Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Evidence for the interaction between ^{t}BuOK and 1,10-phenanthroline: A key step for the activation of aryl bromides by electron transfer

Hong Yi,[a] Anny Jutand,[b]* and Aiwen Lei[a]*

[a] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, P. R. China*

aiwenlei@whu.edu.cn

http://aiwenlei.whu.edu.cn/Main_Website/

[b] *Ecole Normale Supérieure-PSL Research University, Département de Chimie, Sorbonne Universités - UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24 rue Lhomond, F-75231 Paris Cedex 5, France. Anny.Jutand@ens.fr*

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EPR Data Collection and Analysis

1. General Information

EPR spectra were recorded on a Bruker X-band A200 spectrometer. 1,10-phenanthroline, *t*BuOK and PhBr were commercial and used as received. The samples were taken out into a small tube, and then recorded by EPR spectrometer at indicated temperature and parameters.

2. Experimental Details

2.1 The reaction of phen and ^{t}BuOK using toluene as solvent

2.1.1 A dried schlenk tube equipped with a stir bar was loaded with 18.0 mg (0.1 mmol) of 1,10-phenantholine and 44.8 mg (0.4 mmol) of ^{t}BuOK in 2 mL toluene under the atmosphere of nitrogen. The solution was then stirred at 100 ^{o}C. After 120 mins, the solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.435 GHz. Typical spectrometer parameters are shown as follows, scan range: 50 G; center field set: 3367 G; time constant: 81.92 ms; scan time: 40.96 s modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^{3}; microwave power: 2.07 mW.

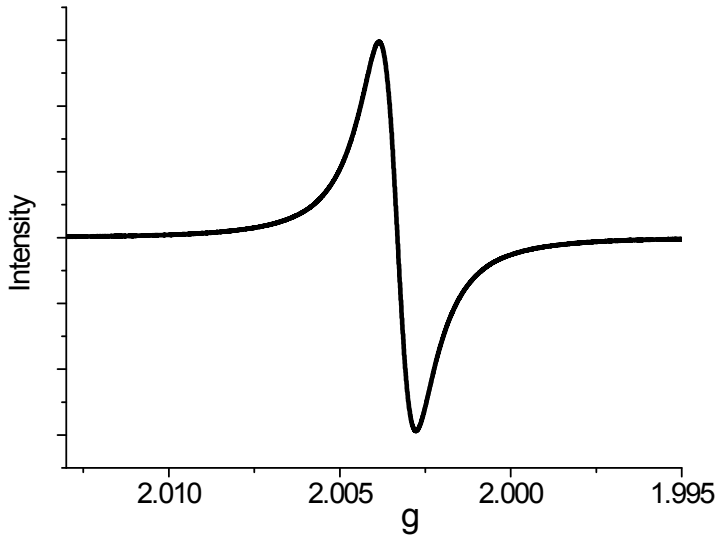

Fig S1

2.1.2 A dried schlenk tube equipped with a stir bar was loaded with 44.8 mg (0.4 mmol) of ^{t}BuOK in 2 mL toluene under the atmosphere of nitrogen. The solution was then stirred at 100 ^{o}C. After 120 mins, the solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.435 GHz. Typical spectrometer parameters are shown as follows, scan range: 50 G; center field set: 3367 G; time constant: 81.92 ms; scan time: 40.96 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^{3}; microwave power: 2.07 mW.

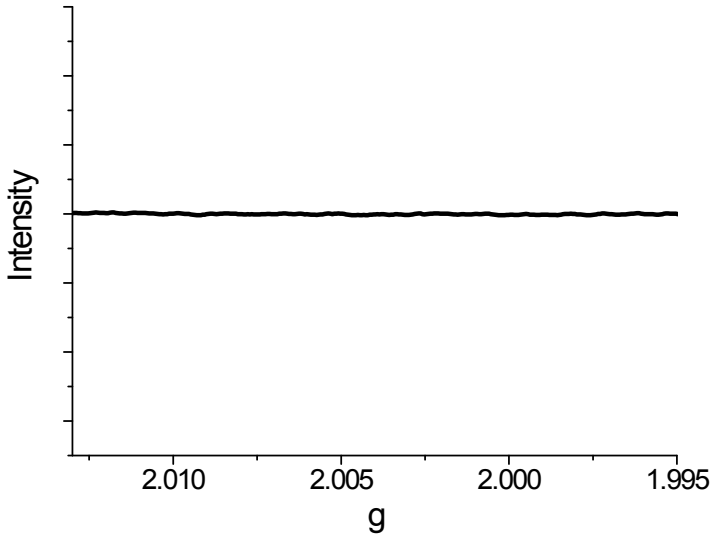

Fig S2

2.2 The reaction of phen and ^{t}BuOK using CH_3CN and Dioxane as solvent

A dried Schlenk tube equipped with a stir bar was loaded with with 18.0 mg (0.1 mmol) of 1,10-phenantholine and 44.8 mg (0.4 mmol) of ^{t}BuOK in 2 mL CH_3CN or 2 mL Dioxane under the atmosphere of nitrogen. The solution was then stirred at 100 ^{o}C. After 120 mins, the solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.435 GHz. Typical spectrometer parameters are shown as follows, scan range: 50 G; center field set: 3367 G; time constant: 81.92 ms; scan time: 40.96 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×103; microwave power: 2.07 mW.

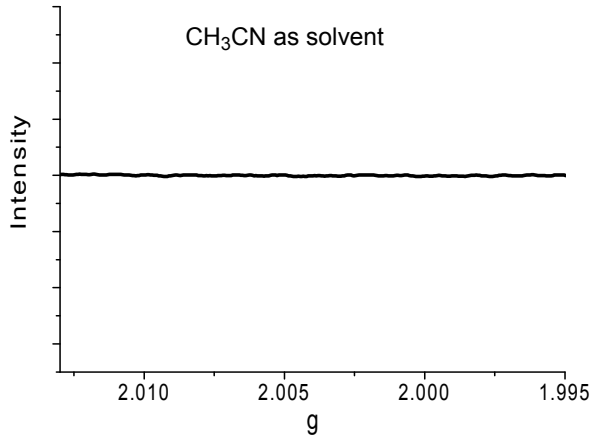

Fig S3

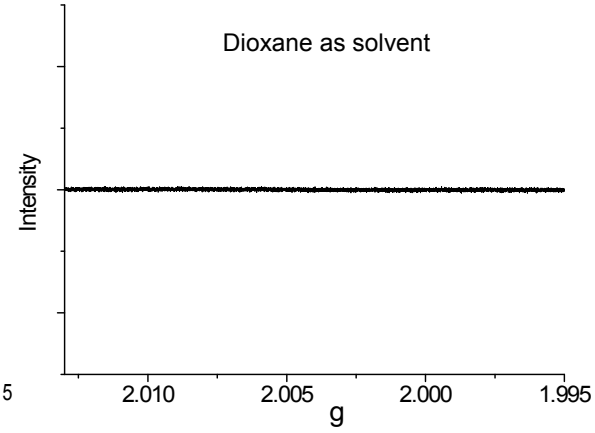

Fig S4

2.3 The reaction of phen and ^{t}BuOK using benzotrifluoride as solvent

A dried schlenk tube equipped with a stir bar was loaded with 18.0 mg (0.1 mmol) of 1,10-phenantholine and 44.8 mg (0.4 mmol) of ^{t}BuOK in 2 mL benzotrifluoride under the atmosphere of nitrogen. The solution was then stirred at 100 ^{o}C. After 120 mins, the solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.434 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3366 G; time constant: 81.92 ms; scan time: 40.96 s; modulation amplitude: 2.5 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^{5}; microwave power: 20.71 mW.

Fig S5

2.3 The reaction of 1,10-phenanthroline derivatives and ^{t}BuOK using DMF as solvent

2.3.1 A dried schlenk tube equipped with a stir bar was loaded with with 0.1 mmol of 1,10-phenantholine derivatives (1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline) and 44.8 mg (0.4 mmol) of ^{t}BuOK in 2 mL DMF under the atmosphere of nitrogen. The solution was then stirred at 100 ^{o}C. After 120 mins, the solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.416 GHz. Typical spectrometer parameters are shown as follows, scan range: 50 G; center field set: 3357 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^{3}; microwave power: 18.51 mW.

2.3.2 A dried schlenk tube equipped with a stir bar was loaded with 44.8 mg (0.4 mmol) of ^{t}BuOK in 2 mL DMF under the atmosphere of nitrogen. The solution was then stirred at 100 ^{o}C. After 120 mins, the solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.416 GHz. Typical spectrometer parameters are shown as follows, scan range: 50 G; center field set: 3357 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^{3}; microwave power: 18.51 mW.

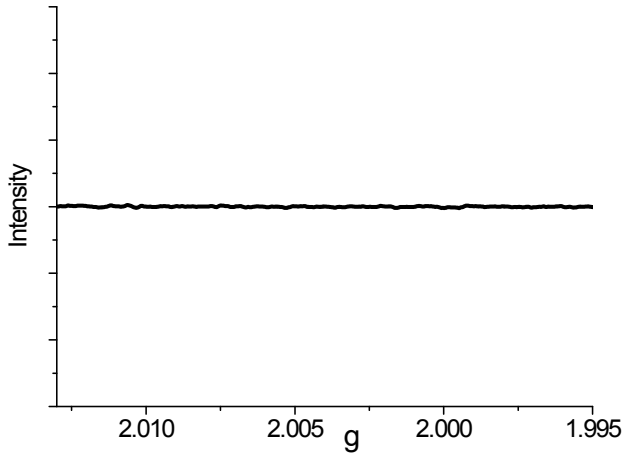

Fig S6

2.4 The reaction of 1,10-phenantholine, ^{t}BuOK and PhBr using toluene as solvent

A dried Schlenk tube equipped with a stir bar was loaded with with 18.0 mg (0.1 mmol) of 1,10-phenantholine, 44.8 mg (0.4 mmol) of ^{t}BuOK, PhBr (1.0 mmol) of PhBr in 2 mL toluene under the atmosphere of nitrogen. The solution was then stirred at 100 ^{o}C. After 120 mins, the solution sample was taken out into a small tube, frozen by liquid nitrogen and then analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.416 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3357 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 0.5 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^{3}; microwave power: 18.51 mW.

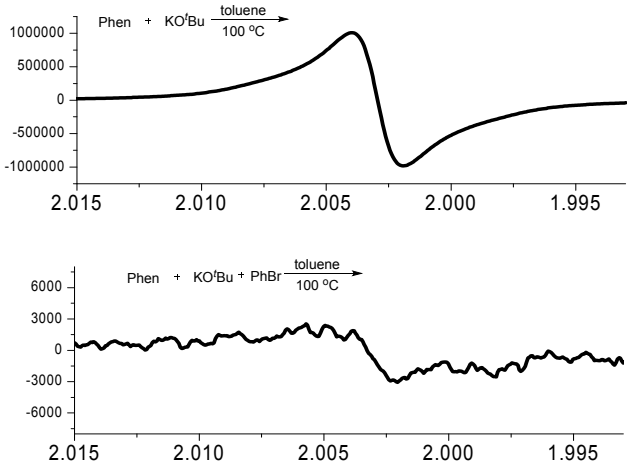

Fig S7

Cyclic Voltammetry Data Collection and Analysis

1. General Information

DMF was distilled on CaH_2, kept in the dark under argon and degassed just before used. 1,10-phenanthroline, ^{t}BuOK were commercial and used as received. Commercial PhBr was filtered on alumina and degassed before used.

2. Experimental Details

2.1 General Procedure for Cyclic Voltammetry. Cyclic voltammetry was performed in a three electrode cell connected to a Schlenk line under argon at 22 °C with a scan rate of 0.5 Vs^{-1}. The working electrode was a gold disk (*d* = 1 mm) or carbon disk (*d* = 1 mm), the counter electrode a platinum wire of ca. 0.2 cm^2 apparent area. The reference was a saturated calomel electrode (SCE) separated from the solution by a bridge filled with a 0.3 M $^nBu_4NBF_4$ solution of 3 mL of DMF. 10 mL of DMF containing 0.3 M $^nBu_4NBF_4$ were poured into the electrochemical cell in all experiments reported below.

2.2 Electrochemical oxidation of ^{t}BuOK

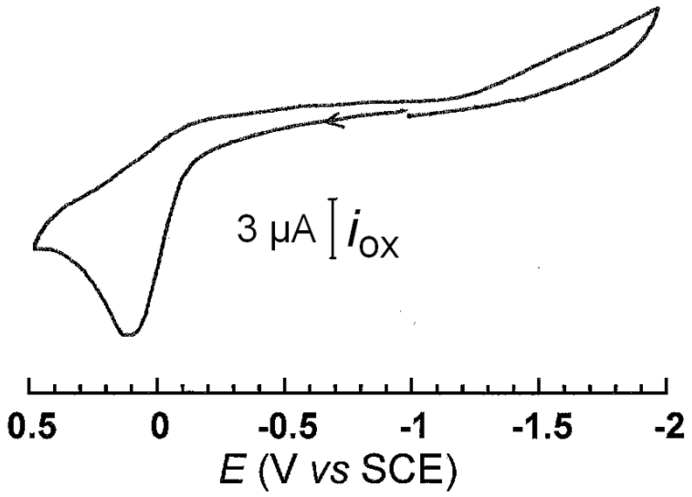

Fig S8. Cyclic voltammetry performed in DMF containing $n$$Bu_4NBF_4$ (0.3 M) at a gold disk electrode (*d* = 1 mm) at the scan rate of 0.5 $V.s^{-1}$ at 22 °C. Oxidation of ^{t}BuOK (19 mg, 0.10 mmol, 10 mM).

2.3 Electrochemical reduction of 1,10-phenanthroline. 8 mg (0.04 mmol, 4 mM) of phen were added to the cell and CV performed just after (Fig 3a).

2.4 Electrochemical reduction of PhBr, alone and in the presence of 1,10-phenantholine (Phen). 4.2 µL (0.04 mmol, 4 mM) of PhBr were added to the cell and the CV was performed just after (Fig S9a). 7.2 mg (0.036 mmol, 3.6 mM) of phen were added to the cell and CV performed just after (Fig S9b). In another experiment, 8 mg (0.04 mmol, 4 mM) of phen were

added to the cell containing 4.2 µL (0.04 mmol, 4 mM) of PhBr and the CV was performed just after (Fig S9c).

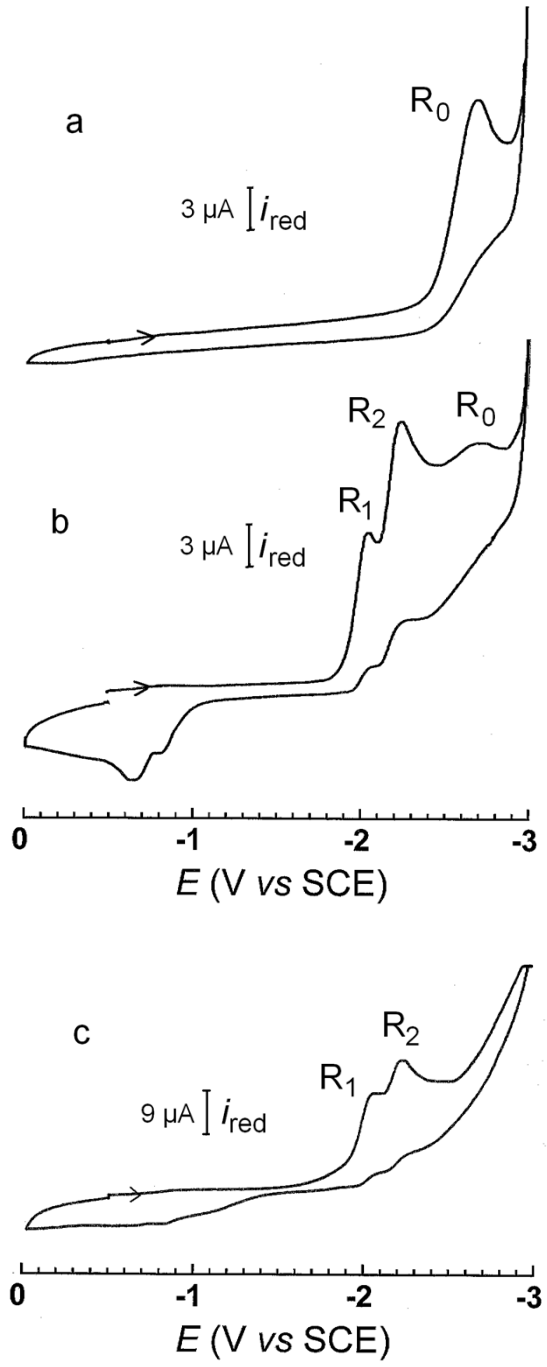

Fig S9. Cyclic voltammetry performed in DMF containing nBu$_4$NBF$_4$ (0.3 M) at a carbon disk electrode (d = 1 mm), at the scan rate of 0.5 V.s^{-1} at 22 °C. a) Reduction of PhBr (4 mM) at R_0. b) PhBr (4 mM) in the presence of Phen (3.6 mM). c) PhBr (4 mM) in the presence of Phen (4 mM) at a gold disk electrode (d = 1 mm)

2.5 Electrochemical reduction of 1,10-phenanthroline in the presence of PhBr.

2.5.1 8.0 mg (0.04 mmol, 4 mM) of phen were added to the cell and CV performed just after. The same CV was performed in the presence of 4.2 µL (0.04 mmol, 4 mM) of PhBr and the direction of the potential scan was reversed just after R_2 (at –2.4 V, Fig 3b). 4.2 µL (0.04 mmol, 4 mM) of PhBr were then added twice (Fig 3b).

2.5.2 The same CV was performed in the presence of 8.4 µL (0.08 mmol, 8 mM) of PhBr (n = 2 equiv.) but the direction of the potential scan was reversed just after R_1 (at –2.1 V, Fig 3c). The same CVs were performed after addition of 8.4 µL (0.16 mmol) of PhBr (total n = 4 equiv.) and finally after addition of 25.2 µL (0.24 mmol) of PhBr (total n = 10 equiv.) (Fig 3c).

2.6 The dianion Phen2– generated at R2 activated PhBr by electron transfer to generate PhBr•– and Phen•–

When the cyclic voltammetry of PhBr (4 mM) was performed in the presence of Phen in substoichiometric amount (3.6 mM), an amplified current intensity was observed for R2 relatively to that of R1 (Fig S9b, to be compare to Fig 3a) due to the catalytic process. The reduction peak of PhBr at R0 was dramatically lower due to its reaction with the electrogenerated Phen2– in the diffusion layer. The clear coexistence on the same CV (Fig S9b) of the reduction peak R2 and the reduction peak R0 of the unreacted PhBr unambiguously indicates that the initial reduction peak of PhBr at R0 did not overlap with the reduction current at R2.