Supporting Material

for

Mechanistic Analysis of *trans* C–N Reductive Elimination From a Square-Planar Macrocyclic Aryl-Copper(III) Complex

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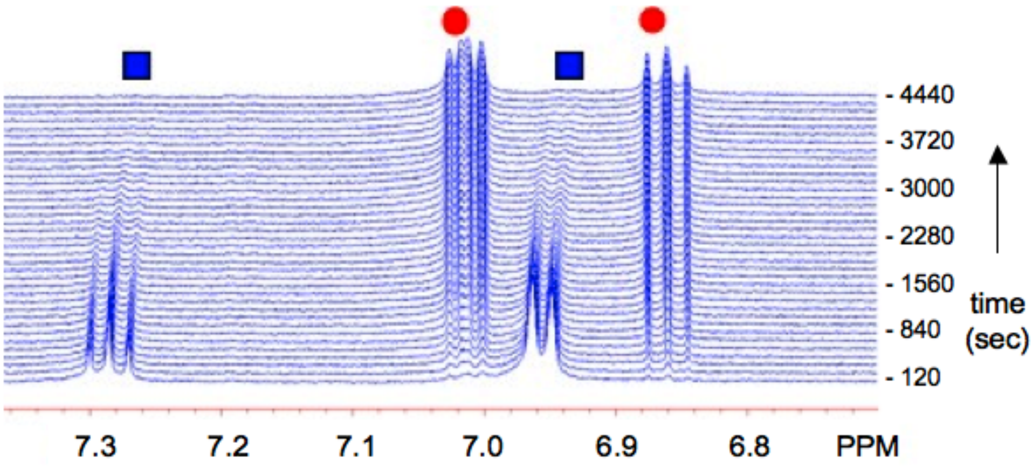


Figure S1: Representative time course of the intramolecular reaction of **1** (blue squares) to afford **3** (red circles), monitored by ^{1}H NMR spectroscopy (aromatic region shown) and corresponding to Fig. 2 in the manuscript. Reaction conditions: [**1**] = 8 mM, CD_3CN, 69 °C; spectra acquired every 2 minutes.

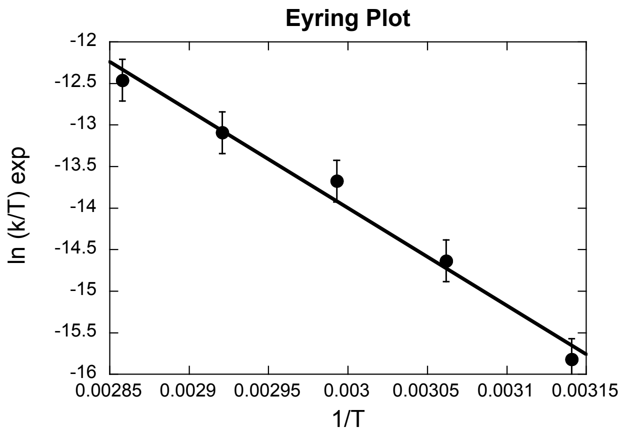


Fig. S2. Eyring plot for intramolecular C–N reductive elimination reaction of aryl–Cu^{III} complex **1** in acetonitrile. Error bars represent standard error obtained by least squares fitting of all temperature data. Reaction Conditions: [**1**] = 8 mM, T = 40-76.8 °C, ^{1}H NMR in CD_3CN, monitored by ^{1}H NMR spectroscopy. ($\Delta H^{\ddagger}$ = 23.3 ± 1.8 kcal/mol•K, $\Delta S^{\ddagger}$ = -5 ± 5 cal/mol•K).

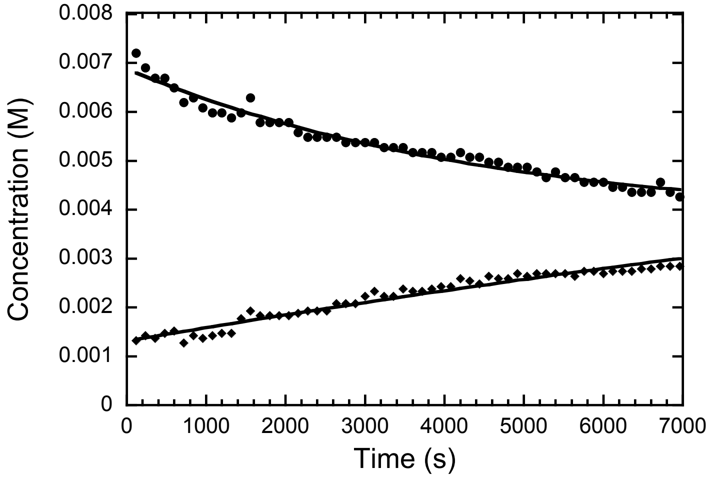


Fig. S3. ^{1}H NMR spectroscopic time course for the conversion of aryl–Cu^{III} complex **1** into **3** in a 1:1 solvent mixture of CD_3CN and DMF-d_6. Reaction conditions: [**1**] = 8 mM, temp = 75 °C.

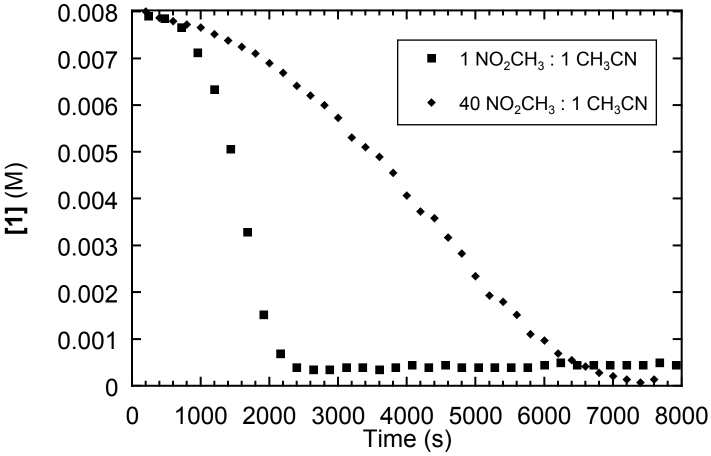
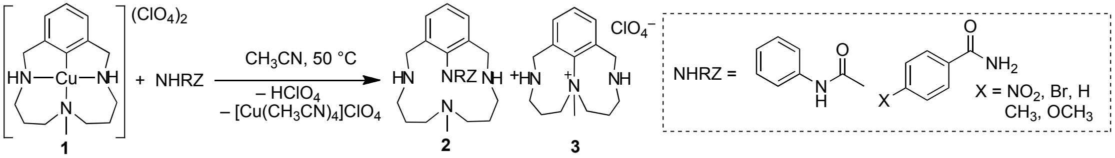


Fig. S4. ^{1}H NMR spectroscopic time courses for the conversion of aryl–Cu^{III} complex **1** into **3** in two solvent mixtures of acetonitrile and nitromethane. [**1**] = 8 mM, 65 °C.

^{1}H NMR Spectroscopic Kinetic Data for Reaction of 1 with Various Nitrogen Nucleophiles.



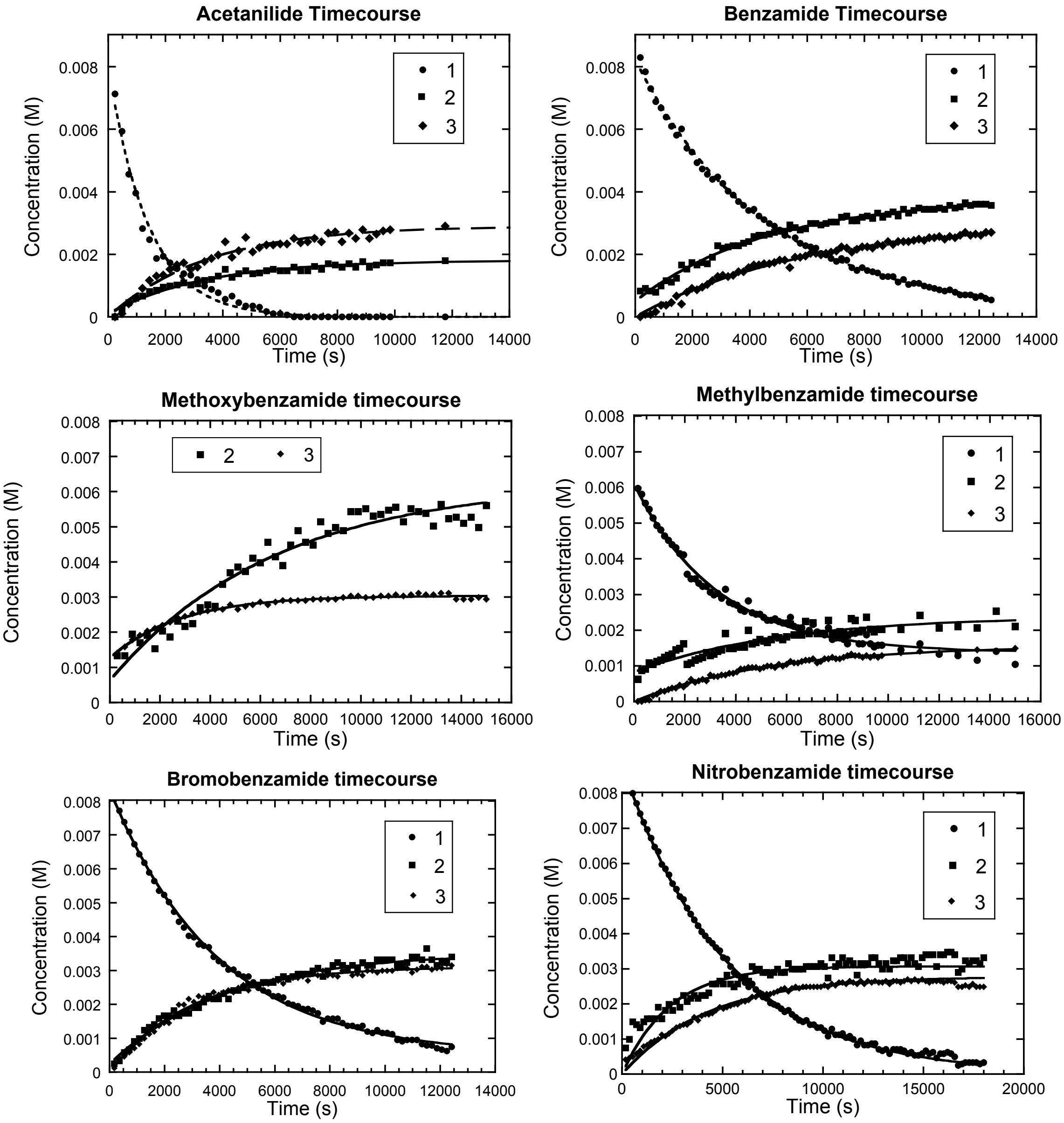


Figure S5. Timecourses for the reaction of the organocopper(III) species **1** with acetanilide and benzamide derivatives to yield both the C—N intermolecular product $\mathbf{2^H}$ and C—N intramolecular product **3**. Reaction conditions: [**1**] = 8 mM, [nucleophile] = 157 mM, ^{1}H NMR, CD_3CN, 70 ˚C for acetanilide and 64 °C for benzamide derivatives respectively. In the methoxybenzamide case, the resonances associated with **1** overlapped with nucleophile and product resonances, interfering with accurate monitoring of copper complex concentration. Reliable NMR monitoring of reaction timecourse for oxazolidinone was not possible due to starting material and product overlap in the spectra.