

Supplementary Information

Activation of Aryl Halides by Cu⁰/1,10-phenanthroline: Cu⁰ as Precursor of Cu^I Catalyst in Cross-Coupling Reactions

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Reaction of 1,10-phenanthroline with CuI in acetonitrile.

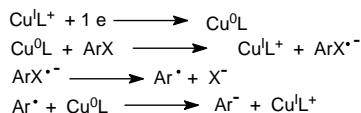
The cyclic voltammetry of CuI (2 mM) was performed in CH₃CN (containing *n*Bu₄NBF₄, 0.3 M). It exhibited an irreversible reduction peak ($E^p = -0.637$ V vs SCE) and two irreversible oxidation peaks ($E^p = +0.506$ V and $+0.854$ V). The first oxidation peak was assigned to the oxidation of I⁻ by comparison to an authentic sample of *n*Bu₄NI. Conductivity measurements performed in acetonitrile revealed that CuI was fully dissociated into ionic Cu(CH₃CN)₄⁺ and I⁻ (conductivity: $\kappa = 110$ μ S cm⁻¹ for CuI (2 mM), Tacussel CDM210 conductivity meter, cell constant = 1 cm⁻¹). Consequently, in acetonitrile CuI behaved as the cationic Cu(CH₃CN)₄⁺ and its reaction with phenanthroline was similar to that performed from Cu(CH₃CN)₄⁺PF₆⁻ in acetonitrile. Indeed, the cyclic voltammogram exhibited three reduction peaks ($E^{p_{R0}} = -1.60$ V, $E^{p_{R1}} = -1.78$ V, $E^{p_{R3}} = -1.96$ V) very similar to those observed when starting from Cu(CH₃CN)₄⁺PF₆⁻ (see text, Fig. 1b).

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Mechanism of the activation of ArX by Cu⁰/phenanthroline by electron transfer. A more sophisticated study should be done to discriminate two mechanisms proceeding by electron transfer (L = phenanthroline):

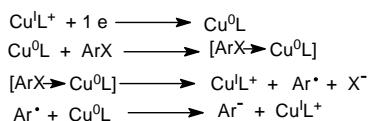
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Outer-sphere mechanism :



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Inner-sphere mechanism :



Such study is beyond the purpose of this work. We are nevertheless inclined to favour an inner-sphere mechanism for the reaction of Cu⁰(phen) with ArX since the catalytic effect was less important in the presence of 2 equiv of phenanthroline. Cu⁰(phen) and Cu⁰(phen)₂ were generated at the same potential (R₁). Since Cu⁰(phen)₂ was less efficient, this suggests that the

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saturated complex Cu⁰(phen)₂ (19-electron instead of 15-electron for Cu⁰(phen)) could not coordinate to PhI as required in an inner-sphere mechanism. Cu⁰(phen)₂ probably reacted via an outer-sphere process which is always slower than an inner-sphere one. The inner-sphere mechanism from Cu⁰(phen) is also supported by the fact that 4-NC-C₆H₄-Cl was more easily reduced than 4-CH₃O-C₆H₄-Br (Table 1) but no NC-C₆H₅ was formed in the electrolysis performed from 4-NC-C₆H₄-Cl whereas 4-CH₃O-C₆H₅ was formed from 4-CH₃O-C₆H₄-Br (Table 1).

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Typical procedure for the analysis of the reaction of Cu(CH₃CN)₄⁺PF₆⁻ and 1,10-phenanthroline by cyclic voltammetry.

The cyclic voltammetry was performed in a air-tight three-electrode cell under argon at room temperature. The working electrode was a glassy carbon disk (d = 3 mm). The counter-electrode was a platinum wire. The reference was a Saturated Calomel Electrode separated from the solution by a bridge filled with 2 mL of degassed and dried acetonitrile containing *n*Bu₄NBF₄ (0.3 M). 15 mL of degassed and dried acetonitrile containing *n*Bu₄NBF₄ (0.3 M) were introduced into the cell followed by 11.2 mg (0.03 mmol) of Cu(CH₃CN)₄⁺PF₆⁻. Cyclic voltammetry was performed at the scan rate of 0.5 Vs⁻¹. 5.4 mg (0.03 mmol) of 1,10-phenanthroline were then introduced and the CV performed under the same conditions. When the CV was performed at higher scan rates (from 20 up to 1000 Vs⁻¹), the size of the electrode was changed (d = 1 mm) to minimize the ohmic drop. Similar experiments were performed in the presence of 11 mg (0.06 mmol) of 1,10-phenanthroline.

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Typical procedure for Cu⁰-catalyzed electrosyntheses of ArH from ArX (Table 1).

Electrosyntheses were performed in a two-compartment air-tight three-electrode cell under argon at room temperature. The two compartments were separated by a sintered glass disk. The cathode was a carbon woven (ca. 4 cm² surface area). The anode was a sacrificial zinc rod (oxidation to Zn²⁺). The reference was a Saturated Calomel Electrode separated from the solution by a bridge filled with 2 mL of degassed and dried acetonitrile containing *n*Bu₄NBF₄ (0.3 M). The cathodic and anodic compartments were charged with 12 mL and 2 mL of degassed and dried acetonitrile containing *n*Bu₄NBF₄ (0.3 M) respectively. 18.6 mg (0.05 mmol) of Cu(CH₃CN)₄⁺PF₆⁻, 9 mg (0.05 mmol) of phenanthroline and 117 mg (0.5 mmol) of 4-MeO-C₆H₄-I were added to the

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cathodic compartment. The electrolysis was carried out at a controlled potential of -1.5 V, using a Tacussel PJT 35-2 potentiostat. The electrolysis was stopped when the current dropped to background level, after 90 min. A charge of 106 C had been passed through the cell. The cathodic compartment was hydrolyzed with 1 mL of aqueous HCl (10 %). After extraction with diethyl ether, the organic phase was dried on MgSO_4 and evaporated. The yield of Ph-OMe (76 %) was determined on the crude mixture by ^1H NMR (250 MHz) using $\text{CHCl}_2\text{CHCl}_2$ (0.2 mmol) as an internal standard. Characterization of Ph-OMe: ^1H NMR (250 MHz, CDCl_3) $\delta = 3.73$ (s, 3H, CH_3), 6.83 (d, 2H, $J = 7.7$ Hz, $o\text{-H}$), 6.87 (t, 1H, $J = 7.7$ Hz, $p\text{-H}$); 7.21 (t, 2H, $J = 7.7$ Hz, $m\text{-H}$); similar to the spectrum of a commercial authentic sample. The ^1H NMR spectra of the arenes (PhCN, PhCH₃) synthesized in Table 1 were identical to those of commercial samples.

Characterization of phenanthroline by cyclic voltammetry

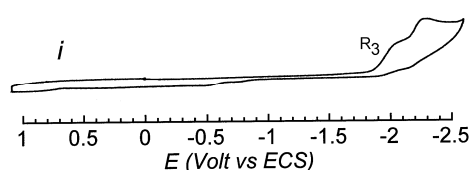


Fig. S11 Cyclic voltammetry of 1,10-phenanthroline (4 mM) performed in acetonitrile containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M) at a steady glassy carbon disk electrode ($d = 3$ mm) at the scan rate of 0.5 V s^{-1} , at 20°C . First reduction peak potential: $E_{R3}^0 = -2.03 \text{ V vs SCE}$.

Activation of PhI by electrogenerated $\text{Cu}^0(\text{phenanthroline})$ as evidenced by cyclic voltammetry.

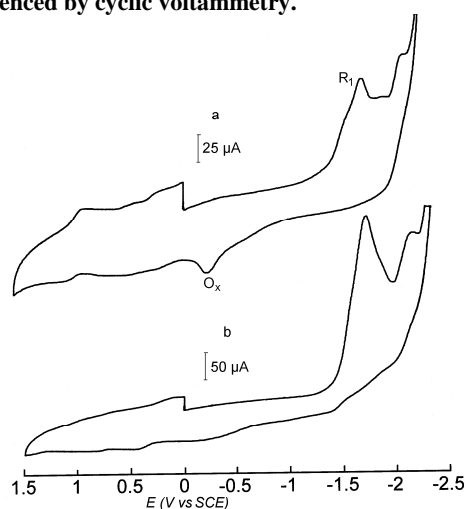


Fig. S12 a) Cyclic voltammetry of $\text{Cu}(\text{CH}_3\text{CN})_4^+\text{PF}_6^-$ (2 mM) in the presence of 1,10-phenanthroline (2 mM), in acetonitrile containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M) at a steady glassy carbon disk electrode ($d = 3$ mm) at the scan rate of 0.5 V s^{-1} , at 20°C . b) After addition of PhI (2 mM). The current scale has been divided by 2 when going from a) to b).

Characterisation of 4-NC-C₆H₄-CuBr(phenanthroline)⁺I⁻.

The ESI MS of the isolated complex 4-NC-C₆H₄-Cu^{III}-Br(phenanthroline)⁺I⁻ generated by oxidative addition of 4-NC-C₆H₄-I to $\text{CuBr}(\text{PPh}_3)(\text{phen})^{\text{I}}$ in toluene at reflux exhibited an isotopic pattern centred at 426 in agreement with the formula $\text{C}_{19}\text{H}_{12}\text{BrCuN}_3$. The ^1H NMR (250 MHz, CD_2Cl_2 , TMS) exhibited two broad signals of same amplitude at 6.88 and 6.60 ppm assigned to the aromatic protons of 4-NC-C₆H₄ ligated to the Cu^{III} center.

References

- 1 For the use of $\text{CuBr}(\text{PPh}_3)(\text{phen})$ as catalyst in cross-coupling reactions see: R. K. Gujadhur, C. G. Bates, D. Venkataraman, *Org. Lett.*, **2001**, 3, 4315.