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PAPER

Reactivity of $[K_3(phen)_8][Cu(NPh_2)_2]_3$—a possible intermediate in the copper(I)-catalyzed N-arylation of *N*-phenylaniline†

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Complex $[K_3(phen)_8][Cu(NPh_2)_2]_3$ (**1**, phen = phenanthroline) was isolated from the catalytic C–N cross coupling reaction based on the CuI-phen-*t*BuOK catalytic system. Complex **1** can react with 4-iodotoluene to give 4-methyl-*N*,*N*-diphenylaniline (**3a**) in 50% yield (based on all available NPh_2^- ligands of complex **1**). In addition, **1** can also work as an effective catalyst for the C–N coupling reactions under the same reaction conditions, indicating that **1** may be an effective intermediate of the catalytic system. In the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), a radical scavenger, the stoichiometric reaction between complex **1** and 4-iodotoluene was significantly quenched to give a low yield of 12%. The results suggest that the radical path dominates in the reaction, with (phen)$KNPh_2$ as the possible radical source. The structures of **1** and (phen)$KNPh_2$ were both determined by single crystal X-ray diffraction studies.

Introduction

The C–N cross coupling reaction is a useful procedure for aryl amine synthesis in biological, pharmaceutical, and chemical materials.[1] The catalytic reaction has been intensively studied due to its economic attractiveness, low toxicity, and air and moisture stability.[2] The formation of the copper complex with the amido ligand may be the first step in the catalytic cycle of the copper-catalyzed N-arylation of amides, followed by the oxidative addition of the aryl halide.[3] We have reported the isolation of $[Na(phen)_3][Cu(NPh_2)_2]$ (**2**) from the CuI-phen-*t*BuONa catalytic system. In addition, $[Cu(NPh_2)_2]^-$, $\{Na[Cu(NPh_2)_2(p\text{-tolyl})]\}^+$ and $[Cu(NPh_2)I]^-$ were observed by *in situ* electrospray ionization mass spectrometry (ESI-MS) analysis for the catalytic reaction, indicating that they are intermediates of the reaction. A catalytic cycle was proposed based on these observations.[4] Mechanisms involving either the 2e oxidative addition path or the free radical path for the activation of aryl halide in the copper-catalyzed C–N cross coupling reaction have also been reported.[5] Among all these studies, the influence of a base is however seldom addressed. Recently, the copper(II) complex $\{K[Cu(phen)(NPh_2)(p\text{-tolyl})]\}^+$ was found by *in situ* ESI-MS study to be present in the CuI-phen-(*t*BuONa/K_2CO_3) mixed-base catalytic system, and a dual reaction path involving both the 2e oxidative addition path and the free radical path was thus proposed.[6] These observations suggest that the cross coupling reaction may undergo a different catalytic path when *t*BuOK is used as the base instead of *t*BuONa.

In this study, we have isolated **1** from the CuI-phen-*t*BuOK catalytic system, which showed quite a different reactivity from **2**, consistent with our finding that the reactivity of the cross coupling reaction depends significantly on the counter cation of the base, *t*BuOM (M = Na, K).

We report herein the isolation, structure characterization and reactivity of complex **1** from the CuI-phen-*t*BuOK catalytic system.

Results and discussion

We followed the general procedure reported in the literature to investigate the copper-catalyzed C–N cross coupling reaction between aryl iodide and amine.[7] Toluene is chosen as the solvent, instead of the frequently used DMF or DMSO, because it is a greener solvent and easier to work up. Typical catalytic reactions were performed by heating a mixture of aniline (1.2 equiv.), aryl iodide (1.0 equiv.), *t*BuOM (M = Na or K; 3 equiv.), CuI (10 mol%) and phen (30 mol%) in toluene at

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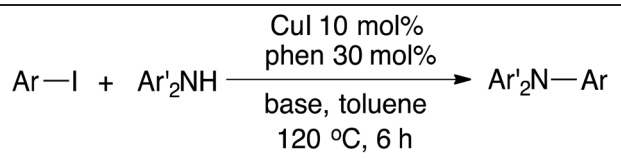
Table 1 Cu(I) catalyzed C–N coupling reaction with different base systems[a]



Entry	ArI	Ar′$_2$NH	Conversion/GC yield (%) *t*BuONa (3 equiv.)	*t*BuOK (3 equiv.)
1	C_6H_5I	Ph_2NH	49/47	98/95
2	4-$MeOC_6H_4I$	Ph_2NH	48/33	91/76
3	4-MeC_6H_4I	Ph_2NH	46/38	99/80
4[b]	4-MeC_6H_4I	Ph_2NH	53/35	100/50
5[c]	4-MeC_6H_4I	Ph_2NH	61/40	90/45
6[d]	4-MeC_6H_4I	Ph_2NH	—	46/43
7[e]	4-MeC_6H_4I	Ph_2NH	—	57/35
8	2-MeC_6H_4I	Ph_2NH	22/12	63/52
9	C_6H_5I	(p-Tolyl)$_2$NH	44/42	100/74

[a] 1.0 mmol ArI, 1.2 mmol *N*-phenylaniline, 4 mL toluene, 0.1 mmol CuI, 0.3 mmol phen, 3 mmol base. [b] Add 3 mmol TEMPO. [c] Add 0.5 mmol cumene. [d] Reaction time: 30 min. [e] Add 0.3 mmol TEMPO and use 30 min reaction time.

120 °C for 6 h. The results are summarized in Table 1; the yields of these catalytic reactions were measured based on the aryl iodides used. The results showed that the reactions based on the CuI-phen-*t*BuOK catalytic system give about twice better yields than those reactions with the CuI-phen-*t*BuONa catalytic system (Table 1, entries 1–3). The reaction of 2-iodotoluene (1 equiv.) with *N*-phenylaniline (1.2 equiv.) catalyzed by CuI-phen-*t*BuONa gave 2-methyl-*N*,*N*-diphenylaniline (**3b**) in 12% yield, which is four times lower than the yield (52%) of the same reaction based on the CuI-phen-*t*BuOK catalytic system (Table 1, entry 8) under the same reaction conditions. The results imply that the more hindered 2-iodotoluene can somehow be better activated by the CuI-phen-*t*BuOK catalytic system. In addition, the free radical path is present because the addition of the free radical scavenger TEMPO or cumene reduces the turnover frequency of the reaction (Table 1, entries 3–5). In order to investigate the reason for their different reactivity behaviours, intermediates $[K_3(phen)_8][Cu(NPh_2)_2]_3$ (**1**) and $[Na(phen)_3][Cu(NPh_2)_2]$ (**2**) were isolated from the corresponding catalytic systems,[4] and their structures and activities were studied.

Structure of 1 and reactivity of 1 and 2

Complex **1** is characterized by single-crystal X-ray analysis and its structure is shown in Fig. 1, which contains three K^+ ions ligated by eight phen and three bis(*N*-phenylanilide)copper(I) anions. Quite interestingly, complex **1** also contains the analogous counter anion $[Cu(NPh_2)_2]^-$ as found in the previously reported complex of $[K(phen)_3][Cu(NPh_2)_2]$, which was synthesized from the reaction mixture of *t*BuOCu, $HNPh_2$, $KNPh_2$ and phen.[8,4b]

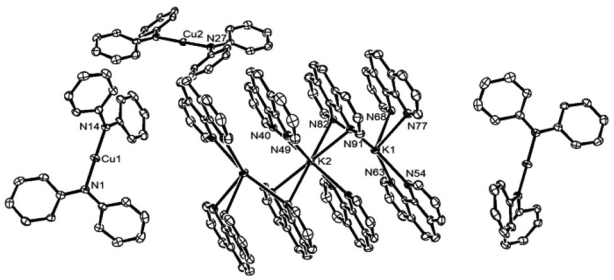


Fig. 1 ORTEP drawing of **1**, with 50% thermal ellipsoids. Hydrogen atoms are omitted.

If **1** is the effective catalytic intermediate, it alone should be sufficient to react with 4-iodotoluene stoichiometrically to form the product **3a** without requiring the use of potassium *tert*-butoxide, assuming that the base only serves to convert *N*-phenylaniline to an *N*,*N*-diphenylamide anion.

Hence, **1** (containing 3 equiv. of Cu species) was allowed to react with an excess amount (12 equiv.) of 4-iodotoluene (with 4-iodotoluene/Cu = 4) in toluene at 120 °C for 6 h to form **3a** in 50.0% yield, counted against all NPh_2^- ligands of complex **1** (Table 2, entry 1). In addition, **1** also works as an effective catalyst for the catalytic C–N cross coupling reaction between *N*-phenylaniline and 4-iodotoluene. For example, when 3.3 mol% of **1** (containing 10 mol% of Cu(I) species) was added into a mixture of *N*-phenylaniline (1.2 equiv.), 4-iodotoluene (1 equiv.), and potassium *tert*-butoxide (3 equiv.) in toluene, the catalytic C–N cross coupling reaction proceeded effectively at 120 °C in 6 h to give **3a** in 47% yield (based on the used 4-iodotoluene). These observations suggest that **1** could be an effective catalytic intermediate in the CuI-phen-*t*BuOK catalyst system.

In order to obtain a better understanding of the catalytic cycle of the C–N cross coupling reaction, we have compared the activities of the stoichiometric reactions between the Cu complexes (**1** and **2**) and 4-iodotoluene, and the results are displayed in Table 2. The yields for these stoichiometric reactions were respectively measured based on all available NPh_2^- ligands within the corresponding complexes. Under the same reaction conditions (*e.g.*, in toluene at 120 °C for 6 h), complex **1** (1 equiv.; corresponding to 3 equiv. of Cu(I) species) reacted with 4-iodotoluene (12 equiv.) to give **3a** in 50.0% yield (based

Table 2 Stoichiometric reaction between Cu(I) complexes and 4-iodotoluene[a]

Entry	Radical scavenger	Cu(I) complex	Conversion/GC yield[d] (%)
1	—	**1**	51/50
2[b]	—	**1**	99/81
3	—	**2**	61/61
4	TEMPO[c]	**1**	12/12
5	TEMPO[c]	**2**	51/50

[a] 0.08 mmol 4-iodotoluene, 0.007 mmol complex **1** or 0.02 mmol complex **2**, 1 mL toluene. [b] Add 0.08 mmol *t*BuOK. [c] 0.02 mmol TEMPO was used; with TEMPO/Cu = 1. [d] Based on all available NPh_2^- ligands in the corresponding complex.

on NPh_2^- ligands of complex **1**) (Table 2, entry 1), while complex **2** (3 equiv.) reacted with 4-iodotoluene (12 equiv.) to give **3a** in 61.0% yield (based on NPh_2^- ligands of complex **2**) (Table 2, entry 3). The higher turnover frequency of **2** than **1** implies that the counter cation may have an influence on the reactivity of the Cu(I) complex, and this may also imply that different catalytic mechanisms may be involved.

It has been reported that when a mixed base (*t*BuONa/K_2CO_3) is used in a copper-catalyzed C–N cross coupling reaction, the radical path is also involved in the mechanism.[6] This may imply that if solely *t*BuOK is used, the radical path may even dominate the mechanism of aryl halide activation. In order to clarify the existence of the free radical path, the effect of free radical scavenger TEMPO on the coupling reaction was examined. When the same amount of TEMPO (*e.g.*, with 1 equiv. TEMPO per Cu species) was added, the yield for the reaction of complex **1** reduced dramatically from 50% to 12% (Table 2, entry 4), while the yield for the reaction of complex **2** reduced only slightly from 61% to 50% (Table 2, entry 5) under the same reaction conditions. The results suggest that the reaction involving complex **1** may mainly go through a radical path, whereas the reaction involving complex **2** mainly undergoes a 2e oxidative addition path.

In situ ESI-MS analyses of the stoichiometric reactions of 1 and 2 with aryl iodide

To further clarify these possibilities, *in situ* ESI-MS analyses were carried out to investigate the reactions. A similar reaction mixture of complex **1** (or complex **2**) and 4-iodotoluene in toluene was stirred at 120 °C for 1 h. The solution was then transferred to a GC vial in a dry box. The temperature was kept at 120 °C by immersing the GC vial in a sand bed, and ESI-MS spectra of the solution were taken.

The ESI-MS results indeed showed different spectral behaviours for these two reaction systems. For complex **2**, all the intermediates previously reported for the reaction based on the CuI-phen-*t*BuONa catalytic system were also observed in the stoichiometric reaction of **2** with 4-iodotoluene, while not all the intermediates were observed in the stoichiometric reaction of **1** with 4-iodotoluene. Only $[K(phen)_3]^+$, $[Cu(phen)_2]^+$ and $[K(phen)_2]^+$ were detected.

For the stoichiometric reaction of **2** with 4-iodotoluene, peaks at m/z = 563.2, 423.1, 383.1 and 513.1 corresponding to $[Na(phen)_3]^+$, $[Cu(phen)_2]^+$, $[Na(phen)_2]^+$ and $\{Na[Cu(NPh_2)_2(p\text{-tolyl})]\}^+$ respectively were observed in the positive-ion mode of ESI-MS, and their measured accurate mass and isotopic distribution patterns are consistent with the assigned species (Fig. 2). These observations indicate that the ligand redistribution had occurred in the stoichiometric reaction. In addition, the ESI-MS in the negative-ion mode shows a peak at m/z = 399.1, which is identified as $[Cu(NPh_2)_2]^-$, and its measured accurate mass and isotopic distribution patterns are consistent with the assigned species (Fig. 3). The observed Cu(III) complex of $\{Na[Cu(NPh_2)_2(p\text{-tolyl})]\}^+$ implies the presence of $Cu(NPh_2)_2(p\text{-tolyl})$ species (that pick up a Na^+ and are detected by the positive-ion mode of the ESI-MS measurement) in the reaction mixture, which may have resulted from $[Cu(NPh_2)_2(p\text{-tolyl})I]^-$ by losing the iodide anion. As expected, the iodide anion was also observed in the negative-ion mode of ESI-MS. The result implies that 4-iodotoluene reacts with $[Cu(NPh_2)_2]^-$ to form $[Cu(NPh_2)_2(p\text{-tolyl})I]^-$ through a 2e oxidative addition path (Scheme 1). Thus, these observations indicate that $[Cu(NPh_2)_2]^-$ is indeed the active catalyst species in the stoichiometric reaction of complex **2**. These results are consistent with the previously reported data for the catalytic reaction using the CuI-phen-*t*BuONa catalyst system.[4]

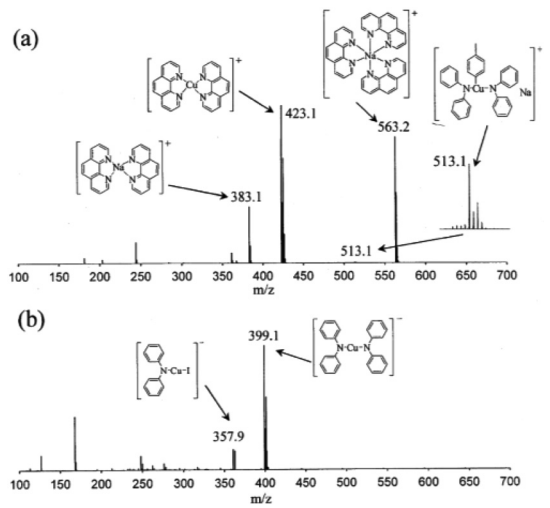


Fig. 2 (a) ESI(+)-MS and (b) ESI(−)-MS from the reaction solution taken during the reaction of 4-iodotoluene, *N*-phenylaniline with complex **2** in toluene at 120 °C.

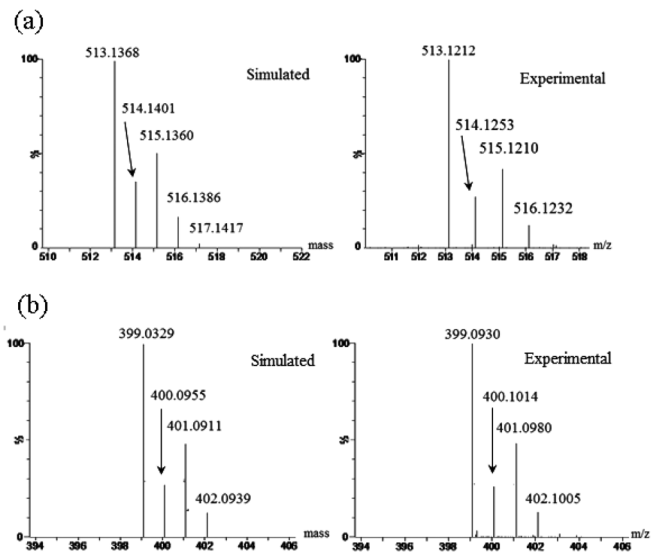
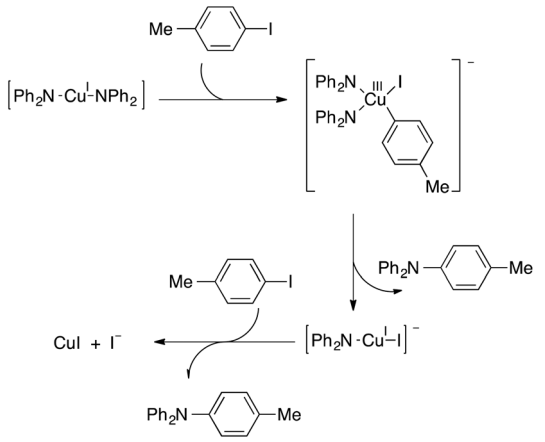


Fig. 3 Simulated and experimental isotopic distributions of (a) $[Cu(NPh)_2(p\text{-tolyl})Na]^+$ and (b) $[Cu(NPh_2)_2]^-$.

Reaction paths of the C–N coupling reactions of 1 and 2

During the reaction of **1** with 4-iodotoluene, redistribution of the phen and NPh_2^- ligands among metal cations may occur



Scheme 1 The proposed mechanism of the reaction between **2** and 4-iodotoluene.

to form the observed cationic complex $[Cu(phen)_2]^+$ (by the ESI-MS spectra in the positive ion mode), and possibly also the neutral complexes such as $Cu(phen)(NPh_2)$ and $(phen)KNPh_2$ (which were not detectable by ESI-MS, because they are neutrally charged). The observed ESI-MS data behaviors may be accounted by the fact that the radical path dominates the reaction mechanism when complex **1** is used. Presumably, the radical mechanism involves neutrally charged intermediate species, which are invisible to ESI-MS.

For example, a *p*-tolyl free radical $[p\text{-}CH_3C_6H_4]^{\bullet}$ may be generated from the radical anions $[p\text{-}CH_3C_6H_4I]^{\bullet-}$ that resulted from the reaction between 4-iodotoluene and a potential single electron donor, such as $(phen)KNPh_2$. The *p*-tolyl free radical may add to the Cu(I) complex, $Cu(phen)(NPh_2)$, to generate a neutral Cu(II) complex, $[Cu(phen)(NPh_2)(p\text{-tolyl})]$, which is not detectable by ESI-MS in this reaction. Actually, such a species has been previously observed by ESI-MS as a K^+ complex, $\{K[Cu(phen)(NPh_2)(p\text{-tolyl})]\}^+$, in other radical-based reaction systems such as the CuI-phen-(tBuONa/K_2CO_3) mixed-base catalytic system.[6]

The (phen)KO*t*Bu complex was reported to act as a single electron donor toward aryl iodide and led to the coupling between aryl halide and benzene without the need of a transition metal catalyst.[9] If $(phen)KNPh_2$ can work as a single electron donor just like (phen)KO*t*Bu, then similar C–C coupling products should also be observed in a similar reaction. For this purpose, $(phen)KNPh_2$ was prepared as a red-brown powder by the reaction between *t*BuOK and *N*-phenylaniline in the presence of 1,10-phenanthroline. The structure of $(phen)KNPh_2$ was characterized by NMR and single crystal X-ray diffraction analysis and is shown in Fig. 4.

A stoichiometric reaction between $(phen)KNPh_2$ (1 equiv.) and 4-iodotoluene (1 equiv.) was carried out in toluene at 120 °C for 6 h. The products of C–C coupling between 4-iodotoluene and toluene, identified by GC-MS, were indeed observed. But, when TEMPO (1 equiv.) was added to the same reaction, the yield of the C–C coupling reaction products reduced from 17.8% to 5.6% (Scheme 2). The results indicate

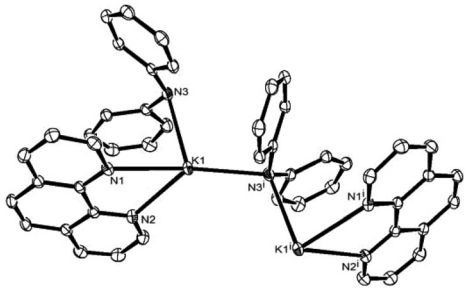
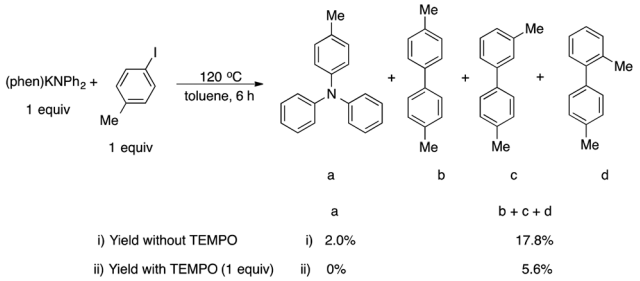


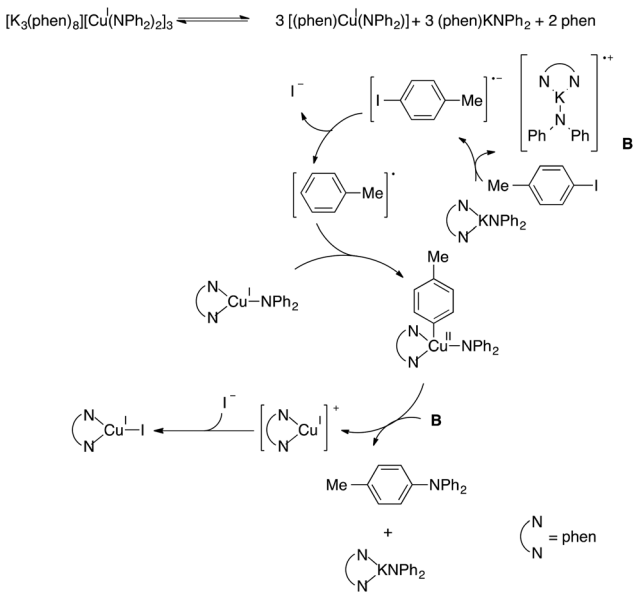
Fig. 4 ORTEP drawing of $(phen)KNPh_2$, with 30% thermal ellipsoids. Hydrogen atoms are omitted.



Scheme 2 Reaction between $(phen)KNPh_2$ and 4-iodotoluene with and without radical scavenger TEMPO.

that $(phen)KNPh_2$, similar to (phen)KO*t*Bu, can act as a single electron donor toward aryl iodide. A plausible mechanism for the reaction between **1** and 4-iodotoluene is shown in Scheme 3.

Although the CuI-phen-*t*BuOK catalytic system produced twice higher turnover frequency than the CuI-phen-*t*BuONa catalytic system, the yield for the stoichiometric reaction of



Scheme 3 The proposed radical path of the reaction between **1** and 4-iodotoluene.

complex **1** with 4-iodotoluene is somewhat lower than that of complex **2** with 4-iodotoluene (Table 2, entries 1 and 3). This may be due to the presence of fewer radical donor species in the stoichiometric reaction of complex **1**. When an additional 4.0 equiv. of *t*BuOK was added to the stoichiometric reaction of complex **1**, the yield increased to 81% (Table 2, entry 2). The additional *t*BuOK provides additional (phen)KO*t*Bu as an electron donor, and thus increases the overall yield of the reaction.

The role of phen and *t*BuOK

In order to evaluate whether the radical path is existing in the absence of phen, catalytic reactions with and without the addition of radical scavenger were carried out using the CuI/*t*BuOK catalytic system. Thus, a toluene solution of *N*-phenylaniline (1.2 equiv.), *t*BuOK (2.0 equiv.), CuI (10 mol%) and 4-iodotoluene (1 equiv.) was stirred at 120 °C for 30 min to give products in 18.9%. With the addition of TEMPO (1 equiv.), the reaction gave almost the same yield (*i.e.*, 17.6%) within the experimental errors. This indicates that, in the absence of phen, the radical path does not exist.

Ligand redistribution (or exchange) between the metal cations has surely occurred in the stoichiometric reactions of both **1** and **2** as well as in the catalytic reaction of CuI-phen-*t*BuOK and CuI-phen-*t*BuONa, as confirmed by the observation of the ligand-exchanged cationic species $[Cu(phen)_2]^+$ in their ESI-MS spectra. Conceivably, the stable complex species formed during the intermediate ligand-exchange stage, *i.e.*, (phen)$CuNPh_2$, should have also existed in all the above reactions. It is envisaged that the complex (phen)$CuNPh_2$ can accept the *p*-tolyl free radical $[p\text{-}CH_3C_6H_4]^\bullet$, which results from the electron transfer reaction between 4-iodotoluene and the single electron donor (phen)MO*t*Bu or (phen)$MNPh_2$ (M = K or Na), to generate the neutrally charged intermediate of [Cu(phen)(NPh_2)(*p*-tolyl)] and further complete the reaction. The fact that reactions of **1** mainly go through the free radical path implies that the electron donation ability of the potassium complex, (phen)$KNPh_2$, is stronger than that of the sodium complex, (phen)$NaNPh_2$. Similarly, the stronger electron donating ability of (phen)KO*t*Bu *versus* (phen)NaO*t*Bu has also been reported in the study of C–H arylation with MO*t*Bu (M = Na or K) in the presence of phen or other ligands.[9] Furthermore, the fact that the CuI/phen/*t*BuONa catalytic system also shows far less radical path contribution than the CuI/phen/*t*BuOK catalytic system further supports the above argument.[6]

Apparently, the use of both phen and *t*BuOK is essential for the reaction to proceed through a radical path, because it provides not only (phen)KO*t*Bu or (phen)$KNPh_2$ as an effective free radical source,[9] but also (phen)$CuNPh_2$ as an acceptor for the *p*-tolyl radical to form $[Cu^{II}(phen)(NPh_2)(p\text{-tolyl})]$.

Conclusions

In summary, complexes **1** and **2** have been isolated from the reaction mixture of catalytic C–N cross coupling reactions catalyzed by CuI-phen-*t*BuONa and CuI-phen-*t*BuOK respectively. Both complexes can catalyze the C–N coupling reaction between aryl iodide and *N*-phenylaniline, indicating that they could be the intermediates of the reaction. The different reactivities of complexes **1** and **2** towards 4-iodotoluene imply that they have undergone different reaction pathways. A drastic yield reduction occurred in the reaction between **1** and 4-iodotoluene in the presence of TEMPO, which implies that the radical path dominates the reaction. In contrast, 2e oxidative addition is the major path for the reaction between **2** and 4-iodotoluene.

Experimental

General procedures

All reagents were purchased from commercial sources and used without further purification. Copper(I) iodide (fine grey powder), *N*-phenylaniline, iodobenzene, 2-iodotoluene, 4-iodoanisole, 4-iodotoluene, 1,10-phenanthroline, *t*BuOK, *t*BuONa, and 1,4-di-*tert*-butylbenzene were purchased from ACROS. Toluene (dried, SeccoSolv®) was purchased from Merck and purged with argon for 15 min before use. All reagents were transferred to the reaction vessel (Pyrex tube with a Teflon screw cap) in a glove box. ^{1}H NMR spectra were recorded using Bruker AV 300 and Bruker AMX 400 instruments. GC-MS experiments were performed on an Agilent 7890A gas chromatograph equipped with a 30 m × 0.25 mm × 3.0 m HP-5 capillary column and an MSD detector. GC experiments were performed on an Agilent 6890N gas chromatograph equipped with a 30 m × 0.53 mm × 3.0 μm HP-1 capillary column and a FID detector. Elemental analysis was performed on a Thermo CHNS-O analyzer (FlashEA 1112 series). High resolution ESI-MS were measured using a Waters LCT Premier XE with a dual ionization ESCi® in the Mass Spectrometry Facility in the Institute of Chemistry, Academia Sinica. Leucine enkephalin $[M + H]^+$ 556.277 was used as a reference standard.

Crystal structure determination of complex 1

A single crystal of a suitable size was attached to a glass fiber and mounted on a goniometer head. Data were collected on a Bruker SMART CCD diffractometer at 100 K using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). A total of 47 735 reflections were sorted and merged using a Bruker SAINT, giving 11 597 independent data. Structure refinement with SHELXL97-2[10] was undertaken using full-matrix least-squares on F^2 and all of the unique data. All of the non-H atoms are refined anisotropically. The refinement details are given in the ESI.† The thermal ellipsoid plot was obtained using ORTEP-3[11] program for Windows; all of the calculations were carried out using the WinGX[12] package.

$[Cu(NPh_2)_2]_3[K_3(phen)_8]$ is crystallized in the monoclinic space group $P2_1/c$. An overview and the numbering scheme are displayed in Fig. 1. The molecule consists of a discrete tricationic $K_3(phen)_8^{3+}$ and three $Cu(NPh_2)_2^-$ anions. For the

$Cu(NPh_2)_2^-$ anions, there are two different Cu atoms in the crystal. The Cu(1) and K(1) sit in general positions in the unit cell, and Cu(2) and K(2) are located at the inversion center. Each Cu atom is coordinated with two NPh_2^- ligands.

The torsion angle between two diphenyl amine ligands built from four phenyl groups is flatter in the Cu(2) fragment than that in the Cu(1) fragment with torsion angles 5.2° (∠C28–N27–$N27^i$–$C34^i$, *i*: $-x$, $-y$, $-z$) and 54.9° (∠C8–N1–N14–C15) respectively.

Crystal structure determination of (phen)$KNPh_2$

Intensity data were collected on an Oxford Atlas-CCD diffractometer for (phen)$KNPh_2$ single crystal at 100 K, using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Integration on the intensity measurement was performed using the CrysAlisPro[13] package. Structure was refined using SHELXL97-2 with full-matrix least-squares on F^2. All programs were performed using WinGX software. Detailed information is summarized in the ESI.†

(phen)$KNPh_2$ is crystallized in an orthorhombic space group *Pbca*. Potassium ion is four-coordinated, with one phen and two NPh_2^- ligands. The nitrogen atom of the NPh_2^- anion bridges two potassium ions and each metal is again linked by two NPh_2^- resulting in an infinite chain type packing.

Typical procedure of the copper(I) catalyzed C–N coupling reaction

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.30 mmol, 30 mol%), base (3.0 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and toluene (4 mL) were transferred to a Pyrex tube with a Teflon screw cap. After stirring for 5 min, aryl amine (1.2 mmol) and aryl halide (1.0 mmol) were added, and the resulting mixture was stirred for an additional 20 min at room temperature. The reaction mixture was then heated at 120 °C in an oil bath for 6 h. After the reaction, the tube was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was first diluted with CH_2Cl_2 (10 mL), and then filtered to remove any insoluble residues by Celite. All products were identified by GC-MS, and the yield was determined by quantitative GC analysis by adding 1,4-di-*tert*-butylbenzene as the internal standard. All GC data are provided in the ESI.†

Reaction of copper(I) catalyzed C–N coupling with different base systems

Similar procedure, amount of reagents and reaction conditions as in the typical procedure stated above was applied to the reaction. For reactions using *t*BuOK as the base, 336.0 mg, 3.0 mmol of *t*BuOK was used. For reactions using *t*BuONa as the base, 288.0 mg, 3.0 mmol of *t*BuONa was used.

Reaction between N-phenylaniline and iodobenzene with tBuOK for 6 h: GC yield: 95% (correction factor for triphenylamine (**3c**): 0.827).

Reaction between N-phenylaniline and 4-iodoanisole with tBuOK for 6 h: GC yield: 76% (correction factor for 4-methoxy-*N*,*N*-diphenylaniline (**3d**): 0.843).

Reaction between N-phenylaniline and 4-iodotoluene with tBuOK for 6 h: GC yield: 80% (correction factor for 4-methyl-*N*,*N*-diphenylaniline (**3a**): 0.818).

Reaction between N-phenylaniline and 4-iodotoluene with tBuOK and 3.0 equiv. of TEMPO (488 mg, 3.0 mmol) for 6 h: GC yield: 50% (correction factor for 4-methyl-*N*,*N*-diphenylaniline (**3a**): 0.818).

Reaction between N-phenylaniline and 4-iodotoluene with tBuOK for 30 min: GC yield: 43% (correction factor for 4-methyl-*N*,*N*-diphenylaniline (**3a**): 0.818).

Reaction between N-phenylaniline and 4-iodotoluene with tBuOK and 3.0 equiv. of TEMPO (488 mg, 3.0 mmol) *for 30 min*: GC yield: 35% (correction factor for 4-methyl-*N*,*N*-diphenylaniline (**3a**): 0.818).

Reaction between N-phenylaniline and 2-iodotoluene with tBuOK for 6 h: GC yield: 52% (correction factor for 2-methyl-*N*,*N*-diphenylaniline (**3b**): 0.818).

Reaction between di-p-tolylaniline and iodobenzene with tBuOK for 6 h: GC yield: 74% (correction factor for 4-methyl-*N*-phenyl-*N*-*p*-tolylaniline (**3e**): 0.735).

Reaction between N-phenylaniline and iodobenzene with tBuONa for 6 h: GC yield: 47% (correction factor for triphenylamine (**3c**): 0.827).

Reaction between N-phenylaniline and 4-iodoanisole with tBuONa for 6 h: GC yield: 33% (correction factor for 4-methoxy-*N*,*N*-diphenylaniline (**3d**): 0.843).

C–N coupling reaction between N-phenylaniline and 4-iodotoluene with tBuONa for 6 h: GC yield: 38% (correction factor for 4-methyl-*N*,*N*-diphenylaniline (**3a**): 0.818).

Reaction between N-phenylaniline and 2-iodotoluene with tBuONa for 6 h: GC yield: 12% (correction factor for 2-methyl-*N*,*N*-diphenylaniline (**3b**): 0.818).

Reaction between di-p-tolylaniline and iodobenzene with tBuONa for 6 h: GC yield: 42% (correction factor for 4-methyl-*N*-phenyl-*N*-*p*-tolylaniline (**3e**): 0.735).

Copper catalyzed C–N cross coupling reaction based on CuI/phen/*t*BuOK

Without TEMPO: In a glove box, CuI (19.0 mg, 0.1 mmol), 4-iodotoluene (218.0 mg, 1.0 mmol), *N*-phenylaniline (203.0 mg, 1.2 mmol), 1,10-phenanthroline (54.0 mg, 30 mol %), *t*BuOK (336 mg, 3.0 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and 4 mL of toluene were transferred into a 15 mL Pyrex tube with a Teflon screw cap. The above mixture was stirred and heated at 120 °C in an oil bath for 30 minutes. The GC yield of **3a** was 43.4% (correction factor for **3a**: 0.688).

Another reaction was carried out for longer reaction time, *i.e.*, 6 h using the same procedure, amount of reagents and reaction conditions. The GC yield of **3a** was 80.0% (correction factor for **3a**: 0.787).

With TEMPO: Similar procedure, amount of reagents and reaction conditions as above was applied to the reaction except that 3.0 equiv. of TEMPO (488 mg, 3.0 mmol) was used. The GC yield of **3a** for 30 min reaction time was 34.7%. The GC yield of **3a** for 6 h reaction time was 50.0% (correction factor for **3a**: 0.688).

Separation of 1 from the reaction mixture

In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (54.0 mg, 0.3 mmol, 30 mol%), *t*BuOK (224.0 mg, 2.0 mmol) and toluene (4 mL) were transferred into a 15 mL Pyrex tube with a Teflon screw cap. After stirring for 5 min, *N*-phenylaniline (203.0 mg, 1.2 mmol) was added, and the resulting mixture was stirred for additional 20 min at room temperature. A reddish brown precipitation was obtained. The mixture was then heated up to 120 °C in an oil bath for 30 min, and a transparent reddish brown solution was obtained. The brown solution was cooled to room temperature, and a reddish brown crystal of $[K_3(phen)_8][Cu(NPh_2)_2]_3$ was separated from other solid precipitates by hand-picking. Yield: 36.0 mg (39.2%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 6.90 (s, br, 18H), 7.02–7.09 (m, 30H), 7.25 (t, J = 7.2 Hz, 16H), 7.58 (d, J = 3.3 Hz, 15H), 7.82 (s, 15H), 8.28 (d, J = 7.8 Hz, 15H), 8.98 ppm (s, br, 15H); elemental analysis calcd (%) for $C_{168}H_{124}Cu_3K_3N_{22}$: C 73.14, H 4.53, N 11.17; found: C 73.01, H 4.51, N 11.14.

Stoichiometric reaction between complex 1 and 4-iodotoluene

Without TEMPO: In a glove box, **1** (18.4 mg, 0.007 mmol), 4-iodotoluene (17.5 mg, 0.08 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and 1 mL of toluene were transferred into a 15 mL Pyrex tube with a Teflon screw cap. The above mixture was stirred and heated at 120 °C in an oil bath for 6 h, and **3a** was obtained with a 50.0% GC yield based on all available NPh_2^- ligands in complex **1** (correction factor for **3a**: 0.818).

With TEMPO: 100 mol% (*vs.* overall Cu species) of TEMPO (3.2 mg, 0.02 mmol) was added into the mixture as stated above. **3a** was obtained with a 12.0% GC yield based on all available NPh_2^- ligands in complex **1** (correction factor for **3a**: 0.818).

Stoichiometric reaction between complex 2 and 4-iodotoluene

Without TEMPO: In a glove box, **2** (19.4 mg, 0.02 mmol), 4-iodotoluene (17.5 mg, 0.08 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and 1 mL of toluene were transferred into a 15 mL Pyrex tube with a Teflon screw cap. The above mixture was stirred and heated at 120 °C in an oil bath for 6 h, and **3a** was obtained with a 61.0% GC yield based on all available NPh_2^- ligands in complex **1** (correction factor for **3a**: 0.818).

Addition with 100 mol% TEMPO: TEMPO (3.2 mg, 0.02 mmol; 100 mol% (*vs.* overall Cu species) was added into the mixture. **3a** was obtained with a 50.0% GC yield based on all available NPh_2^- ligands in complex **2** (correction factor for **3a**: 0.818).

Stoichiometric reaction between complex 1 and 4-iodotoluene plus additional *t*BuOK

In a glove box, **1** (18.4 mg, 0.007 mmol), 4-iodotoluene (17.5 mg, 0.08 mmol), *t*BuOK (9.0 mg, 0.08 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and 1 mL of toluene were transferred into a 15 mL Pyrex tube with a Teflon screw cap. The above mixture was stirred and heated at 120 °C in an oil bath for 6 h, and **3a** was obtained with an 81.0% GC yield based on all available NPh_2^- ligands in complex **1** (correction factor for **3a**: 0.818).

Synthesis of complex (phen)$KNPh_2$

In a glove box, *t*BuOK (180.0 mg, 1.6 mmol), *N*-phenylaniline (676.0 mg, 4.0 mmol), 1,10-phenanthroline (290.0 mg, 1.6 mmol) and 12 mL of toluene were transferred into a 50 mL Pyrex tube with a Teflon screw cap. The above mixture was stirred at room temperature for 24 h. The resultant red precipitation was collected by filtration, which was washed several times with toluene and then dried under reduced pressure. Complex of (phen)$KNPh_2$ was obtain in 187.0 mg (30%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 6.80 (d, J = 1.2 Hz, 2H), 7.08 (m, 2H), 7.16–7.28 (m, 4H), 7.65 (q, J = 2.34 Hz, 2H), 7.83 (d, J = 2.34 Hz, 2H), 8.29 (q, J = 1.74 Hz, 2H), 9.13 ppm (q, J = 1.74 Hz, 2H). Elemental analysis calcd (%) for $C_{24}H_{18}KN_3$: C 74.39, H 4.68, N 10.84; found: C 74.39, H 4.83, N 10.87.

Stoichiometric reaction between (phen)$KNPh_2$ and 4-iodotoluene

Without TEMPO: In a glove box, (phen)$KNPh_2$ (38.7 mg, 0.10 mmol), 4-iodotoluene (21.8 mg, 0.10 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and 2 mL of toluene were transferred into a 15 mL Pyrex tube with a Teflon screw cap. The above mixture was stirred and heated at 120 °C in an oil bath for 6 h, and **3a** was obtained with a 2.0% GC yield (correction factor for **3a**: 0.818). Byproducts (biphenyl isomers) were obtained with a 17.8% GC yield (correction factor for byproduct: 1.17).

With TEMPO: 100 mol% of TEMPO (15.6 mg, 0.1 mmol) was added to the above reaction mixture. **3a** was obtained with a 0% GC yield. Byproducts (biphenyl isomers) were obtained with a 5.6% GC yield (correction factor for byproduct: 1.17).

Copper catalyzed C–N cross coupling reaction based on CuI/*t*BuOK

Without TEMPO: In a glove box, CuI (19.0 mg, 0.1 mmol), 4-iodotoluene (218.0 mg, 1.0 mmol), *N*-phenylaniline (203.0 mg, 1.2 mmol), *t*BuOK (224 mg, 2.0 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and 4 mL of toluene were transferred into a 15 mL Pyrex tube with a Teflon screw cap. The above mixture was stirred and heated at 120 °C in an oil bath for 30 minutes. The GC yield of **3a** was 18.9% (correction factor for **3a**: 0.818).

With 200 mol% TEMPO: Similar procedure, amount of reagents and reaction conditions as above was applied to the reaction except that 2.0 equiv. of TEMPO (312 mg, 2.0 mmol) was used. The GC yield of **3a** was 17.6% (correction factor for **3a**: 0.818).

Copper catalyzed C–N cross coupling reaction based on 1

In a glove box, **1** (47.0 mg, 0.017 mmol), 4-iodotoluene (109.0 mg, 0.5 mmol), *N*-phenylaniline (102.0 mg, 0.6 mmol), *t*BuOK (112.0 mg, 1.0 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.1 mmol) and toluene (2 mL) were transferred into

a 15 mL Pyrex tube with a Teflon screw cap. The above mixture was heated at 120 °C in an oil bath for 6 h, and **3a** was obtained with a 46.5% GC yield (1,4-di-*tert*-butylbenzene as an internal standard; correction factor for **3a**: 0.688).

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