Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

iridium

hydrogenation

pyridinium salts

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Asymmetric Cross-Coupling of Aryl Triflates to the Benzylic Position of Benzylamines
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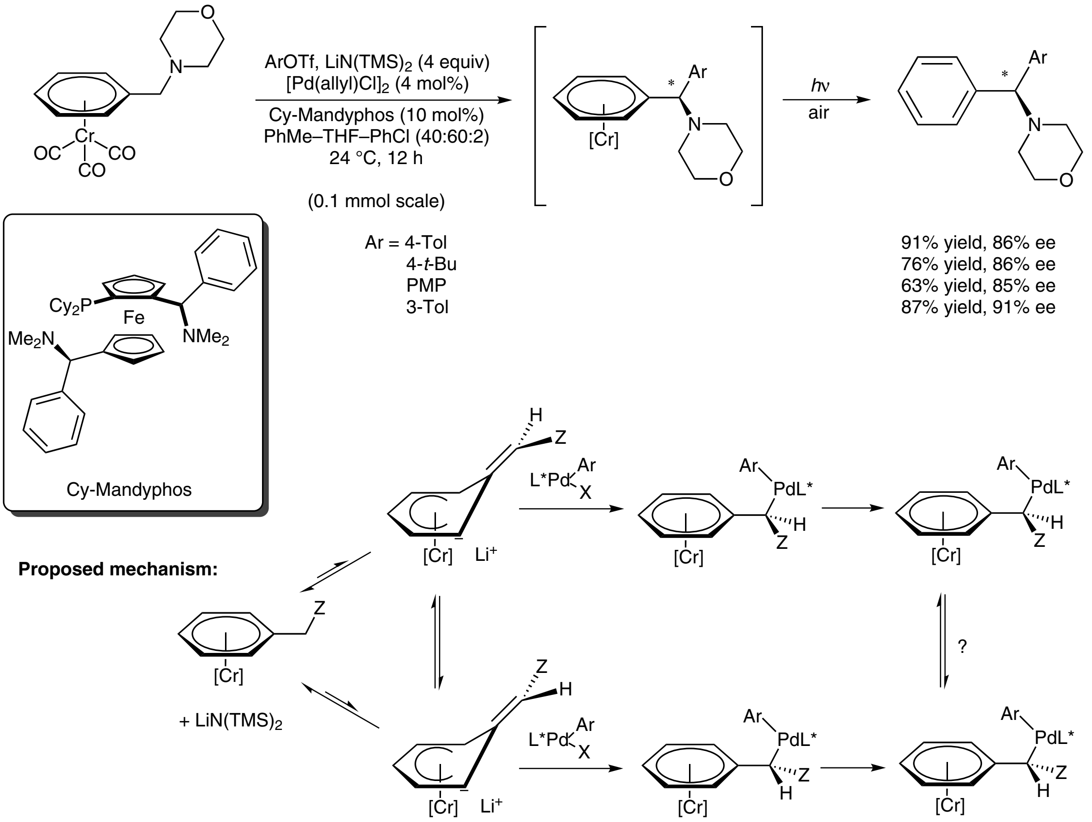
Palladium-Catalyzed Direct Arylation of Chromium-Activated Benzylic C–H Groups



Significance: The authors previously described the application of (η^6-$C_6H_5CH_2R$)$Cr(CO)_3$ complexes as nucleophile precursors in Pd-catalyzed allylic substitution reactions (*J. Am. Chem. Soc.* **2011**, *133*, 20552). They now report the first catalytic asymmetric cross-coupling of benzyllithiums α to tertiary amines using [$Cr(CO)_3$] activation of benzylic C–H bonds. The stabilized organolithium undergoes Pd-catalyzed coupling with aryl triflates by dynamic kinetic resolution to yield enantioenriched Cr-coordinated diarylmethylamines in good to high yield, which can be de-complexed by exposure to sunlight and air.

Comment: Development of an enantioselective version of the previously reported transformation is challenging as it requires the enantioenriched palldium catalyst to select for one of the chromium adducts faster than the other, and also requires the products to be impervious to racemization. High-throughput screening identified the chiral ligand Cy-Mandyphos, and that the addition of PMDETA and toluene as co-solvents increased the yield. The authors report future plans to close the catalytic cycle by focusing on an arene exchange between the chromium-complexed product and the free arene to liberate the product and regenerate the substrate.

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