and shown to proceed exclusively via *five-coordinate* Pt^{IV} intermediates.¹³

The structure of **6b** was determined in a solid-state X-ray diffraction study (Figure 2). The solid-state structural data for **6b** and the NMR solution data for **6a–c** are very similar to that of (PNP)Ir(Ph)(Cl), including the slow rotation about the M–C bond on the NMR time scale (five ¹H NMR resonances for Ph).

Compounds **10–12** were prepared analogously to **6a–c** from the corresponding aryl halides (Scheme 3) to assist in elucidating certain aspects of the presented reactivity. **10** was chosen for the

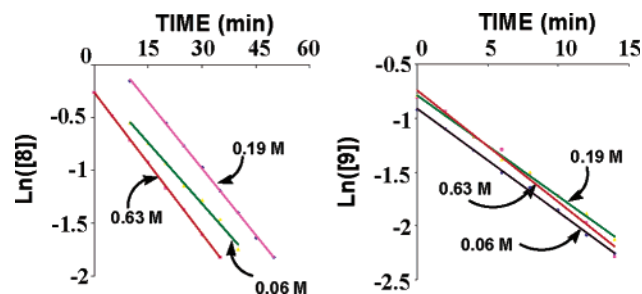


Figure 1. Plots illustrating the first-order reductive elimination of Ph–Me from **8** and of Ph–Ph from **9** at different concentrations of PhBr (shown).

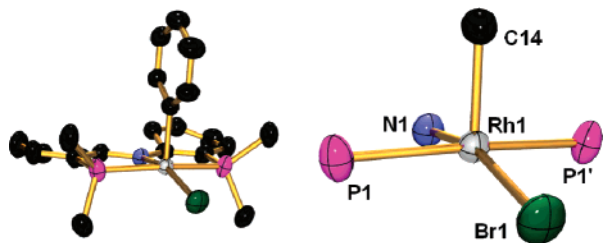
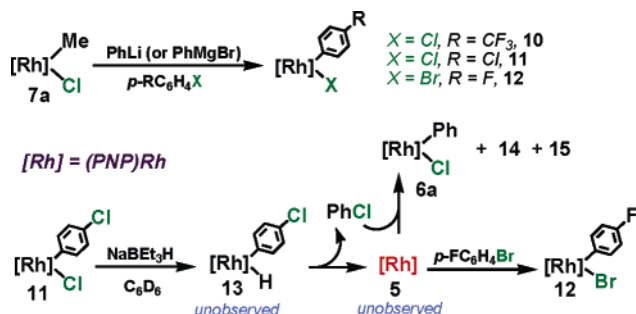


Figure 2. Rendered ORTEP drawing of the solid-state structure of **6b** (thermal ellipsoids set at 50% probability).¹⁵ On the left, all Me groups, all H atoms, the benzene solvent molecule are omitted, disorder not shown for clarity. On the right, the coordination environment about Rh is shown.

Scheme 3



experiments used to quantify the formation of organic C–C coupling products. Addition of PhLi or MeMgCl to a purified sample of **10** resulted (after 24 h at 22 °C) in a high-yield formation of *p*-PhC₆H₄CF₃ (93 ± 5%) and *p*-MeC₆H₄CF₃ (95 ± 5%), respectively, as measured by ¹⁹F NMR.

In sharp contrast to the (PNP)Ir chemistry, we did not observe any products arising from the C–H OA of haloarenes. If the C–C elimination was performed in the absence of PhX, the Rh fragment was found ostensibly to attack the ethereal solvent (from the solution of organolithium or Grignard reagents). In the presence of Et₂O, the major product was (PNP)Rh(η²-C₂H₄) (**14**).

Addition of 1 equiv of NaBEt₃H to **11** in C₆D₆ produced a mixture of **6a**, (PNP)RhH₂ (**15**), and **14** after 10 min at 22 °C (Scheme 3).¹⁶ It appears reasonable to assume that the short-lived (not observed) **13** is formed initially but then undergoes conversion to **6a**. **13** is the C–H OA isomer of **6a**. Although this experiment does not establish whether C–H OA occurs in the reactions of **5** with haloarenes, the isomerization of **13** to **6a** indicates that the C–Cl OA product (**6a**) in the Rh system is thermodynamically preferred just as it was in the Ir system. If the same reaction is performed in the presence of *p*-FC₆H₄Br, the dominant product (93%) is **12** (balance **15**). Since **6a** does not react with *p*-FC₆H₄Br, the isomerization of **13** to **6a** evidently does not proceed intramolecularly but via loss of free PhCl.

In summary, we report a Rh system where the fundamental steps of aryl halide coupling reactions, C–X OA and C–C RE reactions, can be observed at ambient conditions. We also show that in reactions of haloarenes with (PNP)Rh the C–X OA is thermodynamically preferred to the C–H OA. This finding echoes our previous report on (PNP)Ir chemistry, where C–X OA was thermodynamically preferred, as well.⁹ For Ir (5d metal), the C–H OA products were long-lived and the C–X OA accessible only at >100 °C, while in the presently reported Rh (4d metal) system, the C–X OA occurs at ambient temperature and the C–H OA products are too short-lived to be observed. Moreover, we earlier found similar trends (long-lived C–H OA products for Ir, thermodynamic preference for C–N OA)¹⁷ in the intramolecular C–N versus C–H OA chemistry with Rh and Ir.¹⁸ The combined

observations augur that in this PNP system at ambient temperature catalytic processes (a) that involve C–H OA in haloarenes are more likely to be successful with Ir than Rh, and (b) that involve C–X OA are more likely to be successful with Rh than Ir. An intriguing question is whether our findings reflect a broader trend of the behavior of 4d versus 5d metals in C–H versus C–X OA.

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Supporting Information Available: Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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