

Mechanistic Studies of Ni-Catalyzed Electrochemical Homo-Coupling

Reactions of Aryl Halides

Jian Luo,^a Michael T. Davenport,^b Arianna Carter,^b Daniel H. Ess,^{*b} and T. Leo Liu^{*a}

a. Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322

b. Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84604

Corresponding: dhe@chem.byu.edu, leo.liu@usu.edu

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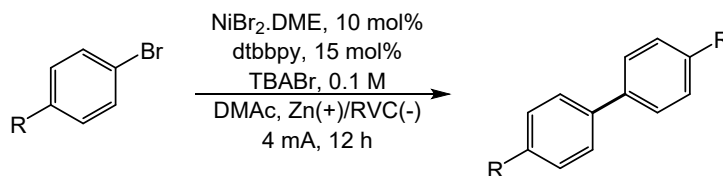
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1. Materials

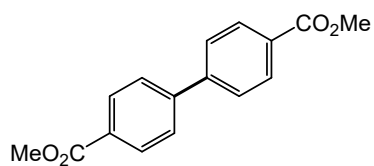
All solvents and reagents were purchased from commercial sources (Sigma Aldrich, TCI Chemicals, and Oakwood Chemical), unless otherwise noted, used without further purification. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ measurements were performed on a Bruker FT-NMR spectrometer (500 MHz). Mass spectra (MS) were collected on a 2020 Shimadzu LC-MS with an APCI ion source. UV-Vis spectra were collected using an Agilent Cary 100 UV-Vis spectrometer. The standard reaction mixture was diluted for 5 times with DMAc for UV-Vis tests of Ni^{II} species and diluted for 50 times for the UV-Vis tests of Ni^{I} intermediate. Electrochemical measurements were performed on a Gamry Instruments 1000 electrochemical workstation. The electrochemical catalytic reactions were investigated using the Chronopotentiometry (CP) method by a Gamry Instruments 5000 electrochemical workstation or a Land battery testing system. Thin-layer chromatography (TLC) was conducted to monitor the reactions. All compounds were purified by flash column chromatography with silica gel.

2. General Procedure

2.1 Ni-catalyzed electrochemical homo-coupling of aryl bromide



In an Ar filled glovebox, a reaction vial was charged with aryl bromide (0.5 mmol, 1.0 eq.), $\text{NiBr}_2 \cdot \text{DME}$ (16 mg, 50 μmol , 10 mol%), dtbbpy ligand (21 mg, 74 μmol , 15 mol%), TBABr (161 mg, 0.1 M), DMAc (5 mL). A homemade Zn metal electrode was used as an anode, and a RVC electrode was used as a cathode. The reaction was performed at room temperature with a constant current of 4.0 mA for 12 h. The reaction was monitored with TLC. After the reaction was done, the electrodes were washed with EtOAc (2×5 mL) in an ultrasonic bath, and the washing solution was combined with the reaction mixture. The reaction mixture was diluted with EtOAc, washed with a saturated NaCl solution, and dried over MgSO_4 . Upon filtration, the organic layer was concentrated under reduced pressure and purified by flash column chromatography (silica gel) to afford the desired product.

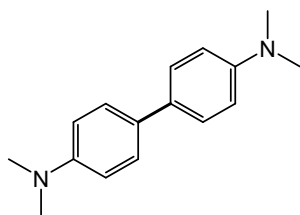


Dimethyl 4,4'-biphenyldicarboxylate

The titled compound was synthesized following the general procedure using methyl 4-bromobenzoate (108 mg) as substrate. The titled compound was obtained as a white solid, 62 mg (92% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 3.97 (s, 6H), 7.72 (d, $J = 5.0$ Hz, 4H), 8.16 (d, $J = 5.0$ Hz, 4H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 52.23, 127.25, 129.70, 130.20, 144.36, 166.80.

APCI-MS m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}_4^+$ ($[\text{M}]^+$) 270.09, found: 270.00.



$\text{N}^4, \text{N}^4, \text{N}^{4'}, \text{N}^{4'}$ -tetramethyl-[1,1'-biphenyl]-4,4'-diamine

The titled compound was synthesized following the general procedure using 4-bromo-N, N-dimethylaniline (100 mg) as substrate, 30 mol% dmobpy as ligand, and 152 mg DBU as the additive. The titled compound was obtained as a colorless oil, 48 mg (81% yield).

^1H NMR (CDCl_3 , 500 MHz, ppm): δ 2.97 (s, 12H), 6.80 (d, $J = 8.5$ Hz, 4H), 7.45 (d, $J = 8.5$ Hz, 6H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 40.97, 113.24, 127.14, 130.01, 149.44.

APCI-MS m/z calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2^+$ ($[\text{M}]^+$) 240.16, found: 240.05.

2.2 Preparation of the $\text{Ni}^{\text{I}}(\text{dtbbpy})\text{Br}$ species

$\text{Ni}^{\text{I}}(\text{dtbbpy})\text{Br}$ intermediate was synthesized by following the literature.¹ $\text{NiBr}_2 \cdot \text{glyme}$ (16 mg, 50 μmol), dtbbpy ligand (14 mg, 50 μmol), and TBABr (161 mg, 1.0 mmol) were mixed in DMAc (5 mL). Control potential electrolysis (50 mV overpotential, 1 hour) or consistent current electrolysis (2.5 mA for 48 min) were conducted using Zn rod as anode and Ni foam as cathode, at room temperature. The resulting dark green solution of $\text{Ni}^{\text{I}}(\text{dtbbpy})\text{Br}$ was used immediately for spectroscopic and reaction studies.

2.3 Synthesis of the Ni^{II}(dtbbpy)(C₆H₄CO₂Me)Br intermediate

The Ni^{II}(dtbbpy)(C₆H₄CO₂Me)Br intermediate was synthesized by following the literature.^{2,3} Ni(COD)₂ (138 mg, 0.5 mmol), dtbbpy ligand (134 mg, 0.5 mmol) were mixed in dry THF (5 mL) under Ar atmosphere. After stirring at room temperature for 12 hours, 1.62 g methyl 4-bromobenzoate was added to the mixture and reacted for another 4 hours. When the reaction is finished, 40 mL pentane was added to the reaction mixture. The Ni^{II}(dtbbpy)(Ar)Br intermediate was obtained as a red precipitate and collected through filtration, 119 mg (44% yield, red powder). The product was stored under Ar atmosphere at -20 °C.

2.4 Electrochemical Measurements

CV measurements were performed on a Gamry Instruments 1000 electrochemical workstation using a three-electrode cell, in which a glassy carbon electrode (GC) was used as a working electrode, a carbon rod as a counter electrode, and an Ag/Ag⁺ electrode as a reference electrode, ferrocenium-ferrocene (Fc⁺⁰) as an internal standard. All potentials were referenced to the internal standard Fc⁺⁰. Before the CV testing, the working electrode was polished using Al₂O₃ (BAS CF-1050) suspended in deionized H₂O, then rinsed with deionized H₂O and dried with airflow. The reference electrode consisted of a silver wire suspended in a solution of 0.2 M KPF₆ and 0.01 M AgNO₃ in dry DMAc.

CV conditions: Aryl halide (0.5 mmol, 1.0 eq.), NiBr₂.DME (16 mg, 50 μmol, 10 mol%), dtbbpy ligand (21 mg, 75 μmol, 15 mol%), TBABr (0.1 mmol), DMAc (5 mL), glassy carbon working electrode, 100 mV/s scan rate, room temperature.

Reference:

- (1) Till, N. A.; Oh, S.; MacMillan, D. W. C.; Bird, M. J. The Application of Pulse Radiolysis to the Study of Ni(I) Intermediates in Ni-Catalyzed Cross-Coupling Reactions. *Journal of the American Chemical Society* **2021**, *143*, 9332-9337.
- (2) Sun, S.-Z.; Martin, R. Nickel-Catalyzed Umpolung Arylation of Ambiphilic α-Bromoalkyl Boronic Esters. *Angewandte Chemie International Edition* **2018**, *57*, 3622-3625.
- (3) Cong, F.; Lv, X.-Y.; Day, C. S.; Martin, R. Dual Catalytic Strategy for Forging sp²-sp³ and sp³-sp³ Architectures via β-Scission of Aliphatic Alcohol Derivatives. *Journal of the American Chemical Society* **2020**, *142*, 20594-20599.