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Synthesis, structure, and activity of $(PhCH_2NH_2)_2CuCl_2$ for oxidative coupling of 2-naphthylamine

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$(PhCH_2NH_2)_2CuCl_2$ (2), an effective oxidation reagent for oxidative coupling of 2-naphthylamine (1) to form 2,2′-diamino-1,1′-binaphthyl (4), is studied. Oxidative coupling of 2-naphthylamine (1) is carried out at room temperature in methanol by $(PhCH_2NH_2)_2CuCl_2$ (2), which is prepared from $CuCl_2 \cdot 2H_2O$ and benzylamine in methanol, to give a novel copper complex, $[\{1,1'\text{-}(C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (3), in good yield. Treatment of 3 with aqueous HCl (37%), followed by addition of $NH_3 \cdot H_2O$ (25%), gives 2,2′-diamino-1,1′-binaphthyl (4) in a moderate yield (total yield from 1: >70%). Both 2 and 3 have been characterized by various techniques, such as infrared spectroscopy, elemental analyses and X-ray diffraction. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: 2-naphthylamine; 2,2′-diamino-1,1′-binaphthyl; copper complexes; oxidative coupling

INTRODUCTION

Both the symmetric and nonsymmetric 2,2′-substituted-1,1′-binaphthyls are widely used as chiral ligands in organic synthesis and asymmetric synthesis.[1–10] In particular, 2,2′-dihydroxy-1,1′-binaphthyl (BINOL),[1–5] 2,2′-bis(diphenylphosphinyl)-1,1′-binaphthyl (BINAP)[2–8] and 2,2′-diamino-1,1′-binaphthyl (BINAM, **4**)[2–5,9,10] have been shown to exhibit good to excellent enantioselectivities in a number of asymmetric reactions. Thus, for example, diamine **4** and its derivatives have been employed as ligands for the enantioselective reduction of ketones,[11,12] hydrogenation of α-acylaminoacrylic acids,[13] and other transformations.[2–5,9,10,14,15]

Three approaches to racemic 2,2′-diamino-1,1′-binaphthyl (**4**) have been reported in the literature: (1) reaction of 2-naphthol with $N_2H_4 \cdot H_2O$ in a sealed bomb for 48–78 h at 170–180 °C, followed by treatment with concentrated HCl and NaOH, gives **4** in 36–55% yield;[13,16] (2) reaction of 2-naphthylamine (**1**) with $NaNO_2$ in the presence of H_2SO_4, followed by addition of NaOAc and Na_2SO_3, gives 2,2′-azonaphthalene, which is reduced by $SnCl_2$ or Zn-NH_4Cl to give 2,2′-hydrazonaphthalene; finally, rearrangement of 2,2′-hydrazonaphthalene in the presence of acid or by heating gives **4** in 40–60% yield (total yield from **1**);[17–19] (3) oxidative coupling of 2-naphthylamine (**1**) by copper(II)-mediated in *situ* gives **4** in 34–74% yield.[20–26] Here, we are interested in this type of oxidative coupling reaction, and recently, we have studied the reaction under various reaction conditions, and found that $(PhCH_2NH_2)_2CuCl_2$ (**2**) is an effective oxidation reagent in this type of oxidative coupling reaction. It can oxidize coupling of 2-naphthylamine (**1**) to give 2,2′-diamino-1,1′-binaphthyl (**4**) in a moderate yield (>70%). Herein we report the preparation of $(PhCH_2NH_2)_2CuCl_2$ (**2**) and its activity for oxidative coupling of 2-naphthylamine (**1**). The effects on the reaction, a facile preparation of 2,2′-diamino-1,1′-binaphthyl (**4**), on a large scale (20–30 g), as well as two copper complexes, oxidation reagent $(PhCH_2NH_2)_2CuCl_2$ (**2**) and intermediate $[\{1,1'\text{-}(C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (**3**), will also be discussed.

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EXPERIMENTAL

General methods

Materials

Methanol, 2-naphthylamine, $CuCl_2 \cdot 2H_2O$, HCl (37%), NH_4OH (25%) and benzene were purchased from Beijing Chemical Co. and used as received. Benzylamine was purchased from Aldrich Chemical Co. and distilled prior to use.

IR spectra

All FTIR spectra were obtained as KBr pellets on an Avatar 360 Fourier transform spectrometer in the range 4000–400 cm^{-1}.

Melting points

All melting points were measured on an X-6 melting point apparatus (Beijing Tech. Instrument Co. Ltd) and were uncorrected.

Elemental analyses

All elemental analyses were performed on a Vario EL elemental analyzer by the analytical laboratory, Beijing Normal University, Beijing, China.

Preparation of $(PhCH_2NH_2)_2CuCl_2$ (2)

$PhCH_2NH_2$ (3.15 g, 29.4 mmol) was added to a methanol (20 ml) solution of $CuCl_2 \cdot 2H_2O$ (2.50 g, 14.7 mmol) with stirring at room temperature. This mixture was stirred for 0.5 h at room temperature. During the course of the reaction, a green precipitate formed, which was filtered and washed with methanol (10 ml × 2) to give $(PhCH_2NH_2)_2CuCl_2$ (**2**) as a green solid. Yield: 4.60 g (90%). Suitable crystals for X-ray diffraction were isolated from the mother liquor, when this mixture was allowed to stand at room temperature overnight; m.p.: 184–185 °C (dec.). IR (KBr, cm^{-1}): ν 3433 (m), 3322 (m), 3209 (m), 3022 (m), 1598 (w), 1561 (m), 1494 (m), 1454 (m), 1153 (s), 1137 (s), 994 (s), 751 (s), 697 (s). Anal. calcd for $C_{14}H_{18}N_2Cl_2Cu$: C, 48.2; H, 5.20; N, 8.03. Found: C, 48.3; H, 5.05; N, 8.07.

General procedure for the oxidative coupling of 2-naphthylamine (1)

A methanol (10 ml) solution of 2-naphthylamine (**1**; 0.29 g, 2.0 mmol) was added to a methanol (20 ml) suspension of $(PhCH_2NH_2)_2CuCl_2$ (**2**; 1.40 g, 4.0 mmol) with stirring at room temperature. After stirring at room temperature for 2 h the solvent was removed to give a brown residue, which was first acidified with concentrated HCl (10 ml), stirred for 10 min, and then treated with concentrated NH_4OH (30 ml) for another 5 min and finally diluted with water (50 ml). The resulting suspension was filtered to give the crude product, which was recrystallized from benzene to yield **4** as a white solid. Yield: 0.20 g (71%).

Preparation of $[\{1,1'\text{-}(C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (3) and 2,2′-diamino-1,1′-binaphthyl (4)

A methanol (550 ml) solution of 2-naphthylamine (**1**; 24.5 g, 0.17 mol) was added to a suspension of $(PhCH_2NH_2)_2CuCl_2$ (**2**) in methanol (200 ml), which was prepared from $CuCl_2 \cdot 2H_2O$ (57.8 g, 0.34 mol) and $PhCH_2NH_2$ (72.8 g, 0.68 mol) using a similar procedure as described above, with stirring at room temperature. This mixture was stirred at room temperature for 2 h. During the course of the reaction, a brown precipitate formed, which was filtered and washed with methanol (50 ml × 3) to give $[\{(1,1'\text{-}C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (**3**) ($MW_{calc} = 789.23$) as a brown solid. Yield: 23.7 g (70%). Brown crystals suitable for an X-ray diffraction experiment were isolated from the mother liquor when this mixture was allowed to stand at room temperature overnight, or grown from a mixed solvent of CH_3OH and CH_2Cl_2 (4 : 1) at room temperature; m.p.: 155–156 °C (dec.). IR (KBr, cm^{-1}): ν 3425 (m), 3230 (m), 3096 (m), 1619 (s), 1597 (s), 1564 (m), 1508 (s), 818 (s), 749 (s). Anal. calcd for $C_{41}H_{42}N_4Cl_2CuO_4$: C, 62.4; H, 5.36; N, 7.10. Found: C, 62.4; H, 5.29; N, 6.93.

To a suspension of $[\{(1,1'\text{-}C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (**3**; 23.7 g, 30.0 mmol) in 200 ml of H_2O, was added 200 ml of 37% aqueous HCl with stirring at room temperature. After this mixture was stirred at room temperature for 30 min, 300 ml of 25% aqueous NH_4OH solution was added slowly with stirring at room temperature, followed by addition of H_2O (500 ml). The precipitate was filtered and washed with H_2O (100 ml × 2). The solid was stirred again with 100 ml of 37% aqueous HCl and 100 ml of H_2O for 10 min. A 25% aqueous solution of NH_4OH (150 ml) was slowly added to the solution and was then diluted with 300 ml of H_2O. The precipitate was filtered and washed with H_2O (100 ml × 2) to give a pink solid, 16.2 g (95%). The pink solid was recrystallized from benzene to give **4** as a white solid. Yield: 15.3 g (90%); m.p.: 192–194 °C (lit. m.p. 193.2–194.5 °C).[16]

X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart CCD diffractometer at 294(2) K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program.[27] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package.[28] Most of the hydrogen atoms (excluding those of the solvated H_2O) were geometrically fixed using the riding model. The crystal data and experimental data for **2** and **3** are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

RESULTS AND DISCUSSION

Treatment of $CuCl_2 \cdot 2H_2O$ with 2 equiv of $PhCH_2NH_2$ in methanol at room temperature for 0.5 h gives $(PhCH_2NH_2)_2CuCl_2$ (**2**) in 90% yield. Complex **2** is soluble in methanol, and insoluble in H_2O, toluene and *n*-hexane. **2** has been characterized by infrared spectroscopy and elemental analyses. The IR spectrum of **2** shows a typical characteristic

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Table 1. Crystal data and experimental parameters for compounds **2** and **3**

Compound	2	3
Formula	$C_{14}H_{18}N_2Cl_2Cu$	$C_{41}H_{42}N_4Cl_2CuO_4$
Formula weight	348.74	789.23
Crystal system	Orthorhombic	Monoclinic
Space group	*P*bca	*C*2
a (Å)	8.226(1)	26.424(4)
b (Å)	12.490(1)	10.745(2)
c (Å)	31.207(3)	14.338(2)
β (deg)	90	100.738(3)
V (Å^3)	3206.3(5)	3999.6(11)
Z	8	4
D_{calc} (g cm^{-3})	1.445	1.311
$\mu(\text{Mo}/\text{K}\alpha)_{\text{calc}}$ (mm^{-1})	1.68	0.72
Size (mm)	0.22 × 0.18 × 0.10	0.32 × 0.26 × 0.20
$F(000)$	1432	1644
2θ range (deg)	5.22 to 56.56	3.14 to 50.04
No. of reflns, collected	18 387	10 200
No. of unique reflns	3959 ($R_{\text{int}} = 0.041$)	5601 ($R_{\text{int}} = 0.035$)
No. of obsd reflns	3959	5601
No. of variables	172	471
Abscorr ($T_{\text{max}}, T_{\text{min}}$)	1.00, 0.61	1.00, 0.69
R	0.055	0.055
R_{w}	0.122	0.149
R_{all}	0.069	0.078
gof	1.18	1.09

Table 2. Selected bond distances (Å) and selected angles (deg) for **2**

Bond distances			
Cu(1)–Cl(1)	2.629(1)	Cu(1)–Cl(2)	2.300(1)
Cu(1)–N(1)	1.983(3)	Cu(1)–N(2)	1.984(3)
Bond angles			
N(1)–Cu(1)–N(2)	169.6(1)	Cl(1)–Cu(1)–Cl(2)	108.9(1)
Cl(1)–Cu(1)–N(1)	84.5(1)	Cl(1)–Cu(1)–N(2)	85.3(1)
Cl(2)–Cu(1)–N(1)	91.0(1)	Cl(2)–Cu(1)–N(2)	94.2(1)
Cu(1)–N(1)–C(1)	118.8(2)	Cu(1)–N(2)–C(8)	118.0(3)

Table 3. Selected bond distances (Å) and selected angles (deg) for **3**

Bond distances			
Cu(1)–Cl(1)	2.333(2)	Cu(1)–N(1)	2.235(5)
Cu(1)–N(2)	2.062(5)	Cu(1)–N(3)	2.062(5)
Cu(1)–N(4)	2.104(5)		
Bond angles			
N(1)–Cu(1)–N(2)	89.5(2)	N(1)–Cu(1)–N(3)	94.1(2)
N(1)–Cu(1)–N(4)	113.2(2)	N(2)–Cu(1)–N(3)	176.1(2)
N(2)–Cu(1)–N(4)	88.0(2)	N(3)–Cu(1)–N(4)	89.2(2)
Cu(1)–N(1)–C(20)	112.4(4)	Cu(1)–N(2)–C(1)	117.9(4)
Cu(1)–N(3)–C(21)	111.9(4)	Cu(1)–N(4)–C(40)	117.0(4)
Cl(1)–Cu(1)–N(1)	104.5(2)	Cl(1)–Cu(1)–N(2)	91.8(2)
Cl(1)–Cu(1)–N(3)	88.7(2)	Cl(1)–Cu(1)–N(4)	142.3(2)

N–H absorption at about 3200 cm^{-1}, and typical characteristic C=C of aryl absorptions at about 1600 cm^{-1}. The solid-state structure of **2** has been further confirmed by single-crystal X-ray analyses.

The solid-state structure of $(PhCH_2NH_2)_2CuCl_2$ (**2**) is shown in Fig. 1. The Cu^{2+} ion is σ-bound to two chlorine atoms and two nitrogen atoms of the amine ligands in a C_{2v} symmetric distorted-tetrahedral geometry. The average distance [1.983(3) Å] of Cu–N is close to that [1.993(4) Å] found in $[H_3NCH_2CH_2CH_2NH_3][(H_2NCH_2CH_2CH_2NH_2)(O_2CCH_2CO_2)CuCl_2]$.[29] Both distances of Cu–Cl [Cu(1)–Cl(1) 2.629(2) Å, Cu(1)–Cl(2) 2.229(2) Å] are much shorter than those [Cu(1)–Cl(1) 2.862 Å, Cu(1)–Cl(2) 3.042 Å] found in $[H_3NCH_2CH_2CH_2NH_3][(H_2NCH_2CH_2CH_2NH_2)(O_2CCH_2CO_2)CuCl_2]$.[29]

The results on copper(II)-mediated oxidative coupling of **1** in methanol are summarized in Table 4. In air, oxidative coupling of **1** by $CuCl_2 \cdot 2H_2O$ gives **4** in 56% yield (Table 4, entry 1),[25] while in the absence of O_2 (under N_2 gas) only 39% **4** is obtained (Table 4, entry 2),[26] which suggests that this reaction involves an oxidation process. A potential reason for this observation is that in the absence of O_2, $CuCl_2$ is

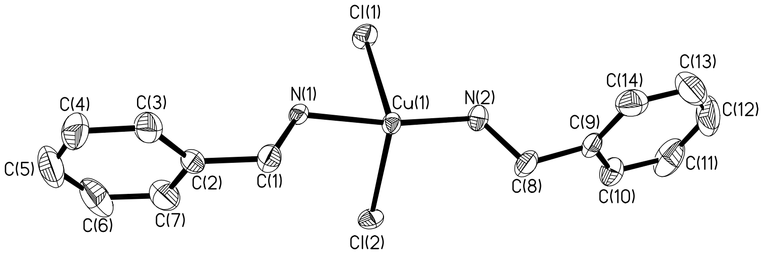

Figure 1. Molecular structure of $(PhCH_2NH_2)_2CuCl_2$ (**2**) (thermal ellipsoids drawn at the 35% probability level).

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Table 4. Copper(II)-mediated oxidative coupling of **1** in methanol

Entry	Cu salt (equiv. to **1**)	Amine (equiv. to **1**)	Atmosphere	Time (h)	Yield[a] of **4** (%)
1	$CuCl_2 \cdot 2H_2O$ (1.5)		Air	24	56[b]
2	$CuCl_2 \cdot 2H_2O$ (1.5)		N_2	48	39[c]
3	$CuCl_2 \cdot 2H_2O$ (2)	Benzylamine (8)	Ar	24	58[d]
4	$Cu(OAc)_2 \cdot H_2O$ (2)	Pyridine (4)	N_2	8	60[e]
5	$CuCl_2 \cdot 2H_2O$ (2)	Ethanolamine (1)	Air or N_2	3	73[c]
6	$(PhCH_2NH_2)_2CuCl_2$ (0.5)		Air	2	56
7	$(PhCH_2NH_2)_2CuCl_2$ (1)		Air	2	62
8	$(PhCH_2NH_2)_2CuCl_2$ (1.5)		Air	2	67
9	$(PhCH_2NH_2)_2CuCl_2$ (2)		Air	2	71
10	$(PhCH_2NH_2)_2CuCl_2$ (2)		N_2	2	70
11	$(PhCH_2NH_2)_2CuCl_2$ (2.5)		Air	2	72
12	$(PhCH_2NH_2)_2CuCl_2$ (3)		Air	2	72

[a] Isolated yields. [b] See Tan *et al.*[25]. [c] See Tan *et al.*[26]. [d] See Smrčina *et al.*[20,21] and Vyskočil *et al.*[23] [e] See Song *et al.*[24]

reduced to CuCl and HCl, and the latter reacts with unreacted **1**, thus leading to decreased reactivity. This problem has been solved by addition of organic amines,[20–24,26] e.g. when $CuCl_2$, benzylamine and **1** are used in a ratio of 2 : 8 : 1, compound **4** is isolated in 58% yield (Table 4, entry 3).[20,21,23] However, decreasing the ratio of amine to copper(II) leads to an increase in the isolated yield of **4** (Table 4, entries 3–5), and the best conversion (73%, Table 4, entry 5) is obtained from a reaction condition of 2-naphthylamine (**1**), ethanolamine and $CuCl_2$ in ratio of 1 : 1 : 2.[26] This can be rationalized by a decreased solubility of the intermediate $CuCl_2$–**4** in the solution, when the amine concentration is reduced, and therefore favoring the complex $CuCl_2$–**4** formation.

In our study, carrying out the reaction under air or N_2 has no effect on the conversion when excess $(PhCH_2NH_2)_2CuCl_2$ (**2**) is used (Table 4, entries 9 and 10). Increasing the ratio of $(PhCH_2NH_2)_2CuCl_2$ (**2**) to 2-naphthylamine (**1**) increases the yield of **4** (Table 4, entries 6–9), and the best conversion (>70%) is obtained when the ratio **2** and **1** is 2 : 1 (Table 4, entries 9 and 10). It is noteworthy that the reaction is complete in 2 h (monitored by GC or TLC for disappearance of **1**), which is faster than reported for the literature procedures.[20–26] These results indicate that $(PhCH_2NH_2)_2CuCl_2$ (**2**) is a very promising oxidation reagent for this kind of transformation, producing high yields and exhibiting enhanced oxidative activity.

In preliminary studies, we have established that $(PhCH_2NH_2)_2CuCl_2$ (**2**) can be successfully used for the oxidative coupling of 2-naphthylamine and 2-naphthol to give 2-amino-2′-hydroxy-1,1′-binaphthyl in 75–85% yield. This work is still underway (Xiang L, Wang Q, Zi G, unpublished data).

Compound $(PhCH_2NH_2)_2CuCl_2$ (**2**) is a potent oxidation reagent for the synthesis of racemic 2,2′-diamino-1,1′-binaphthyl (**4**) in multi-gram quantities (20–30 g) under standard laboratory conditions in a straightforward new manner. Stirring a methanol solution of 2-naphthylamine (**1**), and $(PhCH_2NH_2)_2CuCl_2$ (**2**), in ratio of 1 : 2 at room temperature for 2 h affords a novel brown ionic copper(II) complex $[\{1,1'\text{-}(C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (**3**) in 70% yield. Treatment of complex $[\{1,1'\text{-}(C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (**3**) in aqueous HCl (37%), followed by addition of NH_4OH (25%), gives 2,2′-diamino-1,1′-binaphthyl (**4**) in 95% yield. The total yield from 2-naphthylamine (**1**) to 2,2′-diamino-1,1′-binaphthyl (**4**) is 67%, and the aforementioned transformation is outlined in Scheme 1.

Complex **3** is readily soluble in CH_2Cl_2 and $CHCl_3$, sparely soluble in methanol, and insoluble in H_2O, toluene and *n*-hexane. It has been characterized by infrared spectroscopy and elemental analyses. The IR spectrum of **2** shows a typical characteristic N–H absorption at about 3200 cm^{-1}, and typical characteristic C=C of aryl absorptions at about 1600 cm^{-1}. The solid-state structure of **3** has been further established by a single-crystal X-ray analysis.

The single-crystal structure of complex **3** shows that it consists of well-separated, alternating layers of the complex ion $[\{(1,1'\text{-}C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]^+$ and free anion Cl^- with three H_2O and one CH_3OH molecules of solvent in the lattice. In the complex ion $[\{(1,1'\text{-}C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]^+$, the Cu^{2+} ion is σ-bound to one chlorine atom and four nitrogen atoms of the two ligands **4** in a distorted-tetragonal geometry (Fig. 2). The average distance [2.116(5) Å] of Cu–N is slightly longer than those found in $[H_3NCH_2CH_2CH_2NH_3][(H_2NCH_2CH_2CH_2NH_2)(O_2CCH_2CO_2)CuCl_2]$ [1.993(4) Å],[29] and $(PhCH_2NH_2)_2CuCl_2$ [**2**; 1.983(3) Å]. The distance [2.333(2) Å] of Cu–Cl is close to that [Cu(1)–Cl(2) 2.229(2) Å] found in $(PhCH_2NH_2)_2CuCl_2$ (**2**), but is much shorter than those found in $[H_3NCH_2CH_2CH_2NH_3][(H_2NCH_2CH_2CH_2NH_2)(O_2CCH_2CO_2)CuCl_2]$ [Cu(1)–Cl(1) 2.862 Å, Cu(1)–Cl(2) 3.042 Å],[29] and $(PhCH_2NH_2)_2CuCl_2$ [**2**; Cu(1)–Cl(1) 2.629(2) Å].

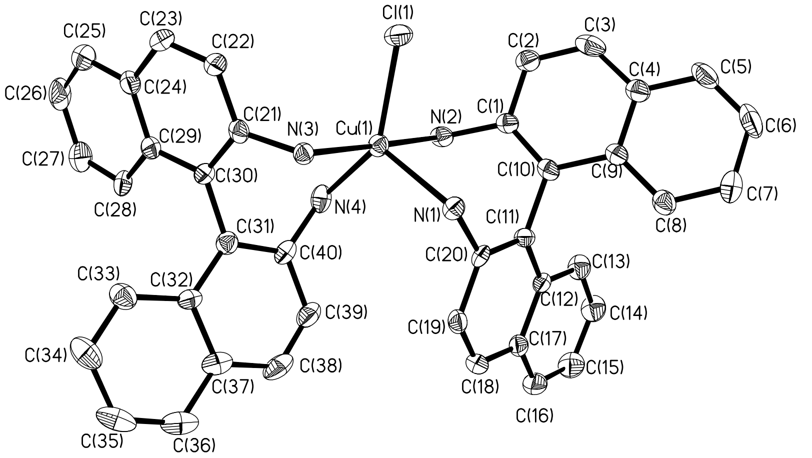
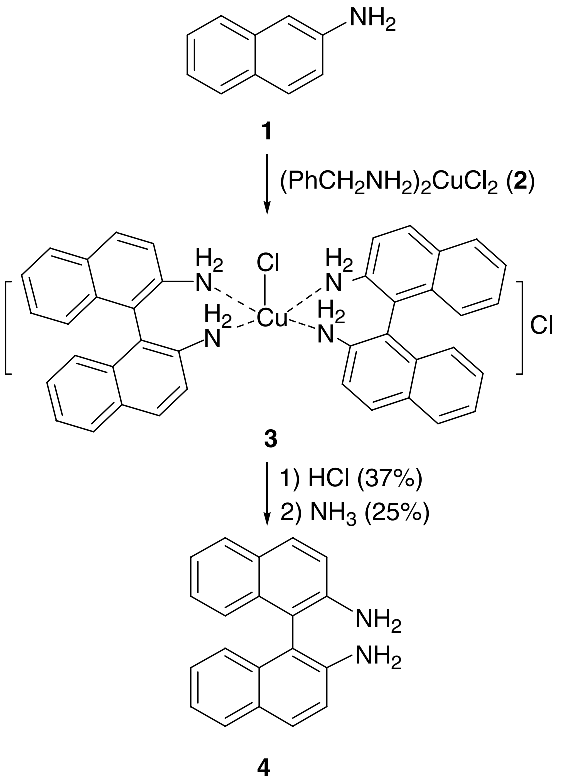


Figure 2. Molecular structure of the ion $[\{(1,1'\text{-}C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]^+$ in **3** (thermal ellipsoids drawn at the 35% probability level).



Scheme 1. .

Under similar oxidative coupling reaction conditions as described in Experimental Section, treatment of $[\{(1,1'\text{-}C_{10}H_6)_2\text{-}2,2'\text{-}(NH_2)_2\}_2CuCl]Cl \cdot CH_3OH \cdot 3H_2O$ (**3**) with 2-naphthylamine (**1**) in ratio of 2 : 1, **3** shows no activity, and indeed, the starting materials are recycled. This supports the assumption that $(PhCH_2NH_2)_2CuCl_2$ (**2**) serves as the oxidation reagent during the course of the reaction.

CONCLUSIONS

In conclusion, $(PhCH_2NH_2)_2CuCl_2$ (**2**) is a useful oxidation reagent for oxidative coupling of 2-naphthylamine (**1**), and a facile preparation of 2,2′-diamino-1,1′-binaphthyl (**4**) is described. Given the ease of accessing multi-gram quantities (20–30 g) of **4** (in isolated yield up to 67%) by the procedure outlined in this paper, this should facilitate its use not only as reported but also possibly in further applications. Further investigation to extend the application of $(PhCH_2NH_2)_2CuCl_2$ (**2**) in organic synthesis is underway.

Supplementary materials

Crystallographic data for the structural analyses of complexes **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 608611 and 608612 for structures **2** and **3**, respectively. Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing deposit@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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