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ARTICLE

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A direct and practical synthetic route to N-heterocyclic carbene copper complexes of [(NHC)CuX] (X = halide) and [(NHC)₂Cu]PF₆ types using commercially available copper powder is described. A number of copper-NHC complexes have been obtained in a range of yields from 26 to 99%. The reactions take place in air without removal of moisture and oxygen, and the excess of copper powder can be easily removed via simple filtration after

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completion. The direct reactions of imidazolium salts and copper powder can also be performed in aqueous media avoiding tedious purification processes. The procedure is also suitable for gram-scale preparation. Introduction Since the first Cu-NHC complex was disclosed in 1993 by Arduengo and co-workers¹, Cu-NHCs have been attracting continuous attention and a number of copper-NHC complexes have been synthesized so far². The structural diversity, ease of modification as well as low cost of Cu-NHCs offer excellent opportunities for their versatile applications. The use of Cu-NHCs such as [(NHC)CuX] (X = halide) type complexes or their derivatives have proven successful^{2b,3} in homogeneous catalysis including hydrosilylation reactions,⁴ conjugate This work **B**^{5a,14a,15-17} Cu powder СпХ **C**^{14a,18} AģX CH₃CN or H₂O R-N

addition reactions,⁵ 1,3-dipolar cycloaddition,⁶ carboxylation,⁷ allylic substitutions and allylation,⁸ borylation of unsaturated hydrocarbons,9 and cross-coupling reactions,10 etc. Besides, researches on the biological activities¹¹ and photoluminescence properties¹² of Cu-NHCs have extended their potential applications to medicine and photoactive functional materials. Recently, it has proven that Cu-NHC complexes are useful carbene transfer agents for the preparation of Au(I)-, Pd(II)-, Ni(II)-, Ru(II)-, Rh(I)-, and Cr(III)-NHC complexes besides the popularly used Ag(I)-NHCs.¹³

Scheme 1. Synthetic Routes to [(NHC)CuX] (X = halide) Complexes

Copper often forms [(NHC)CuX] type complexes when the anions are halide ions.^{2a} The known synthetic routes to these neutral Cu-NHCs are summarized in Scheme 1. Generally, they can be prepared from substitution reactions of free NHCs and copper precursors (method A).^{1,14} This method suffers from the

use of strong bases and high sensitivity of free carbenes. A modified one-pot synthetic strategy involves in situ deprotonation of an imidazolium salt with cuprous halide in the presence of a base such as NaO'Bu, K2CO3, etc (method \mathbf{B})^{5a,14a,15}. This strategy was first reported by Buchwald and co-

Simple Synthesis of Neutral and Cationic Cu-NHC **Complexes**

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workers in 2003.5a Recently, Cisnetti and co-workers found that aqueous ammonia can also be a suitable base.¹⁶ Cazin and coworkers showed that anhydrous solvent and inert gas protection are not necessary for the one-pot strategy in some cases.¹⁷ Although the one-pot strategy simplifies the workup compared to the free carbene route, the bases cannot be avoided. [(NHC)CuX] can also be obtained via transmetallation of their corresponding Ag-NHC complexes (method C).^{13c,14a,18} However, this protocol sacrifices Ag-NHC reagents and generates silver halide as by-product. In situ deprotonation of imidazolium salts with a basic copper precursor such as CuOAc, CuO'Bu, etc represents a convenient route (method **D**)¹⁹. Since reported by Danopoulos and co-workers in 2001,^{19a} basic Cu₂O has been intensively employed for the synthesis of copper complexes.²⁰ [(NHC)CuX] complexes may also be obtained by thermal decomposition of carbene adducts of CO2,²¹ chloroform,²² and I_2^{23} in the presence of a suitable copper precursor (method E). Method E is restricted by the availability of the carbene precursors. In addition, other improvements including continuous synthesis, microwave-assisted, electrochemical procedures were also presented but require special equipments.24

Noteworthily, due to the great importance of such kind of Cu-NHCs,^{2,3,13} seeking their synthetic methods remains the focus of research.^{16,17,20,23,24} Despite above mentioned advances, further simplification of the synthetic procedure of [(NHC)CuX] complexes is highly desirable especially for scalable preparation. We have been interested in exploration of synthetic methods for metal-NHCs,^{13e,24c,25} and have shown that Cu-NHCs can be prepared from imidazolium salts with commercially available copper powder in air.²⁶ However, this protocol is restricted to functionalized imidazolium salts bearing a N-heteroarene such as pyridine or pyrimidine group with the generation of cationic copper products.^{26,27} Herein, we report the facile synthesis of neutral [(NHC)Cu(halide)] and

cationic [(NHC)₂Cu]PF₆ with copper powder in both organic solvent and aqueous media.

Results and Discussion

To explore the scope of the synthetic procedure, a number of imidazolylidene and benzimidazolylidene precursors were selected for this study possessing saturated or unsaturated C4-C5 backbone and various anions, shown in Scheme 2. Ligands IPr, SIPr, IMes and SIMes are among the most frequently used ligands in Cu-NHC-catalyzed organic transformations^{2b,3} (IPr = 1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-2-ylidene, SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydro-1H-imidazol-2ylidene, IMes = 1,3-dimesityl-1*H*-imidazol-2-ylidene, SIMes = 1,3-dimesityl-4,5-dihydro-1*H*-imidazol-2-ylidene). Their hydrochlorides 1a-1d were obtained according to literature procedures.²⁸ IPr•HBr (1e) was obtained in 68% yield via anion exchange of its hexafluorophosphate with an excess of tetrabutylammonium bromide in ethyl acetate/CH₃CN. Similarly, IPr•HI (1f) and SIPr•HI (1g) were readily formed in 60% and 79% yields by anion exchange of IPr•HCl (1a) and SIPr•HCl (1b) with 1 equiv. of NaI in acetone/ethanol. Anion exchange of IMes•HCl (1c) and SIMes•HCl (1d) with NH₄PF₆ in water near-quantitatively gave their hexafluorophosphates IMes•HPF₆ (1h) and SIMes•HPF₆ (1i), respectively.²⁹ Besides, hexafluorophosphates monoimidazolium bearing Nheteroarenes **1j-1l** $(L^{j} = 1,3-bis(pyridin-2-ylmethyl)-1H$ imidazol-2-ylidene, $L^k = 1,3$ -bis(pyridin-2-ylmethyl)-1*H*benzo[d]imidazol-3-ylidene, $L^1 = 1,3$ -bis((1-benzyl-1H-1,2,3triazol-4-yl)methyl)-1*H*-benzo[*d*]imidazol-2-ylidene) and bisimidazolium hexafluorophosphates linked by pyridine or 3,5-dimethylpyrazole 1m-1n ($L^m = 3,3'$ -(pyridine-2,6diyl)bis(1-butyl-1*H*-imidazol-2-ylidene), $L^n = 3,3'-((1H-1))^{n-1}$ pyrazole-3,5-diyl)bis(methylene))bis(1-(pyridin-2-yl)-1Himidazol-2-ylidene)) were also synthesized.



Scheme 2. Schematic Illustration of Carbene Precursors

are

usually

Synthesis of [(NHC)CuX] (X = halide) type complexes with copper powder

hence

Imidazolium chlorides NHC•HCl and their copper complexes

soluble in chlorinated solvents,

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dichloromethane was initially chosen as the solvent. After IPr•HCl (1a) or SIPr•HCl (1b) was treated with 5 equiv. of copper powder in CH₂Cl₂ at 40 °C in air for 24 h, [(IPr)CuCl] (2a) and [(SIPr)CuCl] (2b) were respectively generated in low yields of 24% and 31%, determined by ¹H NMR spectrum of an aliquot of the crude reaction mixture (Table 1, entries 1-2). Under the same reaction conditions, [(SIMes)CuCl] (2d) was isolated in 26% yield (entry 3).

Table 1. Synthesis of [(NHC)CuX] (X = halide) Type
Complexes ^a
- R

	5 equiv. Cu powder	
к ₊ у к	solvent, air, temp., 24 h	
X = Cl, Br, I	- H ₂ O	ĸ

En	Salt	Product	Solvent	Т	Yield
try	Salt	rioduct	Solvent	∕°C	$/\%^b$
1	IPr•HCl	[(IPr)CuCl]	CH CI	40	24^{c}
1	(1a)	(2a)	cn_2cn_2	40	24
2	SIPr•HCl	[(SIPr)CuCl]	CH CI	40	31 ^c
2	(1b)	(2b)	CII_2CI_2 40	51	
3	SIMes•HCl	[(SIMes)CuCl]	CH ₂ Cl ₂	40	26
5	(1d)	(2d)		40	20
4	IPr•HCl	[(IPr)CuCl]	CH ₂ CN	55	90
	(1a)	(2a)	engert	55	70
5	1a	2a	CH ₃ CN	55	88^d
6	1a	2a	CH ₃ CN	55	91 ^e
7	SIPr•HCl	[(SIPr)CuCl]	CH CN	55	88
	(1b)	(2b)	CH3CIV		
Q	IMes•HCl	[(IMes)CuCl]	CH ₂ CN	55	49
0	(1c)	(2c)	CH ₃ CN	55	12
9	IPr•HBr	[(IPr)CuBr]	CH ₂ CN	55	99
	(1e)	(2e)	enger	55	//
10	1e	2e	CH ₃ CN	55	99 ^e
11	IPr•HI	[(IPr)CuI]	CH ₂ CN	55	79
11	(1f)	(2f)	0113011	55	.,
12	SIPr•HI	[(SIPr)CuI]	CH ₂ CN	55	83
	(1g)	(2g)	enger	55	05
13	IPr•HCl	[(IPr)CuCl]	CH ₂ CN	55	82^{f}
	(1a)	(2a)	enger	55	02
14	IPr•HBr	[(IPr)CuBr]	CH ₂ CN	55	93 f
11	(1e)	(2e)	chigen		20
15	IPr•HI	[(IPr)CuI]	CH ₂ CN	55	75 ^f
	(1f)	(2f)	Chigon	55	15

^{*a*} Reaction conditions: imidazolium salt 0.2 mmol, copper powder 1.0 mmol, solvent 5 mL, under air, 40-55 °C, 24 h. ^{*b*} Isolated yields unless otherwise stated. ^{*c*} Determined by ¹H NMR of an aliquot of the crude reaction mixture. ^{*d*} 1.0 equiv. of copper powder was used instead of 5 equiv. ^{*e*} 1.0 equiv. of recovered copper powder was used instead of fresh copper powder. ^{*f*} 1000 mg of imidazolium was used instead of 0.2 mmol.

The yields of Cu-NHC complexes were apparently improved when the reaction was performed in acetonitrile at higher reaction temperature. After stirring the mixture of IPr•HCl (1a) or SIPr•HCl (1b) and 5 equiv. of copper powder in CH₃CN at 55 °C for 24 h, gratifyingly, the imidazolium chlorides were almost completely consumed, and the expected products [(IPr)CuCl] (**2a**) and [(SIPr)CuCl] (**2b**) were afforded in 90% and 88% yields, respectively, after removal of CH₃CN (entries 4 and 7). Although an excess of copper powder was initially employed to promote the complete conversion of imidazolium salts, further studies showed that when 1 equiv. of copper powder was used the yield is not significantly influenced (entry 5). In addition, unreacted copper powder can be quantitatively recovered, and the recovered copper powder showed even better reactivity than commercial copper powder (entry 6). Similarly, IMes•HCl (**1c**) also reacted smoothly with copper powder, and the desired complex [(IMes)CuCl] (**2c**) was isolated in 49% yield after recrystallization of the crude product in diethyl ether/CH₃CN at low temperature (entry 8).

The protocol was also applied to imidazolium bromides and _ iodides. IPr and SIPr based copper(I) bromide and iodide complexes are less soluble in acetonitrile, and cooling the reaction mixture to room temperature gave colorless crystals. Hence removal of unreacted copper powder should be performed while the solution was hot. [(IPr)CuBr] (2e) was obtained in quantitative yield after removal of the solvent (entry 9). The same yield of 2e was obtained when the reaction was carried out with the recovered copper powder (entry 10). [(IPr)CuI] (2f) and [(SIPr)CuI] (2g) were obtained in about 80% yields (entries 11-12). Scale preparation is quite important for potential future application. We attempted the gram-scale preparations of 2a, 2e, and 2f (entries 13-15). The reactions of 1 g of the imidazolium salts IPr•HX with an excess of copper powder were finished within 24 h, and the corresponding complexes [(IPr)CuCl] (2a), [(IPr)CuBr] (2e), and [(IPr)CuI] (2f) were isolated in the yields of 82%, 93%, and 75%, respectively.

The above mentioned neutral [(NHC)CuX] (X = halide) type complexes are colorless solids, and they have been characterized by NMR spectra, and further confirmed by elemental analysis. Their ¹H NMR and ¹³C NMR data are in accordance with those described in the literature.^{4a,5a,14a,15c,17,24a,d}

Synthesis of $[(NHC)_2Cu]PF_6$ type complexes with copper powder

We subsequently examined the efficiency of the strategy for the synthesis of homoleptic [(NHC)₂Cu]PF₆ complexes. Although imidazolium halides NHC•HX have proven to be very reactive towards copper powder as mentioned above, the reactions between their hexafluorophosphate analogues NHC•HPF₆ and copper powder were found to be generally sluggish. It should be noted that the same behavior was also observed in their reactions with Cu₂O.^{20b,24a} The reactions of IMes•HPF₆ (**1h**) and SIMes•HPF₆ (**1i**) with copper powder were performed at 80 °C for 36 h, and the imidazolium salts were not completely consumed. The corresponding complexes [(IMes)₂Cu]PF₆ (**2h**) and [(SIMes)₂Cu]PF₆ (**2i**) were isolated in 20% and 30% yields after recrystallization of the crude product in acetonitrile and ethyl acetate at low temperature. When the reaction time was

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further prolonged to 4 days, the yields of **2h** and **2i** could be accordingly increased to 33% and 42% (Table 2, entries 1-2).

Table 2. Synthesis of [(NHC)₂Cu]PF₆ Type Complexes^a

R∕ ^{_1}	$\frac{1}{N-R} = \frac{5 \text{ equiv. Cu p}}{CH_3CN, \text{ air, 8}}$	o°C, 4 d	+ _ PF ₆
Entry	Salt	Product	Yield/% ^b
1	IMes•HPF ₆	[(IMes) ₂ Cu]PF ₆	33
1	(1h)	(2h)	55
2	SIMes•HPF ₆	[(SIMes) ₂ Cu]PF ₆	42
2	² (1i)	(2i)	42

^{*a*} Reaction conditions: imidazolium 0.4 mmol, copper powder 2.0 mmol, CH₃CN 5 mL, under air, 80 °C, 4 days. ^{*b*} Isolated yields.

We have previously shown that *N*-heteroarene functionalized NHC copper complexes can be easily generated with copper powder even at room temperature.^{26,27} The dramatically different reactivities of NHC•HPF₆ from NHC•HX or functionalized imidazoliums should result from the coordinating abilities of halide ions or *N*-heteroarene, indicating that the formation of Cu-halide bond or Cu-N bond is an important driving force in the reactions.

Synthesis of Cu-NHCs in aqueous media

Water is a green solvent, and some Cu-NHC-catalyzed organic transformations have been realized in water.³⁰ Exploration the synthetic method for Cu-NHCs in water is also attracting. We found that the reactivity of imidazolium halide NHC•HX towards copper powder in water is generally lower than that in CH₃CN probably due to the lower solubility in water. To improve the solubility of imidazolium, the reaction was carried out at 100 °C. As shown in Table 3, imidazolium chlorides **1a**-**1d** were treated with copper powder in refluxing water for 30 h. After removal of water under vacuum and washing with water, the corresponding complexes **2a-2d** were obtained in a range of yields from 30 to 65%. In the case of IPr•HBr (**1e**), [(IPr)CuBr]

(2e) was isolated in 58% yield after recrystallization. Although the yields are not quite high, the procedure is quite practical since imidazolium salts are usually soluble in hot water, and the purification can be avoided.

Although picolyl-based imidazolium salt $[HL^{J}]PF_{6}$ (1j) and benzimidazolium salt $[HL^{k}]PF_{6}(\mathbf{1k})$ are hardly soluble in water at room temperature, they dissolved in water at 100 °C giving - homogeneous solutions. After reacting with copper powder for _ 3 h, white precipitates of copper complexes appeared. After 24 h, the resulting mixture was cooled, and the resulting solid was dissolved in CH₃CN, from which the trinuclear Cu(I) complexes $[Cu_3L_3^{j}](PF_6)_3$ (2j) and $[Cu_3L_3^{k}](PF_6)_3$ (2k) were isolated in 98% and 88% yields after simple filtration and subsequent recrystallization in Et₂O/CH₃CN. It was found that complex 2j could even be obtained in 30% yield when the reaction was performed at room temperature. Under the same conditions, the reaction between 1,2,3-triazole functionalized benzimidazolium salt $[HL^{1}]PF_{6}$ (11) and copper powder could also take place smoothly. A novel Cu₃ complex $[Cu_3L_3^1](PF_6)_3$ (21) was obtained as a colorless solid in 46% yield. However, pyridine-bridged dicarbene precursor $[H_2L^m]PF_6$ (1m) could be hardly converted when it was treated with copper powder in water. To our delight, when the mixed solvent of H2O/CH3CN (v/v=1/1) was used instead of pure water, a novel binuclear Cu(I)-NHC complex $[Cu_2L_2^m](PF_6)_2$ (2m) was isolated as a yellow solid in 54% yield. The reaction of 3,5dimethylpyrazole-linked bisimidazolium salt $[H_2L^n](PF_6)_2$ (1n) with copper powder in refluxing water gave a red turbid mixture, from which tetranuclear Cu(II)-NHC complex $[Cu_4(\mu_3-OH)_2L^n_2](PF_6)_4$ (2n) was obtained in 44% yield. Complexes 2j, 12a,13e 2k, 13e and $2n^{27a}$ have already been reported utilizing other synthetic procedures. Novel complexes 21 and 2m have been confirmed by elemental analysis and NMR spectroscopy. The resonance signal of Cu-Ccarbene was not found in the ¹³C NMR spectrum of **2l**, while the characteristic signal of Cu-C_{carbene} was observed at 178.2 ppm in the ¹³C NMR spectrum of 2m.

Table 3. Synthesis of Cu-NHCs in Aqueous Media^a

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^{*a*} Reaction conditions: imidazolium 0.2-0.3 mmol, copper powder 5.0 equiv., H_2O 10 mL, under air, 100 °C, 24-36 h. Isolated yields unless otherwise stated. ^{*b*} At room temperature for 24 h. ^{*c*} H_2O/CH_3CN (v/v = 1/1) was used instead of pure water.

Single crystal X-ray crystallographic studies

Suitable crystals for X-ray diffraction analysis of 2l and 2m were respectively obtained by slow diffusion of diethyl ether into their CH₃CN solution at room temperature. The structures of 2l and 2m were identified by X-ray single-crystal diffraction analysis. As shown in Figure 1, the cation of 2l consists of a triangular Cu3 core bridged by three triazole based NHC ligands. Each copper ion is coordinated by two triazole and two benzimidazolylidene ligands forming a distorted tetrahedral geometry. The separations of Cu-Cu are at 2.514(1)-2.530(1) Å displaying weak metal-metal interaction, which are comparable to those of other similar trinuclear Cu-NHC complexes (2.46-2.52 Å).^{12a,13e,24c,27b,31} The Cu-N bond distances fall in the range of 2.085(4)-2.111(4) Å. Each benzimidazolylidene forms the 3c-2e bond with two copper ions with Cu-C bond distances of 2.055(5) and 2.084(5) Å, which are within the normal range of Cu-C bonds (*ca.* 1.80-2.20 Å).^{2a} Such a bridging ligand in a μ_2 mode of NHC is rare and only observed in a few silver, copper, and nickel complexes.^{12a,13e,14a,19d,27b,c,32}



Figure 1. ORTEP drawing of the cationic section of $[Cu_3L_3^1](PF_6)_3$ (**2**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu1-C11 2.055(5), Cu1-N7 2.085(4), Cu1-Cu2 2.530(1), Cu2-C38 2.076(5), Cu2-C11 2.084(5), Cu2-N2 2.102(4), Cu2-N11 2.111(4), Cu2-Cu2A 2.514(1), C11-Cu1-C11A 165.2(3), C11-Cu1-N7A 98.0(2), C11-Cu1-N7 91.4(2), N7A-Cu1-N7 100.5(2), C38-Cu2-C11 164.6(2), C38-Cu2-N2 98.7(1), C11-Cu2-N2 92.4(2), C38-Cu2-N11 91.9(1), C11-Cu2-N11 96.7(2), N2-Cu2-N11 99.6(2). Symmetry code: A -x+1, y, -z+1/2.

The structure of **2m** is depicted in Figure 2. The cation consists of a $[Cu_2L^m_2]^{2+}$ dimer situated on a crystallographic inversion center. Complex **2m** is isostructural with previously reported complexes $[Ag_2L^m_2](PF_6)_2$ and $[Au_2L^m_2](PF_6)_2$.³³ The dicarbene ligands are arranged in a helical fashion with pyridine/imidazolylidene ring interplanar angles of 13.1° and 23.2°. Each copper ion is coordinated with two carbenic atoms from two L^m ligands with the bond distances of 1.907(3) and 1.894(4) Å, showing a bent geometry with the C-Cu-C angle of 160.5(2)°. The long Cu-N_{pyridine} distances of 2.685 and 2.797 Å indicated weak interaction between copper ion and pyridyl nitrogen. The intramolecular metal-metal distance of 2.807(1) Å in **2m** is much shorter than that of its Ag(I) and Au(I) isostructural complexes.³³



Figure 2. ORTEP drawing of the cationic section of $[Cu_2L_2^m](PF_6)_2$ (**2m**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, *n*-butyl groups, and counteranions have been removed for clarity. Selected bond distances (Å) and angles (deg): Cu1-C2 1.894(4), Cu1-C1 1.907(3), Cu1-Cu1A 2.807(1), C2-Cu1-C1 160.5(2). Symmetry code: A -x+1, y, -z+3/2.

Conclusions

Published on 27 November 2014. Downloaded by Université Laval on 28/11/2014 18:04:51

In summary, we described a direct approach for the synthesis of neutral [(NHC)CuX] (X = halide) and cationic [(NHC)₂Cu]PF₆ type complexes in a range of yields from imidazolium salts and commercially available copper powder as the simplest copper source. The procedure avoids addition of bases, handling highly sensitive free carbene intermediates, or sacrificing Ag-NHC complexes. The reaction workups are obviously simplified as the reactions take place in air without removal of moisture and oxygen, and the solvent does not require any purification prior to use. In addition, water is the only byproduct, and the excess of copper powder can be easily removed via simple filtration. Further simplification of the procedure is realized in water since imidazolium salts are usually soluble in hot water. This straightforward route is quite practical and suitable for various neutral and cationic Cu complexes of unsaturated and saturated NHCs with different substituents. Especially, the procedure is

suitable for high-yielding scalable preparation which is of significance for future catalytical applications.

Experimental Section

General Details

All reactions were carried out under air. Imidazolium salts IPr•HCl (1a),²⁸ SIPr•HCl (1b),²⁸ IMes•HCl (1c),²⁸ and SIMes•HCl (1d)²⁸ were prepared according to the reported procedures. The synthetic procedures for IPr•HBr (1e), IPr•HI (1f), SIPr•HI (1g), IMes•HPF₆ (1h), SIMes•HPF₆ (1i), $[HL^{j}]PF_{6}$ (1j), $[HL^k]PF_6$ (1k), $[HL^l]PF_6$ (1l), $[H_2L^m](PF_6)_2$ (1m), and $[H_2L^n](PF_6)_2$ (**1n**) are given in the Supporting Information. All other chemicals were obtained from commercial suppliers and used as received without further purification. The copper powder (200 mesh, with purity ≥99.7 wt %) was purchased from Sinopharm Chemical Reagent Co., Ltd, China, and was used directly without any pretreatment. ¹H and ¹³C-{¹H} NMR spectra were recorded at 400 and 100 MHz respectively on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm and coupling constants (J) are expressed in Hz. All NMR spectra were recorded at 298 K in deuterated solvent using the residual solvent peak as reference (CHCl₃ $\delta_{\rm H}$ = 7.26 ppm, $\delta_{\rm C}$ = 77.16 ppm; acetone $\delta_{\rm H}$ = 2.05 ppm, $\delta_{\rm C}$ = 29.84, 206.26 ppm; DMSO $\delta_{\rm H}$ = 2.50 ppm, $\delta_{\rm C}$ = 39.52 ppm; CH₃CN $\delta_{\rm H}$ = 1.94 ppm, $\delta_{\rm C}$ = 1.32, 118.26 ppm). Singlecrystal X-ray diffraction data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with a Mo Ka radiation ($\lambda = 0.71073$ Å). The elemental analyses were performed on a Flash EA 1112 instrument.

General synthetic procedure for [(NHC)CuX] (X = halide) type complexes

A solution of NHC•HX (X = halide) (1.0 equiv.) and copper powder (5.0 equiv.) in CH₃CN (5 mL) was vigorously stirred at 55 °C for 24 hours. The reaction conversion was determined by ¹H NMR spectrum in CDCl₃ of an aliquot of the crude reaction mixture. The resulting solution was filtered through silica to remove the excess of copper powder while it was hot. The desired product was obtained by removal of the solvent under vacuum. When necessary, the solid was further washed with hot water or recrystallized with proper solvent.

[(IPr)CuCl], 2a. This complex was synthesized from IPr•HCl (1a) (0.2 mmol, 85 mg) and copper powder (1.0 mmol, 64 mg). Removal of the solvent under vacuum gave the desired product. Yield: 88 mg (90%), colorless solid. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (t, J = 7.6 Hz, 2H, Ar-H), 7.29 (d, J = 7.6 Hz, 4H, Ar-H), 7.14 (s, 2H, NCHCHN), 2.48-2.59 (m, 4H, $CH(CH_3)_2$, 1.29, 1.23 (both d, J = 6.8 Hz, each 12H, CH_3). ¹³C NMR (100 MHz, CDCl₃): δ 180.7 (Cu-C), 145.6, 134.5, 130.6, 124.3, 123.3, 28.8, 24.9, 24.0. The ¹H NMR and ¹³C NMR data accordance with those described are in in the literature.^{5a,15c,17,24a,d} Anal. Calcd for C₂₇H₃₆ClCuN₂: C, 66.51; H, 7.44; N, 5.75. Found: C, 66.60; H, 7.48; N, 5.67.

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[(SIPr)CuCl], 2b. This complex was synthesized from SIPr•HCl (1b) (0.2 mmol, 86 mg) and copper powder (1.0 mmol, 64 mg). Removal of the solvent under vacuum gave the desired product. Yield: 86 mg (88%), colorless solid. ¹H NMR (400 MHz, CDCl₃): δ 7.38 (t, J = 8.0, 7.6 Hz, 2H, Ar-H), 7.23 (d, J = 8.0 Hz, 4H, Ar-H), 4.00 (br. s, 4H, NCH₂CH₂N), 3.00-3.10 (m, 4H, CH(CH₃)₂), 1.34, 1,33 (both d, J = 7.2 Hz, each 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 203.0 (Cu-C), 146.7, 134.5, 129.9, 124.6, 53.8, 29.0, 25.6, 24.0. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature.^{15c,17,34} Anal. Calcd for C₂₇H₃₈ClCuN₂: C, 66.24; H, 7.82; N, 5.72. Found: C, 66.28; H, 7.78; N, 5.63.

[(IMes)CuCl], 2*c*. This complex was synthesized from IMes•HCl (2*c*) (0.2 mmol, 69 mg) and copper powder (1.0 mmol, 64 mg). Recrystallization in acetonitrile and diethyl ether at -15 °C led to isolation of the desired product. Yield: 39 mg (49%), colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 7.06 (s, 2H, NCHCHN), 7.00 (s, 4H, Ar-H), 2.35 (s, 6H, CH₃), 2.10 (s, 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 179.0 (Cu-*C*), 139.5, 135.1, 134.6, 129.5, 122.4, 21.1, 17.8. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature. ^{15c,17,24d,34} Anal. Calcd for C₂₁H₂₄ClCuN₂: C, 62.52; H, 6.00; N, 6.94. Found: C, 62.50; H, 6.06; N, 6.89.

[(SIMes)CuCl], 2d. This complex was synthesized from SIMes•HCl (1d) (0.2 mmol, 70 mg) and copper powder (1.0 mmol, 64 mg) in CH₂Cl₂ at 40 °C for 24 hours. The solid was washed several times with water and dried in vacuo. Yield: 21 mg (26%), colorless solid. ¹H NMR (400 MHz, CDCl₃): δ 6.95 (s, 4H, Ar-*H*), 3.95 (br. s, 4H, NC*H*₂C*H*₂N), 2.31 (s, 12H, C*H*₃), 2.30 (s, 6H, C*H*₃). ¹³C NMR (100 MHz, CDCl₃): δ 202.7 (Cu-*C*), 138.7, 135.5, 135.1, 129.8, 51.1, 21.1, 18.1. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature.^{4a,15c,24a} Anal. Calcd for C₂₁H₂₆ClCuN₂: C, 62.21; H, 6.46; N, 6.91. Found: C, 62.03; H, 6.59; N, 6.74.

[(IPr)CuBr], 2e. This complex was synthesized from IPr•HBr (1e) (0.2 mmol, 94 mg) and copper powder (1.0 mmol, 64 mg). Removal of the solvent under vacuum gave the desired product. Yield: 105 mg (99%), colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (t, *J* = 7.6, 8.0 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 7.14 (s, 2H, NCHCHN), 2.52-2.61 (m, 4H, CH(CH₃)₂), 1.30, 1.22 (both d, *J* = 6.8 Hz, each 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 181.5 (Cu-*C*), 145.7, 134.4, 130.7, 124.3, 123.2, 28.8, 24.9, 24.0. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature.^{14a,17} Anal. Calcd for C₂₇H₃₆BrCuN₂: C, 60.95; H, 6.82; N, 5.27. Found: C, 60.84; H, 6.76; N, 5.15.

[(IPr)Cu1], 2f. This complex was synthesized from IPr•HI (1f) (0.2 mmol, 104 mg) and copper powder (1.0 mmol, 64 mg). Removal of the solvent under vacuum gave the desired product. Yield: 92 mg (79%), colorless solid. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (t, *J* = 8.0, 7.6 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 7.6 Hz, 4H, Ar-*H*), 7.14 (s, 2H, NC*H*C*H*N), 2.50-2.60 (m, 4H, C*H*(CH₃)₂), 1.29, 1.22 (both d, *J* = 6.8 Hz, each 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 182.9 (Cu-*C*), 145.6, 134.2, 130.5, 124.1, 123.2, 28.7, 24.9, 24.0. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature.^{14a,17}

Anal. Calcd for $C_{27}H_{36}CuIN_2$: C, 56.00; H, 6.27; N, 4.84. Found: C, 55.89; H, 6.27; N, 4.75.

[(SIPr)CuI], 2g. This complex was synthesized from SIPr•HI (1g) (0.2 mmol, 104 mg) and copper powder (1.0 mmol, 64 mg). Removal of the solvent under vacuum gave the desired product. Yield: 97 mg (83%), colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 7.24 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 4.02 (s, 4H, NCH₂CH₂N), 3.02-3.10 (m, 4H, CH(CH₃)₂), 1.36, 1.33 (both d, *J* = 7.2 Hz, each 12H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 204.4 (Cu-*C*), 146.7, 134.2, 129.9, 124.6, 53.8, 29.0, 25.6, 24.1. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature. ^{14a} Anal. Calcd for C₂₇H₃₈CuIN₂: C, 55.81; H, 6.59; N, 4.82. Found: C, 55.92; H, 6.63; N, 4.72.

Scale synthesis of [(IPr)CuX] (X = halide)

A solution of IPr•HX (1000 mg) and copper powder (5.0 equiv.) in CH₃CN (25 mL) was vigorously stirred at 55 °C for 24 hours. The resulting solution was quickly filtered through silica when it was hot, followed by elution with CH₃CN. The solvent was removed under vacuum and washed with *n*-hexane. The solid was dried in vacuo to give the desired product.

[(IPr)CuCl], 2a. 940 mg (82%), Anal. Calcd for C₂₇H₃₆ClCuN₂: C, 66.51; H, 7.44; N, 5.75. Found: C, 66.65; H, 7.49; N, 5.59.

[(IPr)CuBr], *2e*. 1054 mg (93%), Anal. Calcd for C₂₇H₃₆BrCuN₂: C, 60.95; H, 6.82; N, 5.27. Found: C, 60.77; H, 6.79; N, 5.04.

[(IPr)CuI], 2f. 840 mg (75%), Anal. Calcd for C₂₇H₃₆CuIN₂: C, 56.00; H, 6.27; N, 4.84. Found: C, 55.84; H, 6.27; N, 4.70.

General synthetic procedure for [(NHC)₂Cu]PF₆

A solution of NHC•HPF₆ (0.4 mmol) and copper powder (2.0 mmol) in CH₃CN (5 mL) was vigorously stirred at 80 °C for 4 days. The resulting solution was filtered to remove the excess of copper powder. The filtrate was concentrated, and recrystallized with ethyl acetate at -15 °C to isolate the desired products.

[(*IMes*)₂*Cu*]*PF*₆ 2*h*. This complex was synthesized from the reaction of IMes•HPF₆ (**1h**) (0.4 mmol, 181 mg) and copper powder (2.0 mmol, 128 mg). Yield: 54 mg (33%), colorless solid. ¹H NMR (400 MHz, acetone-*d*₆): δ 7.43 (s, 4H, NCHCHN), 7.05 (s, 8H, Ar-H), 2.45 (s, 12H, CH₃), 1.74 (s, 24H, CH₃). ¹³C NMR (100 MHz, acetone-*d*₆): δ 178.3 (Cu-*C*), 140.2, 135.8, 135.4, 130.0, 123.9, 21.2, 17.2. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature.^{16,35} Anal. Calcd for C₄₂H₄₈CuF₆N₄P: C, 61.72; H, 5.92; N, 6.85. Found: C, 61.56; H, 5.82; N, 6.97.

[(SIMes)₂Cu]PF₆ 2i. This complex was synthesized from the reaction of SIMes•HPF₆ (1i) (0.4 mmol, 181 mg) and copper powder (2.0 mmol, 128 mg). Yield: 69 mg (42%), colorless solid. ¹H NMR (400 MHz, acetone- d_6): δ 6.99 (s, 8H, Ar-H), 4.00 (s, 8H, NCH₂CH₂N), 2.40 (s, 12H, CH₃), 1.92 (s, 24H, CH₃). ¹³C NMR (100 MHz, acetone- d_6): δ 202.0 (Cu-C), 139.4, 136.7, 135.8, 130.3, 51.7, 21.2, 17.6. The ¹H NMR and ¹³C

NMR data are in accordance with those described in the literature.³⁵ Anal. Calcd for $C_{42}H_{52}CuF_6N_4P$: C, 61.41; H, 6.38; N, 6.82. Found: C, 61.23; H, 6.45; N, 6.60.

General synthetic procedure of Cu-NHCs in water

A solution of imidazolium salt (1.0 equiv.) and copper powder (5.0 equiv.) in water (10 mL) was vigorously stirred at 100 °C for 24-36 hours. The aqueous solution was then dried under vacuum (for neutral Cu-NHCs) or cooled to room temperature to give the solid (for cationic Cu-NHCs), which was collected and washed several times with water. The solid was dissolved in acetonitrile and filtered through silica. The desired product was obtained after removal of the solvent under vacuum. When necessary, the solid was further recrystallized.

[(IPr)CuCl], 2a. This complex was synthesized from the reaction of IPr•HCl (1a) (0.2 mmol, 85 mg), and copper powder (1.0 mmol, 64 mg) for 30 hours. Yield: 33 mg (34%).

[(SIPr)CuCl], 2b. This complex was synthesized from the reaction of SIPr•HCl (1b) (0.2 mmol, 86 mg), and copper powder (1.0 mmol, 64 mg) for 30 hours. Yield: 29 mg (30%).

[(IMes)CuCl], 2c. This complex was synthesized from the reaction of IMes•HCl (1c) (0.2 mmol, 69 mg), and copper powder (1.0 mmol, 64 mg) for 30 hours. Yield: 52 mg (65%).

[(SIMes)CuCl], 2d. This complex was synthesized from the reaction of SIMes•HCl (1d) (0.2 mmol, 69 mg), and copper powder (1.0 mmol, 64 mg) for 30 hours. Yield: 39 mg (48%).

[(IPr)CuBr], 2e. This complex was synthesized from the reaction of IPr•HBr (1e) (0.2 mmol, 94 mg), and copper powder (1.0 mmol, 64 mg) for 36 hours. The desired product was isolated via recrystallization from *n*-hexane/dichloromethane. Yield: 62 mg (58%).

 $[Cu_3L_3^j](PF_6)_3$, 2j. This complex was synthesized from the reaction of [HL^J]PF₆ (1j) (0.3 mmol, 119 mg), and copper powder (1.5 mmol, 96 mg) for 24 hours. The desired product was isolated via recrystallization from diethyl ether/acetonitrile. Yield: 135 mg (98%), white solid. ¹H NMR (400 MHz, DMSO d_6): δ 8.03 (t, J = 7.6 Hz, 6H, Py-H), 7.64-7.71 (m, 12H, Py-H+NCHCHN), 7.31 (t, J = 6.0, 6.4 Hz, 6H, Py-H), 6.43 (d, J = 4.8 Hz, 6H, Py-H), 5.07 (d, J = 14.4 Hz, 6H, NCHH), 4.97 (d, J = 14.8 Hz, 6H, NCHH). ¹³C NMR (100 MHz, DMSO- d_6): δ 168.3 (Cu-C), 153.9, 148.1, 139.5, 124.7, 124.3, 124.1, 53.3. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literatures.^{12a,13e} Anal. Calcd for C45H42Cu3F18N12P3: C, 39.27; H, 3.08; N, 12.21. Found: C, 39.32; H, 3.10; N, 12.15.

[*Cu*₃*L*^k₃](*PF*₆)₃, 2*k*. This complex was synthesized from the reaction of [HL^k]PF₆ (1k) (0.3 mmol, 134 mg), and copper powder (1.5 mmol, 96 mg) for 24 hours. The desired product was isolated via recrystallization from diethyl ether/acetonitrile. Yield: 134 mg (88%), white solid. ¹H NMR (400 MHz, DMSOd₆): δ 7.97 (t, *J* = 6.8, 8.0 Hz, 6H, Py-*H*), 7.84 (d, *J* = 8.0 Hz, 6H, Py-*H*), 7.77 (dd, *J* = 2.8, 5.6 Hz, 6H, benzimidazole-*H*), 7.51 (dd, *J* = 3.2, 6.0 Hz, 6H, benzimidazole-H), 6.99 (t, *J* = 5.6, 6.4 Hz, 6H, Py-*H*), 5.17 (d, *J* = 16.0 Hz, 6H, NCH*H*). ¹³C NMR (100 MHz, DMSO- d_6): δ 175.5 (Cu-*C*), 153.6, 147.8, 140.0, 134.3, 125.0, 124.9, 124.5, 111.0, 50.2. The ¹H NMR and ¹³C NMR data are in accordance with those described in the literature.^{13e} Anal. Calcd for C₅₇H₄₈Cu₃F₁₈N₁₂P₃: C, 44.85; H, 3.17; N, 11.01. Found: C, 44.76; H, 3.17; N, 11.08.

[*Cu*₃*L*¹₃](*PF*₆)₃, 2*l*. This complex was synthesized from the reaction of [HL¹]PF₆ (**1**) (0.3 mmol, 182 mg), and copper powder (1.5 mmol, 96 mg) for 24 hours. The desired product was isolated via recrystallization from diethyl ether/acetonitrile. Yield: 92 mg (46%), white solid. ¹H NMR (400 MHz, DMSOd₆): δ 8.34 (s, 6H, triazole-*H*), 7.36-7.56 (m, 30H, Ph-*H* + benzimidazole-*H*), 7.20 (d, *J* = 7.2 Hz, 12H, Ph-*H*), 5.41, 5.30 (both d, *J* = 14.8 Hz, each 6H, NC*H*₂), 5.00 (d, *J* = 15.6 Hz, 6H, NC*H*H), 4.81 (d, *J* = 15.2 Hz, 6H, NCH*H*). ¹³C NMR (100 MHz, CD₃CN): δ 142.2, 135.6, 135.2, 130.2, 130.0, 129.1, 125.4, 124.7, 111.3, 55.5, 41.8 (resonance signal of Cu-*C* was not observed). Anal. Calcd for C₈₁H₇₂Cu₃F₁₈N₂₄P₃: C, 48.47; H, 3.62; N, 16.75. Found: C, 48.33; H, 3.70; N, 16.89. Single crystals of **21** were obtained by slow diffusion of diethyl ether to its CH₃CN solution at room temperature.

 $[Cu_2L_2^m](PF_6)_2$, 2m. This complex was synthesized from the reaction of [H₂L^m](PF₆)₂ (1m) (0.2 mmol, 123 mg), and copper powder (1.0 mmol, 64 mg) at 100 °C in 6 mL of water/acetonitrile (v/v = 1/1) for 24 hours. The desired product was isolated via recrystallization from diethyl ether/acetonitrile. Yield: 57 mg (54%), yellow solid. ¹H NMR (400 MHz, DMSO d_6): δ 8.51 (t, J = 7.6, 8.0 Hz, 2H, Py-H), 8.33, 7.63 (both br. s, each 4H, NCHCHN), 8.07 (d, J = 8.0 Hz, 4H, Py-H), 3.61 (t, J = 7.6, 7.2 Hz, 8H, NCH₂CH₂CH₂CH₃), 1.10-1.32 (m, 8H, NCH₂CH₂CH₂CH₃), 0.81-0.92 (m, 8H, NCH₂CH₂CH₂CH₃), 0.57 (t, J = 7.2 Hz, 12H, NCH₂CH₂CH₂CH₂CH₃). ¹³C NMR (100 MHz, DMSO-d₆): δ 178.2 (Cu-C), 148.4, 144.3, 123.5, 118.4, 112.8, 50.7, 31.9, 18.6, 12.9. Anal. Calcd for C₃₈H₅₀Cu₂F₁₂N₁₀P₂: C, 42.90; H, 4.74; N, 13.17. Found: C, 42.72; H, 4.70; N, 13.41. Single crystals of 2m were obtained by slow diffusion of diethyl ether to its CH₃CN solution at room temperature.

 $[Cu_4(\mu_3-OH)_2L^n_2](PF_6)_4$ 2*n*.^{27a} This complex was synthesized from the reaction of $[H_2L^n](PF_6)_2$ (1n) (0.2 mmol, 135 mg), and copper powder (1.0 mmol, 64 mg) for 24 hours. The desired product was isolated via recrystallization from diethyl ether/acetonitrile. Yield: 72 mg (44%), red solid. Anal. Calcd for C₄₂H₃₆Cu₄F₂₄N₁₆O₂P₄: C, 30.93; H, 2.22; N, 13.74. Found: C, 30.71; H, 2.40; N, 13.73. The compound is paramagnetic, and thus no NMR spectrum was obtained.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 21352002) for financial support.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: Synthetic procedures for IPr•HBr (1e), IPr•HI (1f), SIPr•HI (1g), IMes•HPF₆ (1h), SIMes•HPF₆ (1i), $[HL^{j}]PF_{6}$ (1j), $[HL^{k}]PF_{6}$ (1k), $[HL^{l}]PF_{6}$ (1l), $[H_{2}L^{m}](PF_{6})_{2}$ (1m), and $[H_{2}L^{n}](PF_{6})_{2}$ (1n). Copies of ¹H and ¹³C-{¹H} NMR spectra of imidazolium salts and Cu(I)-NHC products. CCDC No. 1025967 (2l), 1025968 (2m) contain the supplementary crystallographic data for this paper. See DOI: 10.1039/b000000x/

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Graphical Abstract

Simple Synthesis of Neutral and Cationic Cu-NHC Complexes

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1. Color Graphic



2. Text (no more than 20 words)

Simple synthesis of [(NHC)CuX] and $[(NHC)_2Cu]PF_6$ complexes with cheap copper powder in both organic solvent and water is described.