Borylation of Simple Arenes Enabled by π-Coordination

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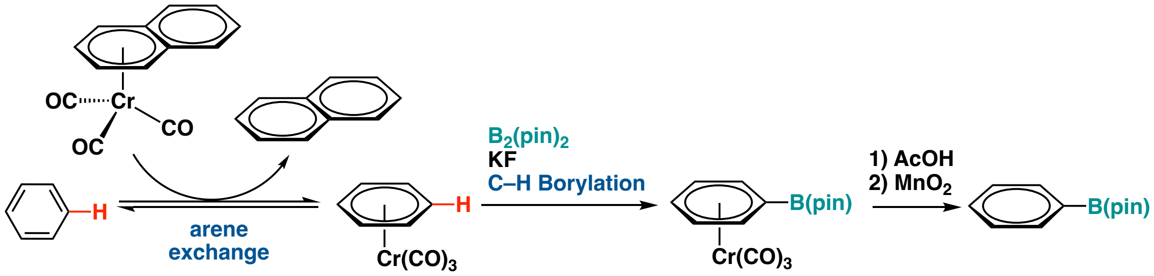
The direct C–H functionalization of simple arenes is a significant challenge in organic synthesis due to the need for strongly coordinating functional groups or electronic bias. To address this challenge, we developed a π-coordination strategy using tricarbonylchromium η^6-arene complexes ([Cr(η^6-arene)(CO)$_3$]) to activate arenes for C–H functionalization.[1] The [Cr(CO)$_3$] fragment decreases electron density on the arene, thus enhancing its reactivity. For example, Larrosa demonstrated the C–H arylation of chromium arene complexes under palladium/silver catalysis, but the synthesis and isolation of the starting complexes was required.[2]

As part of our efforts to utilize p-coordination for organic synthesis,[3] we describe here a method for borylating electron-rich arenes using bis(pinacolato)diboron (B$_2$(pin)$_2$) and a base (K$_2$CO$_3$ or KF), yielding borylated products after oxidative removal of chromium. The reaction proceeds without a transition-metal catalyst, albeit a catalytic amount of Cr(acac)$_3$ slightly improved the yield. π-Coordination was essential, as uncomplexed arenes showed no reactivity. Simple arenes can also undergo borylation via a tricarbonylchromium complex precursor ([Cr(η^6-NP)(CO)$_3$]), which generates the arene complex in situ through arene exchange (**Scheme 1**).

Mechanistic studies suggested an anionic pathway, where a nucleophilic borate species attacks the π-coordinated arene. This transition-metal-free strategy provides an atom economical approach for functionalizing simple arenes, expanding the scope of C–H borylation reactions.



Scheme 1. Borylation of simple arenes via exchange with a chromium complex precursor.

1) Williams, L. J.; Bhonoah, Y.; Wilkinson, L. A.; Walton, J. W. *Chem.—Eur. J.* **2020**, *27*, 3650–3660.
2) (a) Ricci, P.; Krämer, K.; Cambeiro, X. C.; Larossa, I. *J. Am. Chem. Soc.* **2013**, *135*, 13258–13261.
(b) Ricci, P.; Krämer, K.; Larrosa, I. *J. Am. Chem. Soc.* **2014**, *136*, 18082–18086.
3) Nagata, M.; Itonaga, K.; Mutoh, Y.; Endo, K.; Ilies, L. *Chem Lett.* **2024**, *53*, upae233.