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Ligand free copper(I)-catalyzed synthesis of diaryl ether with Cs_2CO_3 *via* a free radical path†

Hong-Jie Chen,[a,b] Mei-Chun Tseng,[a] I-Jui Hsu,[c] Wei-Ting Chen,[a,c] Chien-Chung Han*[b] and Shin-Guang Shyu*[a]

Complexes $[Cu(I)(2,4\text{-dimethylphenoxy})_2]^-$ (A) and $[Cu(II)(2,4\text{-dimethylphenoxy})_2(p\text{-tolyl})]^-$ (B) were observed by *in situ* electrospray ionization mass spectrometry (ESI-MS) analysis of the ligand free copper(I)-catalyzed C–O coupling reaction using Cs_2CO_3 under the catalytic reaction conditions indicating that they could be intermediates in the reaction. The radical scavenger cumene retarded the reaction. Catalytic cycles involving a free radical path are proposed based on these observations.

Ullmann-type C–O cross coupling arylation in the synthesis of aryl ethers usually consists of a ligand, a base and a copper salt.[1] The addition of a ligand usually gives a better yield of the reaction, and different ligands may have different catalytic activities.[2] Thus, a Cu(I) complex with an additive ligand is generally proposed as the intermediate involved in the aryl halide activation step of the catalytic cycle.[3,4] For elucidating the reaction mechanism, complexes LCu(I)(OAr) with the additive ligand L have been prepared, and their catalytic activities have been evaluated.[4] Both the free radical path and concerned 2e oxidative addition path have been proposed for the aryl halide activation step.[3b,c,4] Experimental and theoretical studies support both mechanisms indicating that various factors (such as solvent and substrates used) affect the reaction mechanism.[3b,c,5]

Cesium carbonate is a common base used in the Ullmann type C–O cross coupling reaction since the first report of its application in the reaction.[1a,b,2f,6] The reaction can be carried out in toluene, a relatively environmentally benign solvent, and good yield is obtained under relatively mild reaction conditions without the addition of a ligand.[6a] Cesium carbonate is identified as the key factor for improving the reaction conditions because other metal carbonates and bases do not give similar good results.[6a,c,7] The improvement is proposed due to the nature of cesium because cesium phenoxide is relatively soluble in organic solvents and may also enhance the solubility of the proposed intermediate $[Cu(OAr)_2]^-$.[6a] Recently, we have reported the Ullmann type C–N cross coupling arylation having different reactivities when using different metal *tert*-butoxides.[8] The aryl halide activation step changes from a non-free radical path to a free radical path when sodium *tert*-butoxides in the catalytic system switch to potassium *tert*-butoxides.[8a,b] These discoveries in both Ullmann type C–N and C–O cross coupling reactions may imply that the activity enhancement in the Ullmann type C–O cross coupling reaction using cesium carbonate alone may have a mechanism different from reactions using other metal carbonates. We herein report the *in situ* ESI-MS analysis[9] of a ligand free Ullmann type Cu(I)-catalyzed cross C–O coupling reaction using Cs_2CO_3 as the base. Complexes $[Cu(I)(2,4\text{-dimethylphenoxy})_2]^-$ (denoted as **A**) and $[Cu(II)(2,4\text{-dimethylphenoxy})_2(p\text{-tolyl})]^-$ (denoted as **B**) were observed in the reaction system indicating that they could be the intermediates in the reaction. Addition of the radical scavenger cumene retarded the reaction indicating the existence of a free radical pathway in the catalytic cycle of the reaction. In addition, an *in situ* EPR study of the reaction solution detected a Cu(II) species with a fitted g value of 2.065. A catalytic cycle composed of a free radical path is proposed based on these observations.

We followed the general procedure reported in the literature to investigate the Cu(I)-catalyzed C–O cross coupling arylation between aryl bromide and 2,4-dimethylphenol using Cs_2CO_3 without a ligand. A mixture of 2,4-dimethylphenol (1.2 equiv.), aryl bromide (1 equiv.), Cs_2CO_3 (3 equiv.) and CuI (2.5 mol%) was stirred in toluene at 120 °C for 8 h.[1b,6b] The results of the reactions are summarized in Table 1.

The possibility of a free radical path was evaluated by adding a free radical scavenger (cumene) in the reaction.[10] Under the same reaction conditions, the addition of cumene

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[a] *Institute of Chemistry, Academia Sinica, 128 Academia Road Sec. 2, Nankang, Taipei 115, Taiwan, Republic of China. E-mail: sgshyu@chem.sinica.edu.tw; Fax: +886-2-2783-1237; Tel: +886-2-2789-8593*

[b] *Department of Chemistry, National Tsing Hua University, 101, Sec 2, Kuang-Fu Rd, Hsinchu 30013, Taiwan, Republic of China*

[c] *Department of Molecular Science and Engineering, National Taipei University of Technology, 1, Sec. 3, Zhongxiao E Road, Taipei 10608, Taiwan, Republic of China*

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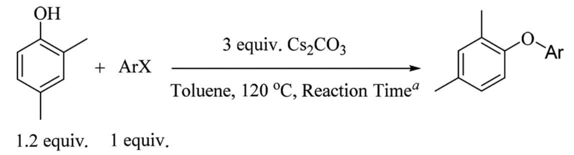
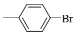
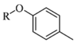
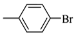
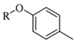
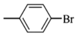
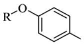
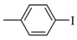
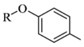
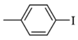
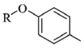
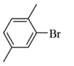
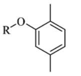
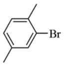
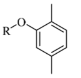
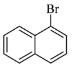
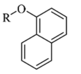
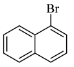
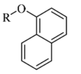
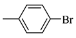
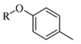
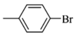
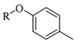
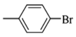
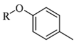
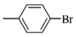
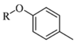
Table 1 Ligand-free C–O cross coupling reactions between aryl halide and 2,4-dimethylphenol using Cs_2CO_3

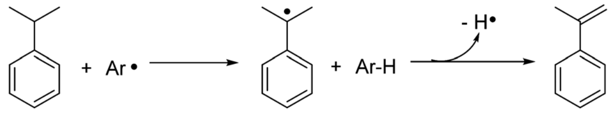


Entry	ArX	Aryl ether[b]	CuI (mol%)	Conv./GC yield[c,d] (%)	Conv./GC yield[c,d] (%) with 50 mol% cumene[e]
1			2.5	76/68(90)	—
2			2.5	—	69/33(48)
3			—	9/4(44)	—
4			—	22/22(99)	—
5			—	—	51/6(12)
6			2.5	42/41(98)	—
7			2.5	—	31/24(77)[f]
8			2.5	25/23(92)	—
9			2.5	—	30/0(0)[g]
10			2.5[h]	67/64(95)	
11			2.5[i]	65/60(92)	
12			2.5[i]		70/49(70)[j]
13			2.5[k]	72/67(90)	

[a] 8 h for reactions with 2.5 mol% of CuI, 2.5 mol% of $CuCl_2$ and 48 h for reactions without CuI. [b] R = 2,4-dimethylphenyl. [c] Yield calculation based on the amount of ArX used; using 1,4-di-*tert*-butylbenzene as an internal standard in GC analysis. [d] Selectivity in the parenthesis. [e] Prop-1-en-2-ylbenzene was detected by GC-MS. [f] *p*-Xylene was detected by GC-MS. [g] Naphthalene was detected by GC-MS. [h] 2.5 mol% CuI and 5 mol% Cs(2,4-dimethylphenoxy) in toluene were stirred at 120 °C for 8 h. Then 2,4-dimethylphenol and 4-bromotoluene were added at RT, and the mixture was stirred at 120 °C for 8 h. [i] 2.5 mol% $CuCl_2$. [j] Prop-1-en-2-ylbenzene was not detected by GC-MS. [k] 2.5 mol% $CuCl_2$ and 5 mol% Cs(2,4-dimethylphenoxy) in THF were stirred at 120 °C for 8 h. After removing THF, 2,4-dimethylphenol, 4-bromotoluene and toluene were added, and the mixture was stirred at 120 °C for 8 h.

reduced the yield from 68% (without cumene) to 33% in the case of 4-bromotoluene indicating the presence of a radical reaction path (Table 1, entries 1 and 2).

Reaction between $[CH_3C_6H_4]^•$ and cumene should produce prop-1-en-2-ylbenzene and toluene because $Ar^•$ reacts with cumene to produce prop-1-en-2-ylbenzene and the corresponding Ar–H (Scheme 1).[11] The detection of prop-1-en-2-ylbenzene by GC-MS confirms the presence of $[CH_3C_6H_4]^•$. The other product toluene cannot be identified because toluene is the reaction medium. In order to reconfirm the presence of $Ar^•$ in the C–O cross coupling reaction, 2-bromo-1,4-dimethylbenzene and 1-bromonaphthalene were used instead, and both prop-1-en-2-ylbenzene and the respective Ar–H products, *i.e.* *p*-xylene and naphthalene, were observed (Table 1 entries 7 and 9).



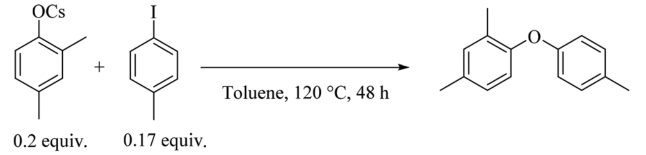
Scheme 1 Reaction between cumene and aryl radical.

The theoretical study suggests that $[(ket)Cu(I)OPh]^-$ (ket = β-diketonate) reacts with ArI to generate $Ar^•$ and I^- through a single electron transfer (SET) process in the C–O cross coupling reaction catalyzed by the CuI-β-diketone-Cs_2CO_3 catalyst system. Similar to $[(ket)Cu(I)(2,4\text{-dimethylphenoxy})]^-$, complex **A** generated by the reaction among 2,4-dimethylphenol, Cs_2CO_3 and CuI may react with 4-bromotoluene to produce $[Cu(II)(2,4\text{-dimethylphenoxy})_2]$ (denoted as **C**), $[CH_3C_6H_4]^•$ and Br^- through SET.[3b]

The other possible path generating $Ar^•$ is the reaction between aryl halide and Cs(2,4-dimethylphenoxy) generated in the reaction. (phen)M(O*t*Bu) (phen = 1,10-phenanthroline; M = Na, K) and (phen)K(NAr'_2) can react with ArI to generate $Ar^•$ which can further react with the solvent toluene to form the C–H arylation product $CH_3C_6H_4Ar'$.[8,11c] The $Ar^•$ is proposed to react with [phenCu(I)NAr'_2)] to generate [phenCu(II)(NAr'_2)-(Ar)] as an intermediate in the C–N cross coupling reaction catalyzed by CuI-phen-(*t*BuONa/K_2CO_3) mixed-base or CuI-phen-*t*BuOK catalytic systems.[8b,c] In order to evaluate the possibility that Cs(2,4-dimethylphenoxy)—similar to (phen)M-(O*t*Bu) (M = Na, K) and (phen)K(NAr'_2)—can react with aryl halide to form $Ar^•$, only Cs_2CO_3 was used in the C–O cross coupling reaction between 2,4-dimethylphenol and 4-iodotoluene (or 4-bromotoluene) under similar reaction conditions (Table 1, entries 3 and 4).

Product yields of 22% and 4% were obtained with selectivity of 99% and 44% for the reactions with 4-iodotoluene and with 4-bromotoluene, respectively. Addition of the radical scavenger cumene to the reaction reduced the product yield to 6% in the case of 4-iodotoluene, and prop-1-en-2-ylbenzene was observed by GC-MS (Table 1, entry 5).

In order to confirm the role of Cs(2,4-dimethylphenoxy) in the electron transfer path, Cs(2,4-dimethylphenoxy), synthesized through transmetalation reaction between K(2,4-dimethylphenoxy) and CsF, was allowed to react with 4-iodotoluene to produce 1-(2,4-dimethylphenoxy)-4-methylbenzene. Again, the addition of cumene to the reaction reduced the product yield from 10% to 3% indicating that Cs(2,4-dimethylphenoxy) is capable of transferring electrons to



i) yield: 10% (conversion: 13%, selectivity; 77%)
ii) with 50 mol% of cumene; yield: 3% (conversion: 6%, selectivity; 50%);
prop-1-2-ylbenzene was detected by GC-Mass

Scheme 2 C–O cross coupling reaction between Cs(2,4-dimethylphenoxy) and iodotoluene.

aryl halide to form Ar$^•$ under the reaction conditions (Scheme 2).

In order to identify the intermediates, *in situ* ESI-MS analysis was carried out at 120 °C—the same temperature as the parent catalytic reaction. A similar reaction mixture in toluene was stirred at 120 °C for 2 h in a dry box. The solution was then transferred to a GC vial. The temperature of the solution was maintained at 120 °C by immersing the GC vial in a sand bed, and ESI-MS spectra of the solution were then recorded. Two peaks at *m*/*z* = 305.64 and *m*/*z* = 397.12 were observed individually in the negative-ion mode of the ESI-MS in four different measurements (Fig. 1). They are identified as **A** and **B** (or [Cu(0)(2,4-dimethylphenoxy)(1-(2,4-dimethylphenoxy)-4-methylbenzene)]$^-$, denoted as **B′**) corresponding to their measured accurate mass and isotope distributions (Fig. 2).

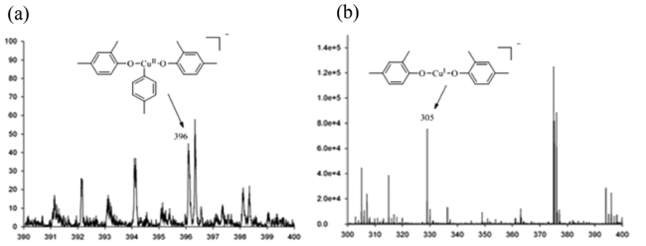


Fig. 1 *In situ* ESI(−)-MS from the solution taken during the reaction of 2,4-dimethylphenol and 4-bromotoluene with Cs_2CO_3 in the presence of CuI in toluene at 120 °C from two individual experiments.

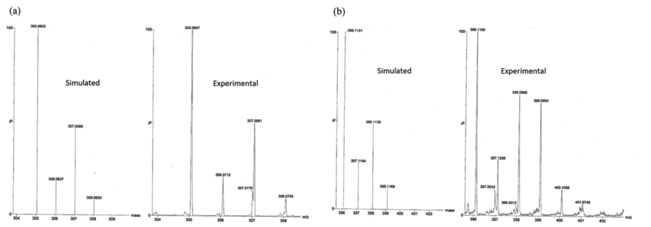
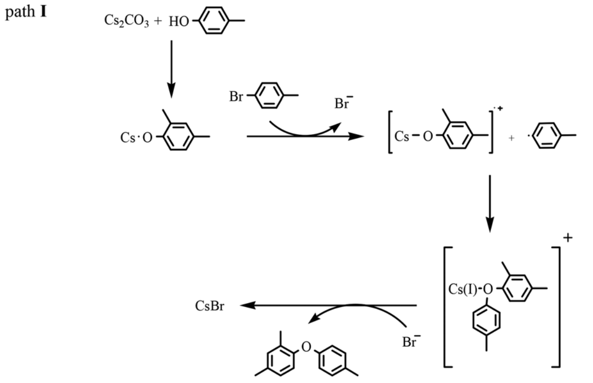
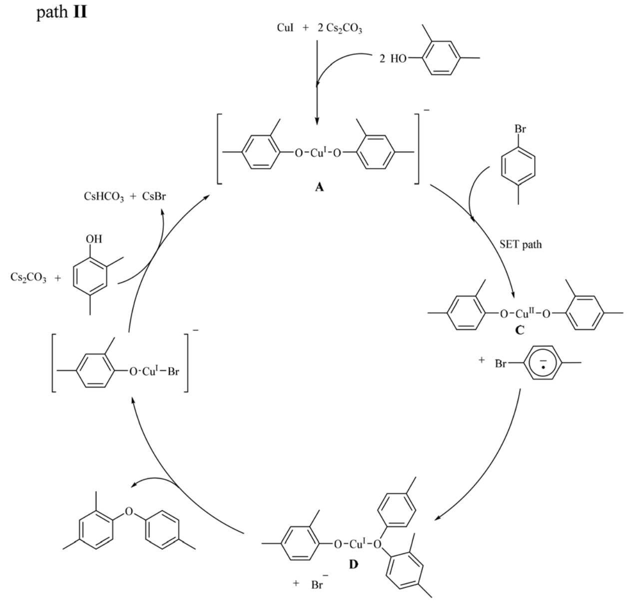


Fig. 2 Simulated and experimental isotopic distributions of (a) **A** and (b) **B** or **B′**.

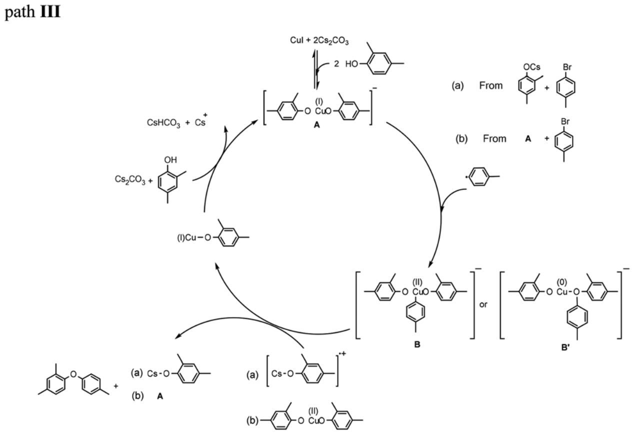


Scheme 3 The proposed mechanism of path **I**.

Based on all the above observations, three possible reaction paths in the Ullmann type C–O cross coupling arylation can be deduced. In path **I**, a free radical [$CH_3C_6H_4$]$^•$, generated through the electron transfer process between Cs(2,4-dimethylphenoxy) and 4-bromotoluene, reacts with [Cs(2,4-dimethylphenoxy)]$^{•+}$ to produce ether (Scheme 3). We consider this path as insignificant because the yield of the reaction with only Cs_2CO_3 is relatively low (Table 1, entry 3). In path **II**, an aryl free radical [$CH_3C_6H_4$]$^•$, generated through the aryl halide SET activation process between **A** and 4-bromotoluene, reacts with **C** to form [Cu(I)(2,4-dimethylphenoxy)(1-(2,4-dimethylphenoxy)-4-methylbenzene)] (denoted as **D**). Substitution of the ligand 1-(2,4-dimethylphenoxy)-4-methylbenzene on **D** by Br^- produces ether and [Cu(I)(2,4-dimethylphenoxy)Br]$^-$, which further reacts with the 2,4-dimethylphenoxy anion to regenerate **A** to complete the catalytic cycle (Scheme 4).[3b] In path **III**, [$CH_3C_6H_4$]$^•$ (generated through path **I** or path **II**) reacts with **A** to form **B** (or **B′**) followed by reductive elimination (in the case of **B**) or substitution of 1-(2,4-dimethyl-



Scheme 4 The proposed mechanism of path **II**.



Scheme 5 The proposed mechanism of path III.

phenoxy)-4-methylbenzene by Br$^-$ (in the case of **B′**) to generate the product 1-(2,4-dimethylphenoxy)-4-methylbenzene and Cu(2,4-dimethylphenoxy) after oxidation of [Cu(2,4-dimethylphenoxy)]$^-$ by [Cs(2,4-dimethylphenoxy)]$^{\bullet+}$ or **C** (Scheme 5).

In order to confirm the role of **A** in the proposed reaction paths, we tried to evaluate the catalytic activity of Cs[Cu(2,4-dimethylphenoxy)$_2$]. Because we failed to obtain pure Cs[Cu(2,4-dimethylphenoxy)$_2$], *in situ* prepared 2.5 mol% of Cs[Cu(2,4-dimethylphenoxy)$_2$]—by reacting 2.5 mol% CuI with 5.0 mol% of Cs(2,4-dimethylphenoxy)—was allowed to react with 2,4-dimethyl phenol (1.2 equiv.), aryl bromide (1 equiv.) and Cs$_2$CO$_3$ (3 equiv.) in toluene under similar reaction conditions, and a comparable yield of ether (64%; Table 1, entry 10) was obtained. In addition, stoichiometric reaction among CuI (1 equiv.), Cs(2,4-dimethylphenoxy) (2 equiv.) and 4-bromotoluene (2 equiv.) under similar reaction conditions producing ether with 84% yield further supports the above argument.

In both paths **II** and **III**, a Cu(II) complex (**C** in path **II**, **B** in path **III**) is involved as an intermediate. The *in situ* EPR study was also carried out at 120 °C in order to evaluate the presence of the Cu(II) moiety in the reaction. A similar reaction mixture in toluene was stirred at 120 °C for 2 h in a sealed tube. The upper portion of the reaction solution was then transferred to an EPR tube in a dry box. We observed a signal around 3000G in the EPR spectrum taken at 25 °C (Fig. 3). After fitting,[12] the isotopic *g* value is 2.065 which is in agreement with a Cu(II) signal.[13] The spectrum was taken at a relatively high temperature (298 K), and all components of *g*-tensor could not be resolved and hence further structural details of the Cu(II) complex could not be obtained.

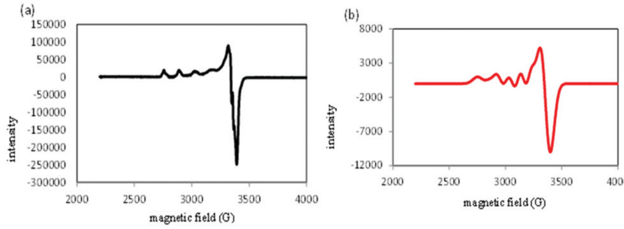


Fig. 3 (a) Experimental and (b) simulated EPR spectra for the reaction between 2,4-dimethylphenol and 4-bromotoluene with Cs$_2$CO$_3$ and CuI in toluene at 298 K.

If path **II** dominates in the reaction, Cu(II) halide should be able to catalyse the C–O coupling reaction[14] because Cu(II) halide can react with Cs(2,4-dimethylphenoxy) to form **C** which is proposed as an intermediate in path **II**. Replacing CuI with CuCl$_2$ in the catalytic system produced ether with comparable yield (60%, Table 1, entry 11) supporting that **C** is a possible intermediate in path **II**. *In situ* preparation of **C** by the reaction of CuCl$_2$ with two equivalents of Cs(2,4-dimethylphenoxy) (attempt to synthesize pure **C** failed) followed by the addition of other reagents obtained ether with 67% yield (Table 1, entry 13) further supporting the above argument.

We propose that the source of [CH$_3$C$_6$H$_4$]$^\bullet$ is mainly from the SET reaction between [Cu(I)(2,4-dimethylphenoxy)$_2$]$^-$ and 4-bromotoluene because the yield of the ether without the addition of Cu(I) salt is very low (Table 1, entry 3) indicating the insignificant contribution of [CH$_3$C$_6$H$_4$]$^\bullet$ generated from the reaction between Cs(2,4-dimethylphenoxy) and 4-bromotoluene (Scheme 3). Also, the addition of cumene in the CuCl$_2$ catalytic system did not effectively retard the reaction (Table 1, entry 12) implying that **C** can react with 4-bromotoluene through a non-radical path. This echoes the partial reduction of the yield of ether from 68% (without cumene) to 33% (addition of cumene) (Table 1, entries 1 and 2) which indicates the presence of a nonradical path if cumene can 100% inhibit the radical path in the reaction (Table 1, entries 1 and 2). Based on the above considerations, recombination of [CH$_3$C$_6$H$_4$]$^\bullet$ and **C** to form **D** in path **II** shown in Scheme 4 is proposed as the major path of the reaction in spite of the detection of **B** (or **B′**) in path **III** which indicates that the combination reaction between [CH$_3$C$_6$H$_4$]$^\bullet$ and **A** exists. The absence of **D** in the ESI-MS analysis does not confirm the non-existence of **D** because neutral species is very difficult to be detected by ESI-MS.

These results echo the findings in the studies of C–O cross coupling using CuI and K$_2$CO$_3$ without the addition of phen as the ligand.[5] A similar intermediate **A** was detected in the ESI-MS of the K$_2$CO$_3$–CuI catalytic system but the yield of the reaction was very low. We did not evaluate the possibility of the radical path in the K$_2$CO$_3$–CuI system because of the low yield. If [Cu(I)(2,4-dimethylphenoxy)$_2$]$^-$ can activate 4-bromotoluene *via* SET, then we should obtain similar yield in both K$_2$CO$_3$–CuI and Cs$_2$CO$_3$–CuI catalytic systems. Different counter cations should be the key factor for the difference in yield because cesium phenoxide has a higher solubility than potassium phenoxide.[6a]

Conclusions

Catalytic cycles with a SET aryl bromide activation step are proposed for the C–O cross coupling reactions catalyzed by the

Cs_2CO_3–CuI system based on the detection of complexes **A** and **B** in the *in situ* ESI-MS study. The *in situ* EPR study confirms the presence of a Cu(II) species in the reaction solution. Addition of the free radical scavenger cumene reduced the yield of the reaction, and the detection of the aryl compound and prop-1-en-2-ylbenzene formed from the reaction between the Ar$^•$ and cumene further supports the existence of Ar$^•$ and thus the free radical path of the aryl halide activation step in the catalytic cycle.

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