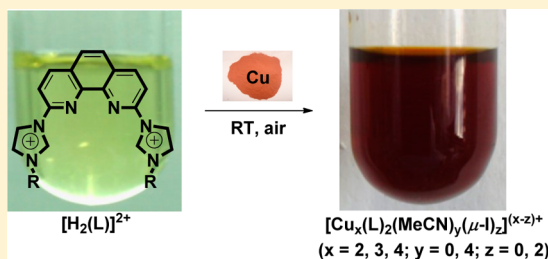


## Di-, Tri-, and Tetranuclear Copper(I) Complexes of Phenanthroline-Linked Dicarbene Ligands

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## Supporting Information

**ABSTRACT:** A family of 2,9-di(3-*R*-1*H*-imidazolium-1-yl)-1,10-phenanthroline iodides and hexafluorophosphates (*R* = allyl, benzyl, mesityl, picolyl) were synthesized from 2,9-diiodophenanthroline and imidazole or *N*-substituted imidazoles. Simple reactions of these diimidazolium salts with copper powder at room temperature have afforded a series of multinuclear copper(I)–NHC complexes in good yields. The structures vary depending on the *N* substituents and counterions. [Cu<sub>4</sub>(L1)<sub>2</sub>(MeCN)<sub>4</sub>](PF<sub>6</sub>)<sub>4</sub> (*R* = allyl) exhibits a zigzag Cu<sub>4</sub> chain with two terminal [Cu(NHC)(MeCN)<sub>2</sub>] and two internal [Cu(phen)(NHC)] moieties. [Cu<sub>3</sub>(L2)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> (*R* = benzyl) contains a strictly linear Cu<sub>3</sub> framework with two [Cu(NHC)<sub>2</sub>] units and a [Cu(phen)<sub>2</sub>] located at the center. Both complexes [Cu<sub>3</sub>(L4)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> (*R* = mesityl) and [Cu<sub>3</sub>(L5)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> (*R* = picolyl) consist of a triangular Cu<sub>3</sub> core in which two copper(I) ions are surrounded by a phen and a NHC group and the third copper(I) is coordinated by two NHC groups. [Cu<sub>3</sub>(L3)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> derived from 2,9-di(3-benzyl-1*H*-benzimidazolium-1-yl)-1,10-phenanthroline hexafluorophosphate can undergo transannulation of the benzimidazolylidene ring giving [Cu<sub>2</sub>(L3')<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. The decomposition process might involve solvent-induced rearrangement of the ligand and hydrolysis of carbene moieties. Treatment of 2,9-di(3-mesityl-1*H*-benzimidazolium-1-yl)-1,10-phenanthroline iodide with copper powder generated dinuclear complex [Cu<sub>2</sub>(L4)<sub>2</sub>][Cu<sub>2</sub>(μ-1)<sub>2</sub>I<sub>2</sub>] (*R* = mesityl) possessing a macrocyclic cation and [Cu<sub>2</sub>(μ-1)<sub>2</sub>I<sub>2</sub>]<sup>2-</sup> anion. Tetranuclear complex [Cu<sub>4</sub>(L5)<sub>2</sub>(μ-1)<sub>2</sub>](CuI<sub>3</sub>) (*R* = picolyl) has been obtained from its diimidazolium iodide and copper powder. All Cu(I) complexes have been characterized by X-ray single diffraction analysis, elemental analysis, and NMR spectra. Their redox behavior and fluorescent properties have also been studied.



## INTRODUCTION

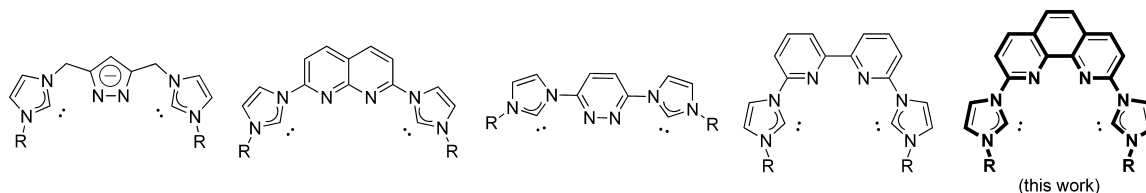
Copper complexes of *N*-heterocyclic carbenes are usually prepared through reactions of isolated or in-situ-generated free carbenes and copper salts,<sup>1</sup> transmetalation of corresponding Ag–NHC complexes,<sup>2</sup> or reactions of imidazolium salts with basic copper salts<sup>3</sup> such as Cu<sub>2</sub>O or CuOAc. More practicably, copper–NHC complexes are even obtained through direct reaction of commercially available copper powder with imidazolium salts in air.<sup>4</sup> The copper–NHC complexes not only show interesting luminescent properties<sup>5</sup> but have also found wide applications in catalytic organic transformations<sup>6</sup> such as hydrosilylation reactions,<sup>1c,7</sup> conjugate addition reactions,<sup>1b,8</sup> 1,3-dipolar cycloaddition,<sup>1c,4c,e,9</sup> carboxylation,<sup>10</sup> allylic substitutions and allylation,<sup>11</sup> borylation of unsaturated hydrocarbons,<sup>12</sup> and cross-coupling reactions.<sup>13</sup> Recently, Cu(I)–NHC complexes have proven to be good alternative NHC transfer reagents besides the popularly used Ag(I)–NHCs.<sup>12b,14</sup> Among the structurally defined copper–NHC complexes, most of them are [Cu(NHC)X] (*X* = halide) and [Cu(NHC)<sub>2</sub>]X (*X* = halide, PF<sub>6</sub><sup>-</sup>, etc.) complexes. Thus far relatively few polynuclear copper complexes of NHCs have been known compared to its polysilver complexes.<sup>4a,b,5a,13,14e,15</sup> We have been interested in the organometallic chemistry of dicarbene ligands bridged by 3,5-bismethyl-1*H*-pyrazole,<sup>4b,16</sup>

1,8-naphthyridine,<sup>17</sup> and pyridazine.<sup>18</sup> As shown in Scheme 1, the tetratentate ligand offers an excellent opportunity to construct multinuclear metal complexes. In particular, such compounds have proven to be suitable binucleating ligands for construction of dimetallic complexes in which two metals are held together in close proximity.<sup>4b,16–18</sup> We demonstrated that the pyrazole-bridged dicarbene ligands are able to construct Ag(I), Au(I) clusters, and dinuclear Ni(II) and Cu(II) complexes.<sup>4b,16</sup> Others also applied these ligands to prepare polynuclear Ag(I) and dinuclear Pd(II), Ru(II), Rh(I), and Ir(I) complexes.<sup>19</sup> Naphthyridine-bridged dicarbenes can construct trinuclear Ag(I)<sup>17</sup> and dinuclear Pd(II)<sup>20</sup> complexes. Pyridazine-bridged dicarbenes were initially applied to synthesize dinuclear Hg(II) complexes,<sup>21</sup> and we found that these ligands can also serve for construction of Ag(I), Cu(I) clusters, and dinuclear Pd(II), Ru(II) complexes.<sup>18</sup> Besides, dicarbene ligands bridged by 2,2'-bipyridine are also known to form polynuclear metal complexes.<sup>22</sup> As a continuation, we report herein the synthesis of a new class of phenanthroline-bridged bisimidazolylidene ligands and their copper complexes.

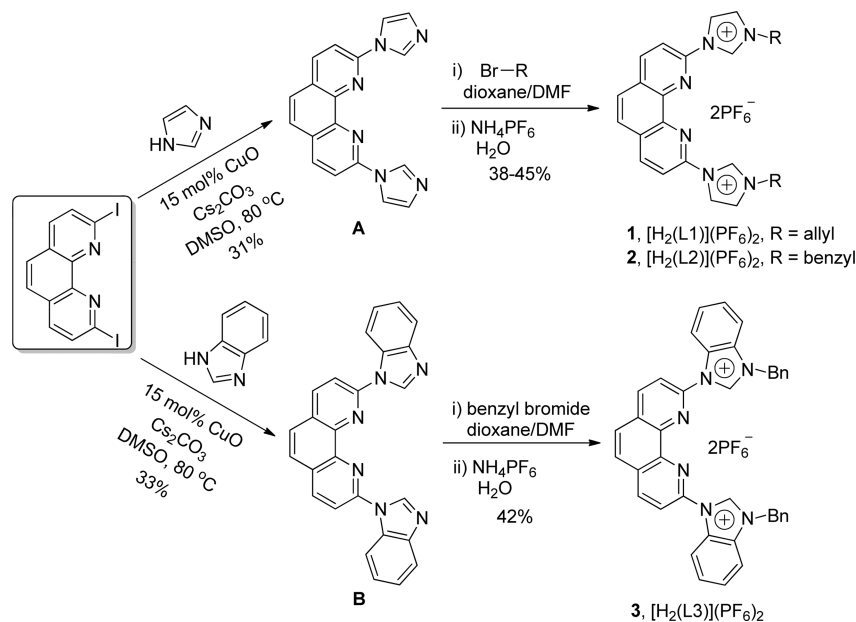
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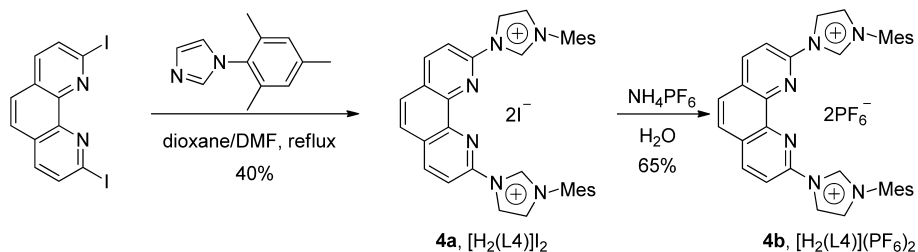
Scheme 1. Bis-Imidazolylidene Ligands Bridged by a N-Heteroarene



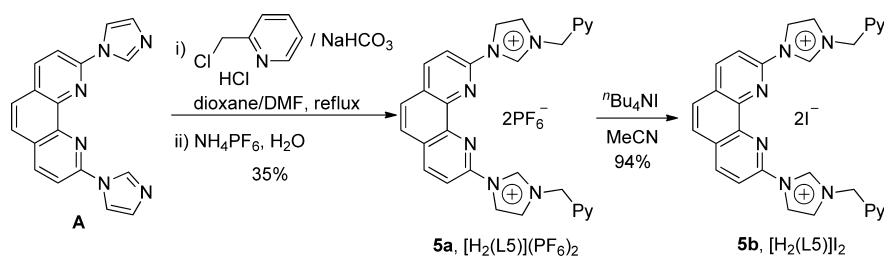
Scheme 2. Synthesis of Phenanthroline-Bridged Diimidazolium Salts 1–3



Scheme 3. Synthesis of Phenanthroline-Bridged Diimidazolium Salts 4a,b



Scheme 4. Synthesis of Phenanthroline-Bridged Diimidazolium Salts 5a,b



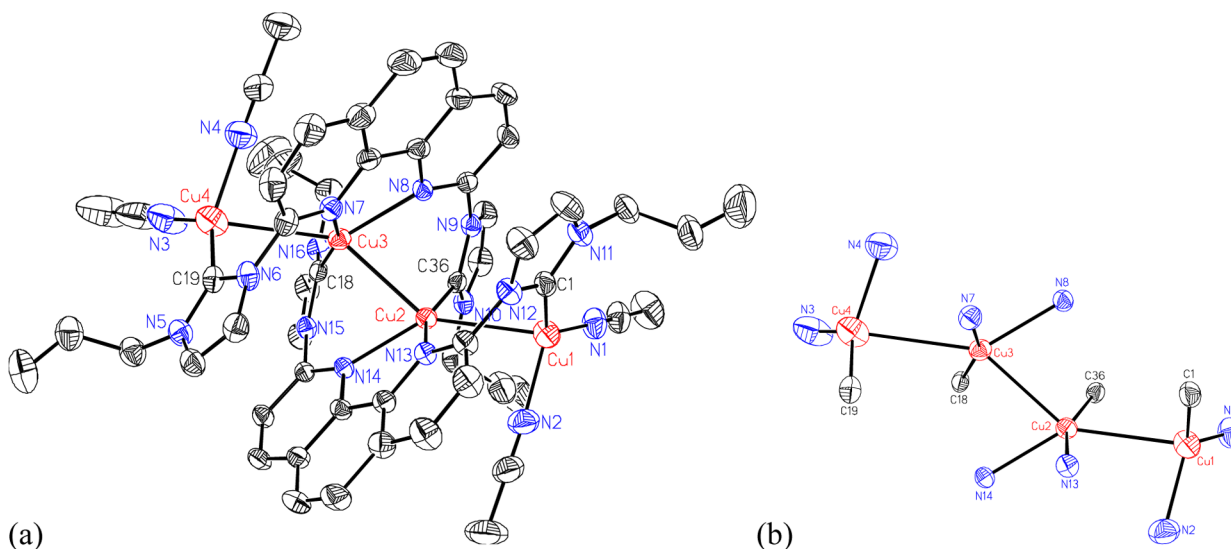
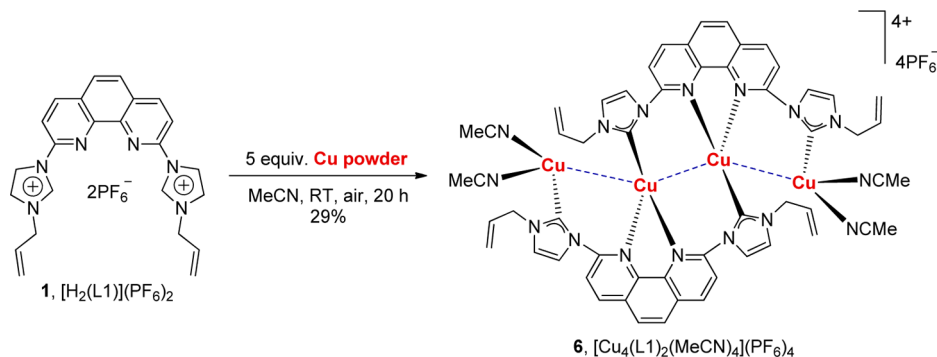
## RESULTS AND DISCUSSION

### Preparation of Phenanthroline-Bridged Diimidazolium Salts

2,9-Diiodo-1,10-phenanthroline was prepared according to the reported literature procedure<sup>23</sup> from 1,10-phenanthroline in an overall yield of 25%. Reaction of 2,9-diiodo-1,10-phenanthroline with an excess of imidazole or benzimidazole in the presence of CuO afforded 2,9-di(1*H*-imidazol-1-yl)-1,10-

phenanthroline (**A**) and 2,9-bis(1*H*-benzo[*d*]imidazol-1-yl)-1,10-phenanthroline (**B**) in ca. 30% yields (Scheme 2).

There are two different strategies for synthesis of phenanthroline-linked diimidazolium salts. Both reactions of compound **A** or **B** with suitable alkyl halides and reactions of 2,9-diiodo-1,10-phenanthroline with *N*-substituted imidazole can generate the NHC precursors (Schemes 2–4).  $[\text{H}_2(\text{L}1)](\text{PF}_6)_2$  (**1**) and  $[\text{H}_2(\text{L}2)](\text{PF}_6)_2$  (**2**) were obtained in 38% and

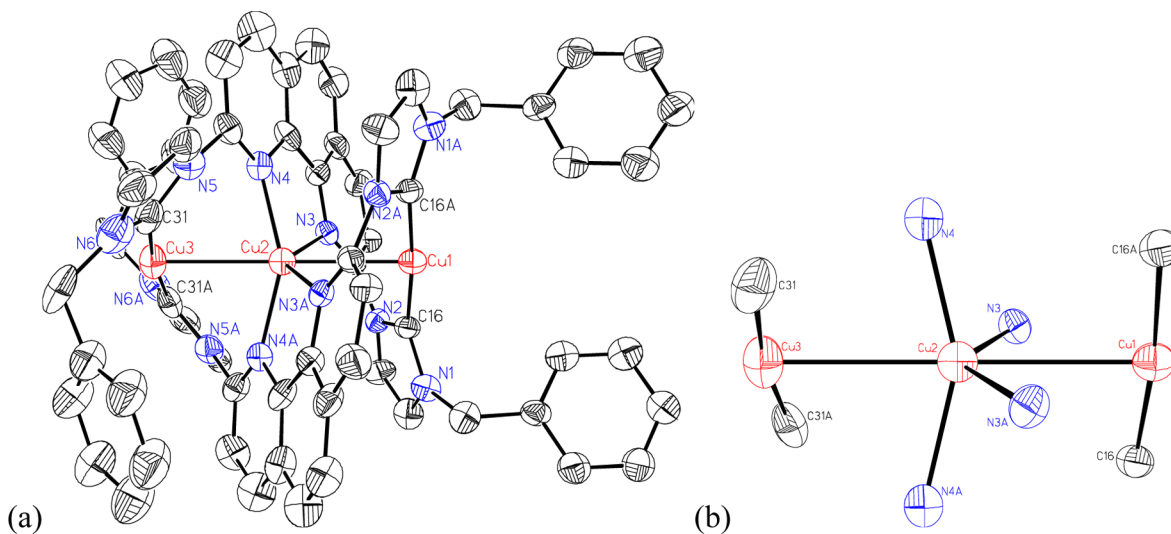
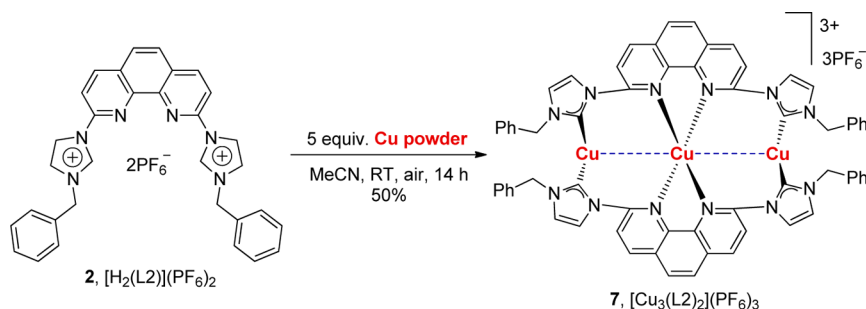
Scheme 5. Synthesis of  $[\text{Cu}_4(\text{L1})_2(\text{MeCN})_4](\text{PF}_6)_4$  (**6**)

**Figure 1.** (a) ORTEP drawing of the cationic section of  $[\text{Cu}_4(\text{L1})_2(\text{MeCN})_4](\text{PF}_6)_4$  (**6**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Angstroms) and angles (degrees): Cu1–C1 1.925(6), Cu1–N1 1.963(6), Cu1–N2 2.014(6), Cu2–C36 1.910(5), Cu2–N13 2.040(4), Cu2–N14 2.158(4), Cu3–C18 1.905(5), Cu3–N7 2.027(4), Cu3–N8 2.174(4), Cu4–C19 1.915(6), Cu4–N3 1.951(6), Cu4–N4 2.032(7), C1–Cu1–N1 127.8(2), C1–Cu1–N2 121.8(2), N1–Cu1–N2 106.0(2), C36–Cu2–N13 157.4(2), C36–Cu2–N14 122.7(2), N13–Cu2–N14 79.1(2), C18–Cu3–N7 158.8(2), C18–Cu3–N8 122.3(2), N7–Cu3–N8 78.4(2), C19–Cu4–N3 131.5(3), C19–Cu4–N4 125.8(2), N3–Cu4–N4 100.5(3). (b) Simplified illustration of the coordination environment of **6**.

45% yield from **A** and 6 equiv of 3-bromopropene or benzyl bromide in dioxane and DMF at 85 °C for 36 h, followed by anion exchange with  $\text{NH}_4\text{PF}_6$  (Scheme 2). Under similar conditions,  $[\text{H}_2(\text{L3})](\text{PF}_6)_2$  (**3**) was prepared from **B** in a yield of 42% (Scheme 2). Refluxing the mixture of 2,9-diiodo-1,10-phenanthroline with 4 equiv of *N*-mesitylimidazole in dioxane and DMF for 48 h led to formation of diimidazolium iodide salt  $[\text{H}_2(\text{L4})]\text{I}_2$  (**4a**) in a yield of 40%. Further reaction of **4a** with an excess of  $\text{NH}_4\text{PF}_6$  generated  $[\text{H}_2(\text{L4})](\text{PF}_6)_2$  (**4b**) (Scheme 3). Refluxing the mixture of **A** with 5 equiv of 2-(chloromethyl)pyridine hydrochloride in the presence of  $\text{NaHCO}_3$  for 24 h followed by anion exchange with  $\text{NH}_4\text{PF}_6$  resulted in isolation of  $[\text{H}_2(\text{L5})](\text{PF}_6)_2$  (**5a**) in 35% yield.  $[\text{H}_2(\text{L5})]\text{I}_2$  (**5b**) was readily obtained in nearly quantitative yield via anion exchange of  $[\text{H}_2(\text{L5})](\text{PF}_6)_2$  (**5a**) with tetrabutylammonium iodide (TBAI) in MeCN (Scheme 4). These imidazolium salts are colorless to pale yellow solids. The hexafluorophosphate salts **1–3**, **4b**, and **5a** have good solubilities in MeCN, while iodide salt **5b** is poorly soluble in MeCN but dissolves in DMSO. All these salts have been fully characterized. In their  $^1\text{H}$  NMR spectra, the chemical shifts of C2–H are located between 10.40 and 11.03 ppm.

UV–vis absorption spectra of **1** and **2**, **4a,b**, and **5a** in MeCN at room temperature showed three maximum absorptions at 235–237, 251–254, and 287–289 nm associated with the  $\pi$ – $\pi^*$  transition of phenanthroline, while **3** shows two main maximum absorptions at 229 and 278 nm. The weak shoulders at ca. 315 nm were also observed in their electronic absorption spectra. Fluorescent emission spectra of these imidazolium salts in MeCN at room temperature exhibited unstructured emission bands centered at ca. 376 nm upon excitation at 290 nm (see Supporting Information).

**Synthesis and Characterization of Cu(I)–NHC Complexes.** According to our previously reported method, copper NHC complexes can be directly obtained from reaction of the corresponding imidazolium salts with copper powder.<sup>4</sup> As shown in Scheme 5, we treated the imidazolium salt  $[\text{H}_2(\text{L1})](\text{PF}_6)_2$  (**1**) with an excess of copper powder in MeCN at room temperature. During the reaction the solution was gradually changed from colorless to red. Red crystals of tetranuclear complex  $[\text{Cu}_4(\text{L1})_2(\text{MeCN})_4](\text{PF}_6)_4$  (**6**) were obtained in 29% yield after recrystallization by diffusion of diethyl ether into its MeCN solution. Complex **6** is stable in its solid state, but the color of its solution turns to green very

Scheme 6. Synthesis of  $[\text{Cu}_3(\text{L}2)_2](\text{PF}_6)_3$  (7)

**Figure 2.** (a) ORTEP drawing of the cationic section of  $[\text{Cu}_3(\text{L}2)_2](\text{PF}_6)_3$  (7). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Angstroms) and angles (degrees): Cu1–C16 1.873(1), Cu2–N4 2.042(7), Cu2–N3 2.188(8), Cu3–C31 1.924(1), C16–Cu1–C16A 174.6(6), N4A–Cu2–N4 153.5(5), N4A–Cu2–N3 111.3(3), N4–Cu2–N3 79.7(3), N3–Cu2–N3A 132.6(4), C31–Cu3–C31A 171.5(7). Symmetry code: A  $-x, -y + 1, z$ . (b) Simplified illustration of the coordination environment of 7.

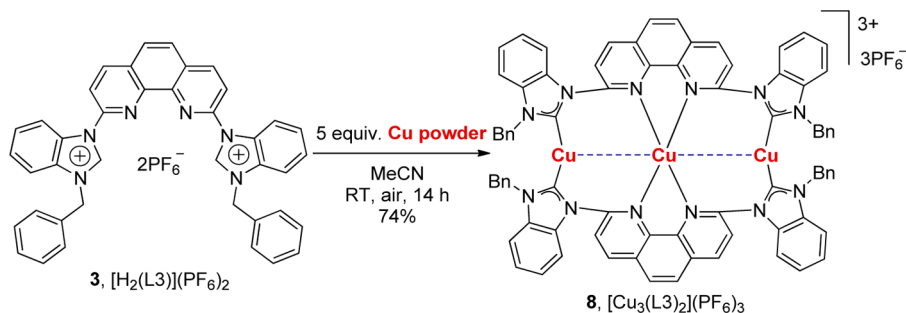
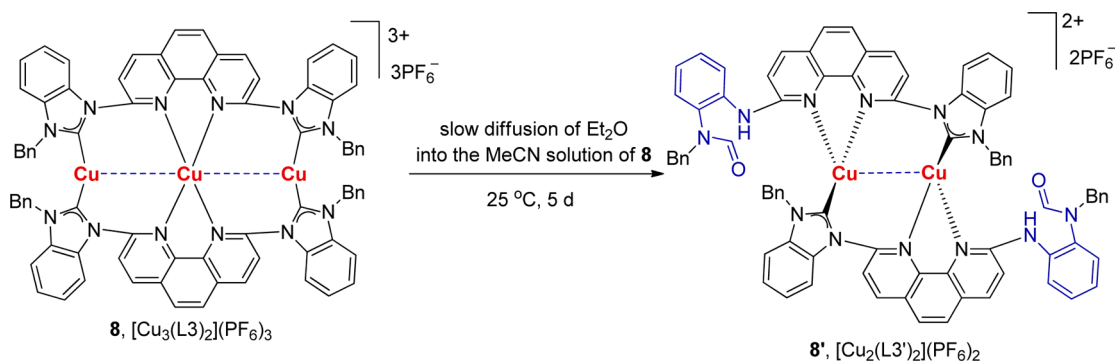
slowly, indicating its oxidation. The structure of **6** has been characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and elemental analysis. Elemental analysis shows that the molar ratio of copper and 1,10-phenanthroline-2,9-diimidazolylidene is 2:1. In its  $^1\text{H}$  NMR spectrum, only one set of resonance signals of ligands was observed illustrating the phen-NHC moieties are magnetically equivalent. The chemical shift of the carbenic carbons appears at 178.8 ppm in the  $^{13}\text{C}$  NMR spectrum of **6**, which falls in the range of  $^{13}\text{C}$  chemical shifts for Cu(I)–NHC complexes (ca. 157.6–219.4 ppm).<sup>24</sup> Although the two carbenic carbons coordinate in different coordination spheres, they show the same chemical shifts.

Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into the MeCN solution of **6** at room temperature. The structure of **6** was unambiguously identified by X-ray single-crystal diffraction analysis. Complex **6** crystallizes in the monoclinic space group  $C2/c$ . It is a cationic tetranuclear copper complex consisting of a zigzag  $\text{Cu}_4$  chain. The molecular structure of the cationic section is represented in Figure 1 along with the principal bond lengths and bond angles. The four copper atoms are held together by two L1 ligands with short Cu–Cu contacts, in which the Cu–Cu separations are between 2.637(1) and 2.899(1) Å. The Cu–Cu separations are comparable to the reported results in other copper–NHC cluster complexes (ca. 2.4–2.9 Å).<sup>15,24</sup> In the complex, the two external copper atoms are each tricoordinated to one carbene

carbon and two acetonitrile molecules in an approximate trigonal geometry. The two internal copper atoms are also tricoordinated by a phenanthroline and a NHC of the second ligand. The Cu–C bond distances are found in the range of 1.905(5)–1.925(6) Å, which is normal for copper carbene complexes (ca. 1.85–2.18 Å).<sup>15,24</sup> Linear tetranuclear  $\text{Ag}_4$  complexes of NHC ligands have already been reported;<sup>24,25</sup> to the best of our knowledge, complex **6** represents the first example of a linear  $\text{Cu}_4$  complex supported by NHCs. Linearly arranged  $\text{Cu}_4$  complexes supported by multidentate P and N ligands are also rare.<sup>26</sup>

$[\text{H}_2(\text{L}2)](\text{PF}_6)_2$  (**2**) also reacted with copper powder in acetonitrile at room temperature giving a red solution from which  $[\text{Cu}_3(\text{L}2)_2](\text{PF}_6)_3$  (**7**) was isolated as red crystals in 50% yield (Scheme 6). Complex **7** is stable both in solution and in the solid state. The composition of the tricopper complex **7** was confirmed by elemental analysis. The  $^1\text{H}$  NMR spectrum of **7** displays only one set of resonance signals assignable to L2, indicating two magnetically equivalent ligands. In its  $^{13}\text{C}$  NMR spectrum, the chemical shift of the four carbenic carbons was found to be 179.3 ppm, close to that of **6**.

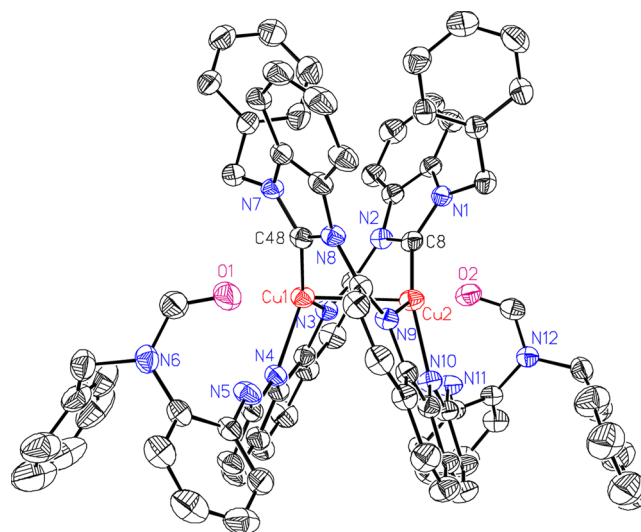
The structure of **7** determined by X-ray single-crystal analysis is presented in Figure 2. The molecular structure shows a cationic tricopper complex consisting of a strictly linear  $\text{Cu}_3$  chain with a  $180.0^\circ$  angle of Cu1–Cu2–Cu3 bridged by two L2 ligands. The two terminal  $\text{Cu}(\text{NHC})_2$  units are arranged in an

Scheme 7. Synthesis of  $[\text{Cu}_3(\text{L3})_2](\text{PF}_6)_3$  (**8**)Scheme 8. Transannulation of Complex **8**

eclipsed conformation. Two external Cu1 and Cu3 are each bicoordinated by two carbenic carbons in a slightly bent geometry with C–Cu–C angles of  $174.6(6)^\circ$  and  $171.5(7)^\circ$ , respectively, while the internal copper atom is tetracoordinated with two phenanthroline moieties in a distorted tetrahedral coordination sphere. The Cu–C distances in **7** are between 1.873(1) and 1.924(1) Å. The separation of neighboring copper(I) centers is at 2.687(2)–2.711(2) Å, indicating weak metal–metal interactions.

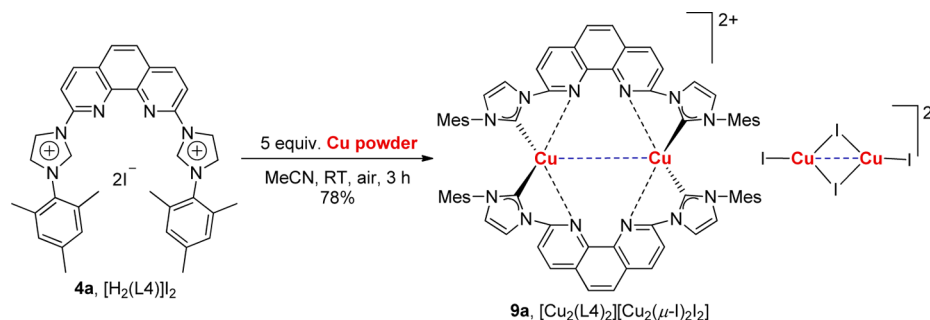
Under similar reaction conditions, reaction of benzimidazolium salt  $[\text{H}_2(\text{L3})](\text{PF}_6)_2$  (**3**) with copper powder proceeded smoothly in MeCN at 25 °C. After 14 h, addition of  $\text{Et}_2\text{O}$  into the MeCN solution gave complex **8** as a red solid (Scheme 7). Elemental analysis of **8** showed that the molar ratio of the L3 ligands and copper ions is 2:3. A set of resonance signals ascribed to the L3 ligand was observed in the  $^1\text{H}$  NMR spectrum of **8**, illustrating that the ligands are magnetically equivalent. Its  $^{13}\text{C}$  NMR spectrum displayed a resonance signal at 188.7 ppm characteristic of Cu–C<sub>carbene</sub> bonds. The complex is reasonably assumed to have the same structure as **7**. Unexpectedly, slow diffusion of diethyl ether into the MeCN solution of **8** at 25 °C for 5 days gave orange crystals of **8'** (Scheme 8). The  $^1\text{H}$  NMR spectrum showed two resonance signals at 7.97 and 5.67 ppm corresponding to  $\text{Ar}_2\text{NCHO}$  and  $\text{Ar}_2\text{NH}$  protons resulting from the transannulation of the NHC rings, and the resonance signals ascribed to the carbon atoms of Cu–C and  $\text{Ar}_2\text{NCHO}$  are, respectively, located at 191.2 and 163.1 ppm in the  $^{13}\text{C}$  NMR of **8'**. Deterioration of the NHC ring was further confirmed by X-ray single-crystal diffraction, elemental analysis, and ESI-MS spectrum. Positive-ion ESI-MS analysis shows the most intense  $m/z$  peak at 674.3 amu corresponding to  $[\text{Cu}(\text{L3}')^+]^+$  or  $[\text{Cu}_2(\text{L3}')_2]^{2+}$ .

X-ray single-crystal diffraction showed that complex  $[\text{Cu}_2(\text{L3}')_2](\text{PF}_6)_2$  (**8'**) consists of two tricoordinated copper(I) centers bridged by two ligands (Figure 3). The structure



**Figure 3.** ORTEP drawing of the cationic section of  $[\text{Cu}_2(\text{L3}')_2](\text{PF}_6)_2$  (**8'**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Angstroms) and angles (degrees): Cu1–C48 1.885(4), Cu1–N4 2.028(3), Cu1–N3 2.082(3), Cu2–C8 1.889(4), Cu2–N10 2.016(3), Cu2–N9 2.090(3), C48–Cu1–N4 139.3(2), C48–Cu1–N3 138.8(1), N4–Cu1–N3 81.8(1), C8–Cu2–N10 139.8(1), C8–Cu2–N9 138.9(1), N10–Cu2–N9 81.2(1).

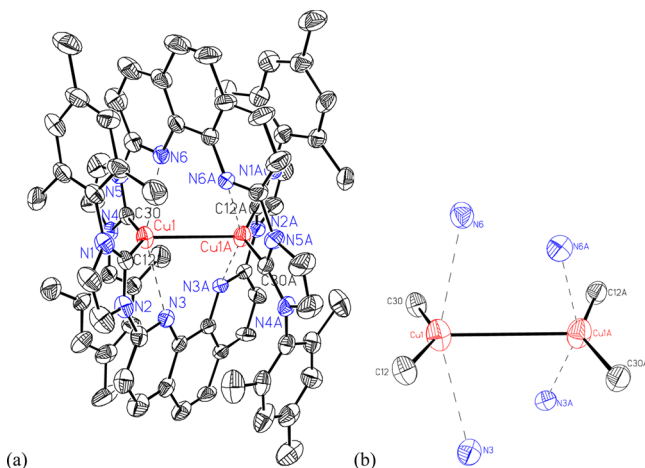
clearly showed the decomposition of one NHC ring of the L3 giving formamide, while the other NHC is coordinated to the copper center as usual. The formamide group is not coplanar with its neighboring phenyl ring, and the carbonyl points to the NH group due to hydrogen bonding at distances of 2.237–2.264 Å. Each copper center of **8'** is located in the triangle tricoordination geometry of one carbenic carbon and one phenanthroline molecule. Cu–C distances are 1.885(4) and

Scheme 9. Synthesis of  $[\text{Cu}_2(\text{L4})_2][\text{Cu}_2(\mu\text{-I})_2\text{I}_2]$  (**9a**)

1.889(4) Å. The two copper centers are separated by 2.652(1) Å.

As described in Scheme 9, it was found that diimidazolium iodide salt  $[\text{H}_2(\text{L4})]\text{I}_2$  (**4a**) is quite reactive toward copper powder in MeCN at room temperature. The colorless solution of **4a** turned to red within a few minutes when it was treated with copper powder.  $[\text{Cu}_2(\text{L4})_2][\text{Cu}_2(\mu\text{-I})_2\text{I}_2]$  (**9a**) was isolated as orange crystals in 78% yield after 3 h. Complex **9a** is well soluble in DMSO. The  $^1\text{H}$  NMR spectrum displays a set of resonance signals assignable to phenanthroline, imidazolylidene, and mesityl groups as expected. In the  $^{13}\text{C}$  NMR spectrum of **9a**, the resonance signal ascribed to the carbenic carbon atom appears at 175.5 ppm.

The structure of complex **9a** further characterized by X-ray single-crystal diffraction is shown in Figure 4. The structure of



**Figure 4.** (a) ORTEP drawing of the cationic section of  $[\text{Cu}_2(\text{L4})_2][\text{Cu}_2(\mu\text{-I})_2\text{I}_2]$  (**9a**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranion have been removed for clarity. Selected bond distances (Angstroms) and angles (degrees): Cu1–C30 1.908(6), Cu1–C12 1.912(6), Cu1–N3 2.546(4), Cu1–N6 2.557(5), C30–Cu1–C12 144.8(2), C30–Cu1–N3 115.3(2), C12–Cu1–N3 74.5(2), C30–Cu1–N6 74.5(2), C12–Cu1–N6 112.0(2), N3–Cu1–N6 154.2(2). Symmetry code: A  $-x, y, -z + 1/2$ . (b) Simplified illustration of the coordination environment of **9a**.

**9a** is composed of centrosymmetric  $[\text{Cu}_2(\text{L4})_2]^{2+}$  and  $[\text{Cu}_2(\mu\text{-I})_2\text{I}_2]^{2-}$ . The macrocyclic cation consists of two Cu(I) ions coordinated by two carbenic carbons from two L4 ligands with bond distances of 1.908(6) and 1.912(6) Å. In addition, the Cu(I) ions also weakly interact with the nitrogen atoms of phenanthroline with distances of 2.546(4) and 2.557(5) Å. As a result, the bond angle of C–Cu–C was bent to 144.8(2)°,

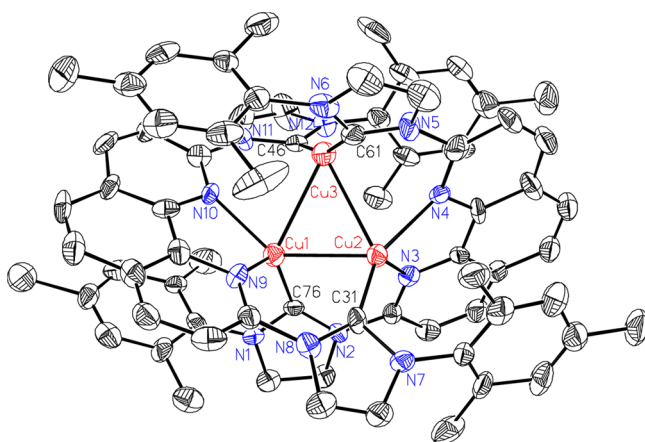
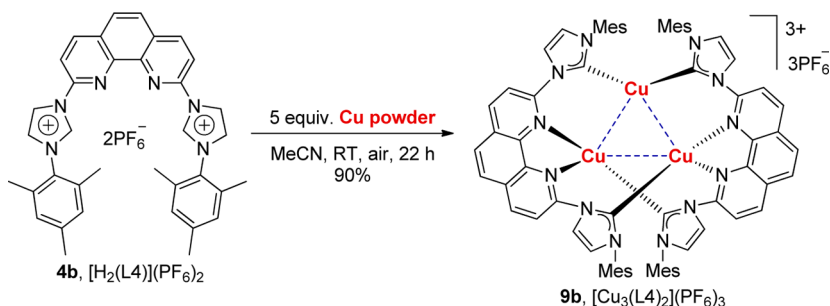
obviously much smaller than those of Cu(I) dicarbene complexes which typically adopt nearly linear coordination geometry.<sup>24,27</sup> The separation of Cu1 and Cu1A is at 2.955(2) Å in **9a**.

Reaction of  $[\text{H}_2(\text{L4})](\text{PF}_6)_2$  (**4b**) with copper powder at room temperature generated trinuclear complex  $[\text{Cu}_3(\text{L4})_2](\text{PF}_6)_3$  (**9b**) as yellow crystals in 90% yield (Scheme 10). Elemental analysis of **9b** shows the molar ratio of ligand to copper center is 2:3. In addition, a set of resonance signals of the ligand was observed in the  $^1\text{H}$  NMR spectrum of **9b**. The chemical shift of the carbenic carbon atoms was found to be 175.7 ppm in its  $^{13}\text{C}$  NMR spectrum.

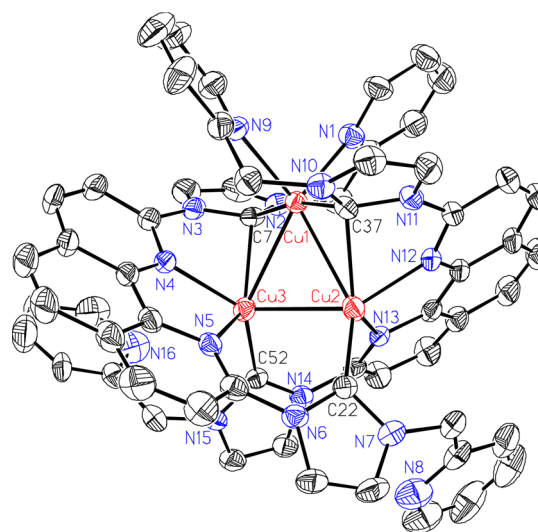
The structure of complex **9b** was finally determined by X-ray single-crystal diffraction analysis, shown in Figure 5. The cell unit consists of two independent molecules that are essentially the same, and thus, only one is given in Figure 5. In the structure of **9b**, the spatial arrangement of the ligands makes the structure form a triangular  $\text{Cu}_3$  core. Copper centers Cu1 and Cu2 are in triangular pyramid geometry with coordination of one carbenic carbon atom and phenanthroline of the other ligand. Cu3 is dicoordinated by two carbenic carbon atoms in a bent geometry. The separation of copper centers is at 2.579(1)–2.714(1) Å. Triangular  $\text{Cu}_3$  complexes bearing NHC ligands have been reported by us and others, and the Cu–Cu distance is usually among 2.47–2.90 Å.<sup>4a,5a,13b,14e,15d–f</sup> Cu–C bond distances in **9b** are among 1.852(6)–1.918(6) Å, which are similar to those of Cu–C bonds described above.

As shown in Scheme 11,  $[\text{H}_2(\text{L5})](\text{PF}_6)_2$  (**5a**) containing additional pyridine groups reacted with copper powder in MeCN at room temperature for 24 h affording a new trinuclear Cu(I)–NHC complex  $[\text{Cu}_3(\text{L5})_2](\text{PF}_6)_3$  (**10a**) in 73% yield. Complex **10a** is orange and stable toward air and moisture. **10a** has been characterized by elemental analysis and NMR spectra. A set of signals ascribed to the L5 ligand was observed in the  $^1\text{H}$  NMR spectrum of **10a**. The chemical shift of carbenic carbon atoms appears at 177.9 ppm in its  $^{13}\text{C}$  NMR spectrum.

The molecular structure of complex **10a** is shown in Figure 6. The structure of **10a** is similar to that of **9b** containing a triangular  $\text{Cu}_3$  core. In contrast with **9b**, **10a** exhibits two carbenic carbon atoms in  $\mu_2$  coordination mode with Cu–C bond distances of 1.958(6)–2.436(6) Å, which are longer than normal Cu–C bonds of Cu(I)–NHC complexes. Such a bridging coordination mode of NHC has also been found in a few Ag, Cu, and Ni complexes.<sup>1c,3f,4b,5a,14e,18b,28</sup> Meanwhile, two NHCs of terminal coordination mode are bonded with the corresponding Cu centers in 1.935(6) and 1.940(6) Å. Due to the bridging coordination effect, the separations of each two copper centers are between 2.544(1) and 2.647(1) Å, slightly shorter than those of **9b**. In the structure, each copper center is

Scheme 10. Synthesis of  $[\text{Cu}_3(\text{L4})_2](\text{PF}_6)_3$  (**9b**)

**Figure 5.** ORTEP drawing of the cationic section of  $[\text{Cu}_3(\text{L4})_2](\text{PF}_6)_3$  (**9b**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Angstroms) and angles (degrees): Cu1–C76 1.911(6), Cu1–N9 2.086(5), Cu1–N10 2.073(5), Cu2–C31 1.918(6), Cu2–N4 2.040(5), Cu2–N3 2.135(5), Cu3–C46 1.852(6), Cu3–C61 1.897(7), C76–Cu1–N9 124.1(2), C76–Cu1–N10 133.5(2), N9–Cu1–N10 79.7(2), C31–Cu2–N4 137.9(2), C31–Cu2–N3 117.5(2), N4–Cu2–N3 79.9(2), C46–Cu3–C61 159.0(2).

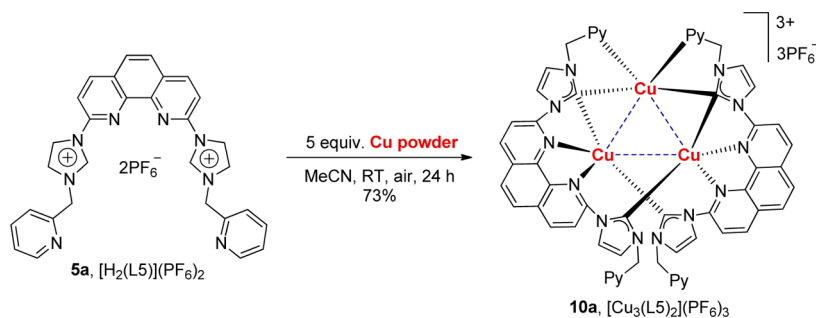


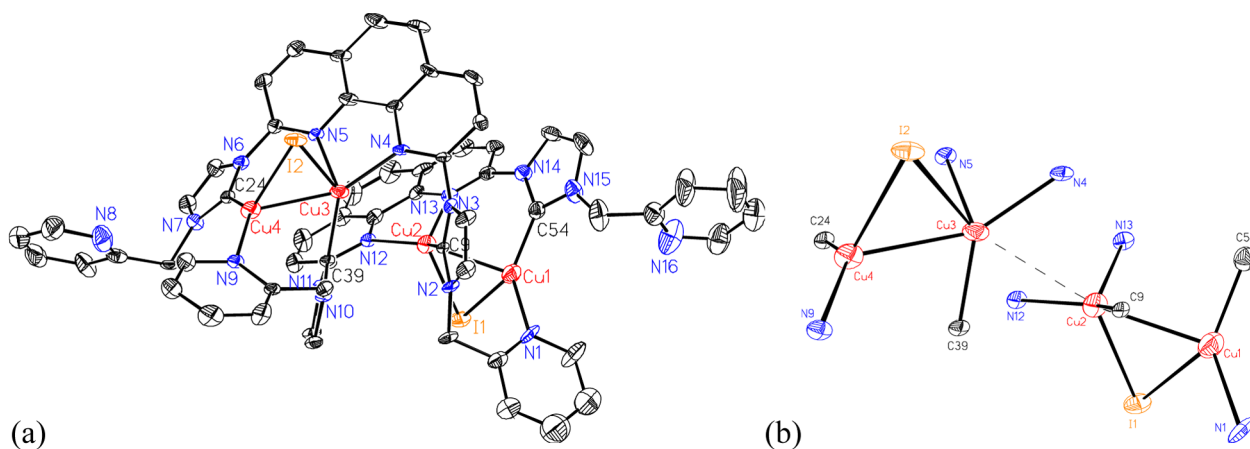
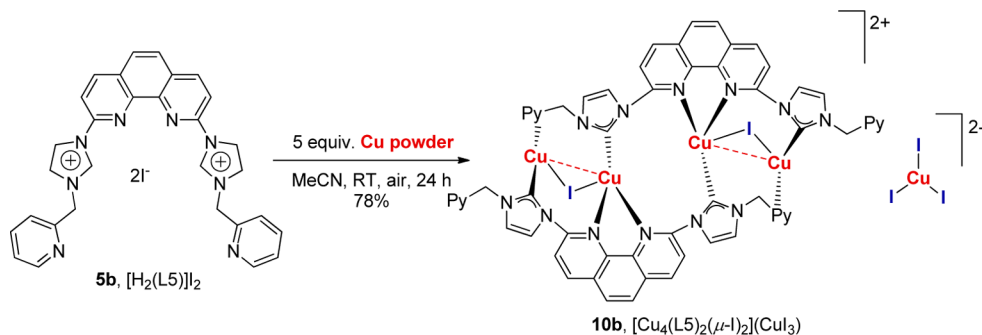
**Figure 6.** ORTEP drawing of the cationic section of  $[\text{Cu}_3(\text{L5})_2](\text{PF}_6)_3$  (**10a**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranions have been removed for clarity. Selected bond distances (Angstroms) and angles (degrees): Cu1–C37 1.958(6), Cu1–C7 1.964(6), Cu1–N9 2.196(5), Cu1–N1 2.222(6), Cu2–C22 1.935(6), Cu2–N12 2.039(5), Cu2–N13 2.382(5), Cu2–C37 2.436(6), Cu3–C52 1.940(6), Cu3–N4 2.043(5), Cu3–N5 2.326(5), Cu3–C7 2.402(6), C37–Cu1–C7 166.9(3), C37–Cu1–N9 90.3(2), C7–Cu1–N9 99.5(2), C37–Cu1–N1 100.1(2), C7–Cu1–N1 88.0(3), N9–Cu1–N1 93.5(2), C22–Cu2–N12 129.6(2), C22–Cu2–N13 106.8(2), N12–Cu2–N13 73.8(2), C22–Cu2–C37 117.1(2), N12–Cu2–C37 73.7(2), N13–Cu2–C37 135.7(2), C52–Cu3–N4 129.4(2), C52–Cu3–N5 108.0(2), N4–Cu3–N5 74.6(2), C52–Cu3–C7 114.4(2), N4–Cu3–C7 73.3(2), N5–Cu3–C7 137.0(2).

located in a distorted tetrahedral geometry. Two pyridine rings from two L5 ligands are simultaneously coordinated with Cu1, while the other two are free from coordination.

As shown in Scheme 12, although diimidazolium iodide salt  $[\text{H}_2(\text{L5})]\text{I}_2$  (**5b**) is poorly soluble in MeCN, reaction of **5b** with copper powder proceeded smoothly in MeCN even at room temperature, as identified by the dark red color of the solution. After 24 h,  $[\text{Cu}_4(\text{L5})_2(\mu\text{-I})_2](\text{CuI}_3)$  (**10b**) was isolated as a red solid in 78% yield. It is not soluble in common solvent but strong polar DMF and DMSO. The

chemical shift of the carbenic carbon atoms was found to be 179.0 ppm in its  $^{13}\text{C}$  NMR spectrum.

Scheme 11. Synthesis of  $[\text{Cu}_3(\text{L5})_2](\text{PF}_6)_3$  (**10a**)

Scheme 12. Synthesis of  $[\text{Cu}_4(\text{L5})_2(\mu\text{-I})_2](\text{CuI}_3)$  (**10b**)

**Figure 7.** (a) ORTEP drawing of the cationic section of  $[\text{Cu}_4(\text{L5})_2(\mu\text{-I})_2](\text{CuI}_3)$  (**10b**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and counteranion have been removed for clarity. Selected bond distances (Angstroms) and angles (degrees): Cu1–C54 1.921(1), Cu1–N1 2.057(9), Cu1–I1 2.692(2), Cu2–C9 1.917(7), Cu2–N12 2.015(6), Cu2–N13 2.161(7), Cu2–I1 2.881(1), Cu3–C39 1.916(8), Cu3–N4 2.042(7), Cu3–N5 2.141(6), Cu3–I2 2.873(1), Cu4–C24 1.936(7), Cu4–N9 2.032(7), Cu4–I2 2.674(1), C54–Cu1–N1 133.3(4) 133.2(4), C54–Cu1–I1 128.5(3) 128.5(3), N1–Cu1–I1 96.0(3) 96.1(3), C9–Cu2–N12 137.3(3), C9–Cu2–N13 128.6(3), N12–Cu2–N13 80.9(3), C9–Cu2–I1 114.9(2), N12–Cu2–I1 91.3(2), N13–Cu2–I1 90.7(2), C39–Cu3–N4 133.9(3), C39–Cu3–N5 131.1(3), N4–Cu3–N5 80.4(2), C39–Cu3–I2 115.2(2), N4–Cu3–I2 93.9(2), N5–Cu3–I2 89.8(2), C24–Cu4–N9 137.2(3), C24–Cu4–I2 123.8(2), N9–Cu4–I2 96.1(2). (b) Simplified illustration of the coordination environment of **10b**.

Red crystals of complex **10b** were grown by slow diffusion of diethyl ether to its DMF solution at room temperature. X-ray single diffraction analysis indicated that **10b** consists of a tetranuclear copper(I) NHC cation and a  $\text{CuI}_3^{2-}$  anion (Figure 7). The cationic section of **10b** contains four copper centers, two L5 ligands, and two bridging iodide ions. Both internal copper centers Cu2 and Cu3 are tetracoordinated by one carbene, one phenanthroline of the other ligand, and one  $\text{I}^-$  in a distorted tetrahedral geometry. The separation of Cu2 and Cu3 is at 3.223 Å, excluding any interaction. The external copper Cu1 and Cu4 are tricoordinated by one carbenic carbon, one pyridine, and one iodide ion. The adjacent internal and external copper centers are bridged by an iodide ion, forming a butterfly conformation with the Cu–Cu separation by 2.536(2) and 2.550(2) Å. Cu–C and Cu–N bond distances are comparable to those of the above Cu(I)–NHC complexes. In the anionic section, the copper center is located in a triangular geometry with coordination of three iodide ions. Cu–I bond distances are between 2.537(2) and 2.553(2) Å, shorter than those of the bridging Cu–I bonds in **10b**.

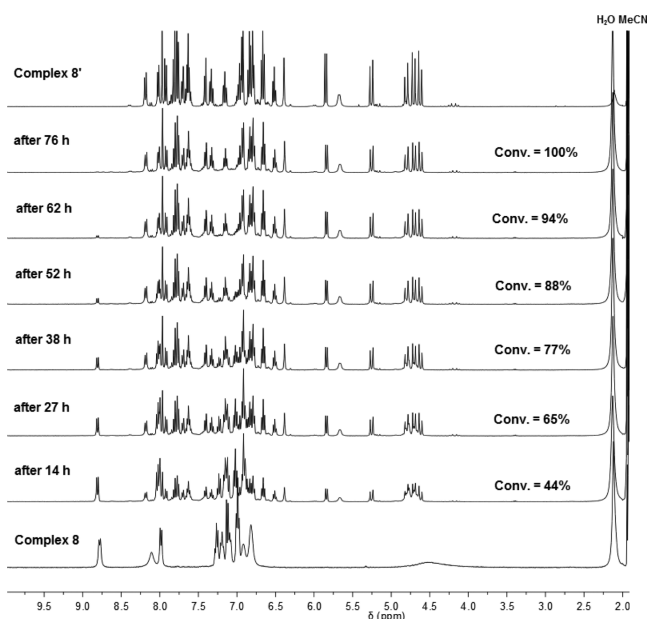
All of the Cu(I) complexes presented above were constructed by two ligands, and the two NHC moieties can adopt two different orientations. The two NHC moieties of L1, L2, and L5 in complexes **6**, **7**, and **10b** are located at different sides of the phenanthroline plane; thus, the copper centers in

these complexes are linearly arranged. In contrast, the two NHC moieties of L4 and L5 in **9b** and **10a** are oriented to the same side of the phenanthroline plane. As a result, the copper ions in **9b** and **10a** are arranged in a cyclic fashion. For comparison, our previously reported tridentate *N*-(1,10-phenanthroline-2-yl)imidazolylidene ligands form dicopper complexes independent of the N substituents.<sup>4c</sup>

**Study of the Conversion of 8 into 8'.** Hydrolysis of free imidazolylidenes is known.<sup>29</sup> Metal complexes of NHCs are usually considered to be resistant toward water, and some catalytic applications can even be performed in aqueous media.<sup>30</sup> Hydrolysis of Cu–NHCs has been scarcely observed or studied so far.<sup>31</sup> To clarify the hydrolysis we monitored the  $^1\text{H}$  NMR spectrum of **8** in  $\text{MeCN-}d_3$ . In the solid state, **8** is quite stable toward air and moisture, and it did not show any changes after it was stored in open air for 2 months.

Degradation of **8** into **8'** can be easily observed through  $^1\text{H}$  NMR measurements of **8** in commercial  $\text{MeCN-}d_3$  at 25 °C (Figure 8). The characteristic proton resonance signals at 7.97 and 5.67 ppm attributed to NCHO and NH clearly showed the concentration change of **8'**. After standing in an NMR tube for 14, 27, 38, 52, and 62 h, conversions are 44%, 65%, 77%, 88%, and 94%, respectively. After 76 h, **8** was completely decomposed into **8'**. The process is described as a first-order reaction where the rate is proportional to the concentration of





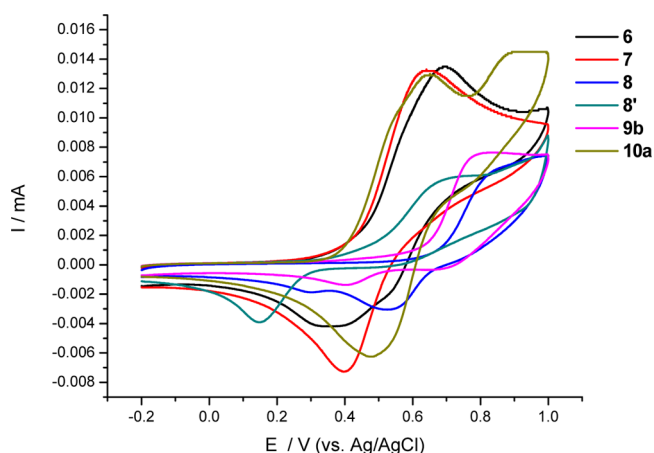
**Figure 8.** Conversion of **8** to **8'** in MeCN- $d_3$  at 25 °C shown by  $^1\text{H}$  NMR spectrum variation.

**8** with a rate constant of  $0.04378\text{ h}^{-1}$ . Hydrolysis of **8** is much slower in DMSO- $d_6$  at 25 °C (see Supporting Information). No **8'** was observed within 4 days. After 7 and 14 days, only 10% and 23% of **8** was converted into **8'**, respectively. Hydrolysis is quite clean, and no other byproduct or intermediate such as free NHC and carbene–water adduct<sup>29d</sup> was observed in both MeCN- $d_3$  and DMSO- $d_6$ . Although **8** in MeCN decomposes slowly, reaction of  $[\text{H}_2(\text{L}3)](\text{PF}_6)_2$  and 5 equiv of copper powder in MeCN at room temperature for 14 h gave **8** almost quantitatively without **8'** as indicated by  $^1\text{H}$  NMR of the crude product in DMSO- $d_6$ .

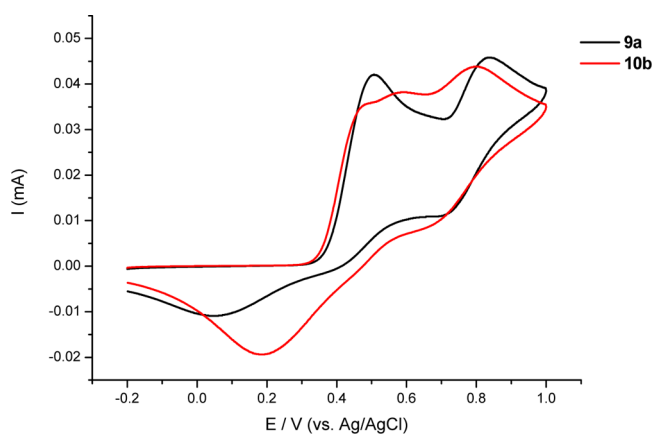
The lability of the Cu–NHC bonds is known since a number of Cu–NHC complexes have been successfully employed as carbene-transfer reagents.<sup>12b,14</sup> We assumed that hydrolysis of **8** is initiated by solvation of the external copper ion and uncoordination of one NHC group. In contrast with complex **7**, larger steric repulsion may accelerate hydrolysis.

**UV–Vis Absorption and Emission Spectra.** All copper complexes presented above are yellow to red crystals due to a metal-to-ligand charge-transfer process. UV–vis absorption spectra of Cu(I)–NHCs **6**, **7**, **8'**, **9a,b**, and **10a,b** in MeCN at room temperature show two maximum absorptions at 232–243 and 286–293 nm. Complex **8'** also exhibits a red shift absorption at 341 nm, probably ascribed to the formamide group. For comparison, the dicopper complexes of *N*-(1,10-phenanthrolin-2-yl)imidazolylienes show two bands centered at 225 and 275 nm, which are very close to their corresponding imidazolium salts.<sup>4c</sup> The multinuclear copper complexes are emissive at room temperature in their acetonitrile solutions. The emission spectra upon excitation at 290 nm show one nonstructured emission band with maximum emission located at 390–406 nm, and the emission intensity is obviously weaker than that of the corresponding ligand precursor (see Supporting Information). When excited at 290 nm, emission spectra of the dicopper complexes of *N*-(1,10-phenanthrolin-2-yl)imidazolylienes display structured emission with two not well-resolved bands at ca. 350 and 370 nm.<sup>4c</sup>

**Electrochemistry.** The redox behavior of the above-mentioned Cu(I)–NHC complexes were studied by cyclic voltammetry in MeCN at 25 °C at a concentration of  $5.5 \times 10^{-4}\text{ M}$ . Experiments were performed with a three-electrode system (glass carbon working electrode, platinum counter electrode, and Ag/AgCl reference electrode) using  $\text{Bu}_4\text{NPF}_6$  (0.10 M) as the supporting electrolyte. Cyclic voltammograms of **6–8**, **8'**, **9a,b**, and **10a,b** shown in Figures 9 and 10



**Figure 9.** Cyclic voltammograms of **6–8**, **8'**, **9b**, and **10a**.



**Figure 10.** Cyclic voltammograms of **9a** and **10b**.

illustrated that these complexes are electrically active substances, and they can undergo a quasi-reversible redox process ( $\Delta E_p > 59\text{ mV}$ ,  $I_{pa}/I_{pc} \neq 1$ ). Their peak separations and peak current ratios vary over a wide range depending on the structures of the complexes. Oxidation of these copper complexes involves removal of an electron from the highest occupied molecular orbital, i.e., the d orbital of the Cu(I) ion. Complexes **6** and **7** can undergo a quasi-reversible redox process with close half-wave potentials and peak separations. The oxidation potential of complex **7** is less positive than the corresponding values for **8** and **8'**, indicating that the energy of the copper-centered HOMO can be decreased by replacement of benzimidazolyliene with stronger electron-donating imidazolyliene. A decrease in the oxidation potential in **9a** and **10b** was observed, probably resulting from an electron density increase of the Cu center due to participation of the iodide ion in coordination. The copper centers in **9a** and **9b** are entrapped by the mesityl-based bulky ligands; thus, it is difficult for direct heterogeneous electron transfer between the electroactive

centers and the electrode surface to occur. Consequently, the reversibility of the redox processes of **9a** and **9b** is poor.

## CONCLUSION

We described the facile synthesis of a number of di-, tri-, and tetranuclear Cu(I)–NHC complexes supported by a new class of dicarbene ligands linked by a phenanthroline. The copper complexes were obtained via simple reactions of corresponding imidazolium salts with copper powder at room temperature and have been structurally characterized. The phenanthroline dicarbene ligands bearing less steric N-substituted groups such as allyl and benzyl tend to form Cu<sub>3</sub> and Cu<sub>4</sub> chain complexes, whereas the phenanthroline dicarbene ligands bearing more sterically hindered groups favor cyclic Cu<sub>3</sub> complexes. The presented complexes show interesting structures, and their synthetic procedures are simple. Their potential applications as NHC transfer reagents in the preparation of other metal complexes and as catalysts in various organic transformations are currently ongoing.

## EXPERIMENTAL SECTION

All chemicals were obtained from commercial suppliers and used without further purification. The copper powder (200 mesh, with purity ≥ 99.7 wt %) was purchased from Sinopharm Chemical Reagent Co., Ltd., China, and used directly without any pretreatment. MeCN used for reactions and crystallization was distilled prior to use with a water content of ca. 0.3 wt %. Elemental analyses were performed on a Flash EA 1112 instrument. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} 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 Hertz. All NMR spectra were recorded at 298 K in deuterated solvent using the residual solvent peak as reference (DMSO δ<sub>H</sub> = 2.50 ppm, δ<sub>C</sub> = 39.52 ppm; MeCN δ<sub>H</sub> = 1.94 ppm, δ<sub>C</sub> = 1.32, 118.26 ppm). Single-crystal X-ray diffraction data were collected at 293(2) K on a Siemens Smart/CCD area-detector diffractometer with Mo Kα radiation (λ = 0.71073 Å). ESI-mass spectral data was acquired using a Waters Micromass ZQ mass spectrometer (positive mode, ESI source). CV measurements were performed at room temperature under nitrogen in MeCN with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup> using a CHI610D electrochemical analyzer.

**2,9-Di(1H-imidazol-1-yl)-1,10-phenanthroline, A.** The mixture of 2,9-diiodo-1,10-phenanthroline (4320 mg, 10.0 mmol), imidazole (1360 mg, 20.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (6500 mg, 20.0 mmol), and CuO (120 mg, 1.5 mmol) in DMSO (30 mL) was stirred under nitrogen at 80 °C for 24 h. After the reaction, the mixture was added into 500 mL of chloroform and washed with water (100 mL × 6). The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. Solvent was removed under reduced pressure to give the product. Yield: 970 mg (31%), brown solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.88 (br s, 2H), 8.63 (br s, 2H), 8.29 (br s, 2H), 8.19 (br s, 2H), 7.95 (br s, 2H), 7.23 (br s, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 147.4, 143.2, 140.1, 135.6, 130.3, 127.6, 125.5, 116.9, 113.5.

**2,9-Bis(1H-benzo[d]imidazol-1-yl)-1,10-phenanthroline, B.** This compound was synthesized via a similar procedure for **A** from 2,9-diiodo-1,10-phenanthroline (4320 mg, 10.0 mmol), 1H-benzo[d]imidazole (2360 mg, 20.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (6500 mg, 20.0 mmol), and CuO (120 mg, 1.5 mmol). Yield: 1360 mg (33%), gray solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.27 (s, 2H, NCHN), 9.15 (d, J = 7.6 Hz, 2H, benzimidazole), 8.78, 8.41 (both d, J = 8.4 Hz, each 2H, phen), 8.09 (s, 2H, phen), 7.83 (d, J = 7.6 Hz, 2H, benzimidazole), 7.39 (t, J = 6.8, 7.2 Hz, 2H, benzimidazole), 7.15 (t, J = 6.8, 7.2 Hz, 2H, benzimidazole). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 149.2, 143.7, 142.3, 140.0, 132.0, 127.3, 125.7, 124.3, 123.3, 119.7, 115.3, 115.2.

**[H<sub>2</sub>(L1)](PF<sub>6</sub>)<sub>2</sub>, 1.** A mixture of 2,9-di(1H-imidazol-1-yl)-1,10-phenanthroline (936 mg, 3.0 mmol) and 3-bromopropene (2178 mg, 18.0 mmol) in 30 mL of dioxane and DMF was stirred at 85 °C

for 36 h. The gray precipitate was isolated and dissolved in water. The solution was added into an aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (1630 mg, 10.0 mmol). Then the resulting precipitate was isolated and dried in vacuo. Yield: 779 mg (38%), white powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.40 (s, 2H, NCHN), 9.02, 8.50 (both d, J = 8.8 Hz, each 2H, phen), 8.96, 8.12 (both s, each 2H, NCHCHN), 8.26 (s, 2H, phen), 6.16–6.27 (m, 2H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 5.50–5.53 (m, 2H, NCH<sub>2</sub>CH=CHH), 5.48 (d, J = 3.6 Hz, 2H, NCH<sub>2</sub>CH=CHH), 5.08 (d, J = 6.0 Hz, 4H, NCH<sub>2</sub>CH=CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 145.3, 142.5, 141.2, 135.5, 131.0, 129.2, 127.0, 123.7, 121.0, 119.6, 114.4, 51.8. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>: C, 42.12; H, 3.24; N, 12.28. Found: C, 42.17; H, 3.41; N, 12.02.

**[H<sub>2</sub>(L2)](PF<sub>6</sub>)<sub>2</sub>, 2.** This compound was synthesized via a similar procedure for [H<sub>2</sub>(L1)](PF<sub>6</sub>)<sub>2</sub> (**1**) from 2,9-di(1H-imidazol-1-yl)-1,10-phenanthroline (936 mg, 3.0 mmol) and benzyl bromide (3078 mg, 18.0 mmol). Yield: 1056 mg (45%), white powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.54 (s, 2H, NCHN), 9.03, 8.49 (both d, J = 8.8 Hz, each 2H, phen), 8.92, 8.19 (both s, each 2H, NCHCHN), 8.27 (s, 2H, phen), 7.59 (d, J = 7.2 Hz, 4H, Ph), 7.42–7.52 (m, 6H, Ph), 5.65 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 145.6, 142.7, 141.3, 135.9, 134.4, 129.4, 129.1, 129.0, 128.5, 127.2, 123.8, 120.1, 114.8, 52.9. Anal. Calcd for C<sub>32</sub>H<sub>26</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>: C, 48.99; H, 3.34; N, 10.71. Found: C, 48.78; H, 3.39; N, 10.84.

**[H<sub>2</sub>(L3)](PF<sub>6</sub>)<sub>2</sub>, 3.** This compound was prepared via a similar procedure for [H<sub>2</sub>(L1)](PF<sub>6</sub>)<sub>2</sub> (**1**) from 2,9-bis(1H-benzo[d]imidazol-1-yl)-1,10-phenanthroline (1236 mg, 3.0 mmol) and benzyl bromide (3078 mg, 18.0 mmol). Yield: 1113 mg (42%), white powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 11.03 (s, 2H, NCHN), 9.24 (d, J = 8.4 Hz, 2H, benzimidazole), 9.15, 8.56 (both d, J = 8.4 Hz, each 2H, phen), 8.39 (s, 2H, phen), 8.08 (d, J = 8.4 Hz, 2H, benzimidazole), 7.69–7.77 (m, 6H, benzimidazole + Ph), 7.34–7.51 (m, 8H, benzimidazole + Ph), 5.97 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 147.4, 143.4, 143.3, 141.3, 133.3, 131.3, 130.0, 129.1, 129.0, 128.9, 128.5, 128.0, 127.5, 127.4, 117.4, 117.1, 114.2, 50.8. Anal. Calcd for C<sub>40</sub>H<sub>30</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>: C, 54.31; H, 3.42; N, 9.50. Found: C, 54.47; H, 3.44; N, 9.73.

**[H<sub>2</sub>(L4)]<sub>2</sub>, 4a.** A mixture of 2,9-diiodo-1,10-phenanthroline (1296 mg, 3.0 mmol) and 1-mesityl-1H-imidazole (2232 mg, 12.0 mmol) in 30 mL of dioxane and DMF was refluxed for 48 h. The brown precipitate was washed with dioxane and diethyl ether and dried in vacuo. Yield: 964 mg (40%), white powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.64 (s, 2H, NCHN), 9.26 (s, 2H, phen), 9.09, 8.58 (both d, J = 8.0 Hz, each 2H, phen), 8.33 (s, 4H, NCHCHN), 7.22 (s, 4H, Mes), 2.38 (s, 6H, Me), 2.17 (s, 12H, Me). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 145.7, 142.6, 141.4, 140.5, 136.4, 134.2, 130.9, 129.7, 129.3, 127.4, 125.2, 120.6, 115.4, 20.6, 17.2. Anal. Calcd for C<sub>36</sub>H<sub>34</sub>I<sub>2</sub>N<sub>6</sub>: C, 53.75; H, 4.26; N, 10.45. Found: C, 53.62; H, 4.26; N, 10.64.

**[H<sub>2</sub>(L4)](PF<sub>6</sub>)<sub>2</sub>, 4b.** A solution of [H<sub>2</sub>(L4)]<sub>2</sub> (**4a**) (402 mg, 0.5 mmol) in 100 mL of water was added into the aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (1467 mg, 9.0 mmol). The precipitate was isolated, washed with water, and dried in vacuo. Yield: 272 mg (65%), off-white powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.64 (s, 2H, NCHN), 9.26 (s, 2H, phen), 9.07, 8.56 (both d, J = 9.2 Hz, each 2H, phen), 8.31 (s, 4H, NCHCHN), 7.21 (s, 4H, Mes), 2.39 (s, 6H, Me), 2.16 (s, 12H, Me). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 145.8, 142.8, 141.4, 140.6, 136.6, 134.3, 131.0, 129.7, 129.3, 127.5, 125.2, 120.6, 115.3, 20.6, 17.0. Anal. Calcd for C<sub>36</sub>H<sub>34</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>: C, 51.44; H, 4.08; N, 10.00. Found: C, 51.58; H, 4.05; N, 9.81.

**[H<sub>2</sub>(L5)](PF<sub>6</sub>)<sub>2</sub>, 5a.** This compound was synthesized via a similar procedure for [H<sub>2</sub>(L1)](PF<sub>6</sub>)<sub>2</sub> (**1**) from 2,9-di(1H-imidazol-1-yl)-1,10-phenanthroline (936 mg, 3.0 mmol), 2-(chloromethyl)pyridine hydrochloride (2445 mg, 15.0 mmol), and NaHCO<sub>3</sub> (1764 mg, 21 mmol). Yield: 827 mg (35%), white powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.56 (s, 2H, NCHN), 9.04 (d, J = 8.4 Hz, 2H, phen), 8.95, 8.19 (both br, each 2H, NCHCHN), 8.58 (d, J = 4.4 Hz, 2H, Py), 8.52 (d, J = 8.0 Hz, 2H, phen), 8.28 (s, 2H, phen), 7.94 (td, J = 7.6, 1.6 Hz, 2H, Py), 7.64 (d, J = 8.0 Hz, 2H, Py), 7.44 (td, J = 7.2, 2.0 Hz, 2H, Py), 5.80 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 153.1, 149.6, 145.4, 142.7, 141.4, 137.6, 136.4, 129.4, 127.2, 124.6,

123.9, 122.7, 119.7, 114.7, 53.8. Anal. Calcd for  $C_{30}H_{24}F_{12}N_8P_2$ : C, 45.81; H, 3.08; N, 14.25. Found: C, 45.62; H, 3.10; N, 14.33.

**[H<sub>2</sub>(L5)]<sub>2</sub>, 5b.** A solution of [H<sub>2</sub>(L5)](PF<sub>6</sub>)<sub>2</sub> (**5a**) (394 mg, 0.5 mmol) in 15 mL of MeCN was treated with tetrabutylammonium iodide (TBAI) (1107 mg, 3.0 mmol) at room temperature. After the mixture was stirred for several minutes, the generated precipitate was isolated and dried in vacuo. Yield: 352 mg (94%), pale yellow powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.60 (s, 2H, NCHN), 9.02 (d, *J* = 8.4 Hz, 2H, phen), 8.95, 8.20 (both br, each 2H, NCHCHN), 8.59 (d, *J* = 4.0 Hz, 2H, Py), 8.51 (d, *J* = 8.8 Hz, 2H, phen), 8.26 (s, 2H, phen), 7.94 (td, *J* = 8.0, 1.6 Hz, 2H, Py), 7.66 (d, *J* = 7.6 Hz, 2H, Py), 7.44 (td, *J* = 6.8, 2.0 Hz, 2H, Py), 5.86 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 153.0, 149.5, 145.4, 142.7, 141.4, 137.5, 136.2, 129.4, 127.2, 124.6, 123.7, 122.7, 119.7, 114.8, 53.7. Anal. Calcd for  $C_{30}H_{24}I_2N_8$ : C, 48.02; H, 3.22; N, 14.93. Found: C, 48.17; H, 3.29; N, 15.12.

**General Procedure for Preparation of Cu(I)–NHC Complexes.** Cu(I) complexes **6–8**, **9a,b**, and **10a,b** were synthesized by the following route: a solution of imidazolium salt (0.2 mmol) in 3 mL of MeCN was treated with an excess of copper powder (64 mg, 1.0 mmol). The mixture was allowed to react at room temperature for 3–24 h under air. After reaction, the solution was filtered through Celite. Then the product was obtained via recrystallization from its solution with diethyl ether.

**[Cu<sub>4</sub>(L1)<sub>2</sub>(MeCN)<sub>4</sub>](PF<sub>6</sub>)<sub>4</sub>, 6.** This complex was synthesized from reaction of [H<sub>2</sub>(L1)](PF<sub>6</sub>)<sub>2</sub> (**1**) (137 mg, 0.2 mmol) with copper powder (64 mg, 1.0 mmol) for 20 h. Yield: 50 mg (29%), red crystals. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.13 (d, *J* = 8.0 Hz, 4H, phen), 8.46 (br s, 4H, phen), 8.26 (d, *J* = 8.8 Hz, 4H, phen), 8.08, 7.21 (both br s, each 4H, NCHCHN), 4.58–4.73 (m, 4H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 4.43 (d, *J* = 9.2 Hz, 4H, NCH<sub>2</sub>CH=CHH), 4.38 (d, *J* = 16.8 Hz, 4H, NCH<sub>2</sub>CH=CHH), 3.64 (br, 8H, NCH<sub>2</sub>CH=CH<sub>2</sub>), 2.06 (s, 12H, CH<sub>3</sub>CN). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 178.8 (Cu–C), 148.3, 140.9, 139.6, 131.5, 128.4, 126.5, 122.4, 120.1, 119.6, 117.8, 117.5, 51.1, 0.5. Anal. Calcd for  $C_{56}H_{52}Cu_4F_{24}N_{16}P_4$ : C, 37.72; H, 2.94; N, 12.57. Found: C, 37.60; H, 2.98; N, 12.73. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its MeCN solution at room temperature.

**[Cu<sub>3</sub>(L2)<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>, 7.** This complex was synthesized from reaction of [H<sub>2</sub>(L2)](PF<sub>6</sub>)<sub>2</sub> (**2**) (158 mg, 0.2 mmol) with copper powder (64 mg, 1.0 mmol) for 14 h. Yield: 80 mg (50%), red crystals. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.15 (d, *J* = 8.0 Hz, 4H, phen), 8.49 (s, 4H), 8.28 (d, *J* = 8.4 Hz, 4H, phen), 8.02 (s, 4H), 7.27 (s, 4H), 6.97–7.15 (m, 12H, Ph), 6.49–6.56 (m, 8H, Ph), 4.03 (s, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 179.3 (Cu–C), 148.7, 141.4, 139.7, 135.0, 128.7, 128.5, 128.3, 127.8, 127.1, 123.0, 120.5, 120.2, 52.5. Anal. Calcd for  $C_{64}H_{48}Cu_3F_{18}N_{12}P_3$ : C, 47.72; H, 3.00; N, 10.44. Found: C, 47.70; H, 3.07; N, 10.69. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its MeCN solution at room temperature.

**[Cu<sub>3</sub>(L3)<sub>2</sub>(PF<sub>6</sub>)<sub>3</sub>, 8.** This complex was synthesized from reaction of [H<sub>2</sub>(L3)](PF<sub>6</sub>)<sub>2</sub> (**3**) (177 mg, 0.2 mmol) with copper powder (64 mg, 1.0 mmol) for 14 h. Yield: 135 mg (74%), red powder. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.97, 8.27 (both d, *J* = 8.4 Hz, each 4H, phen), 8.13 (s, 4H, phen), 7.39 (d, *J* = 8.0 Hz, 4H, benzimidazole), 7.29 (t, *J* = 7.6, 8.0 Hz, 4H, benzimidazole), 7.18 (t, *J* = 8.0, 6.8 Hz, 8H, Ph), 7.01–7.08 (m, 16H, benzimidazole + Ph), 6.90 (d, *J* = 8.0 Hz, 4H, benzimidazole), 4.98, 4.65 (both d, *J* = 14.8 Hz, each 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 188.7 (Cu–C), 147.9, 141.8, 140.9, 135.4, 132.6, 130.7, 128.4, 128.0, 127.7, 126.8, 125.1, 125.0, 122.0, 112.4, 110.6, 50.7. Anal. Calcd for  $C_{80}H_{56}Cu_3F_{18}N_{12}P_3 \cdot H_2O$ : C, 52.54; H, 3.20; N, 9.19. Found: C, 52.25; H, 3.02; N, 9.12.

**[Cu<sub>2</sub>(L3')<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>, 8'.** This complex was obtained as orange crystals from the hydrolysis process of **8** by slow diffusion of diethyl ether into the MeCN solution of **8** at 25 °C for 5 days. <sup>1</sup>H NMR (400 MHz, MeCN-*d*<sub>3</sub>): δ 8.19 (d, *J* = 8.4 Hz, 2H), 8.00–8.04 (m, 2H), 7.97 (s, 2H, CHO), 7.92 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.75–7.79 (m, 4H), 7.69–7.73 (m, 2H), 7.61–7.65 (m, 4H), 7.41 (d, *J* = 16.0 Hz, 2H), 7.33 (t, *J* = 14.8 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 6.90–6.97 (m, 6H), 6.83 (t, *J* = 7.6 Hz, 4H), 6.79 (d, *J* = 7.2 Hz, 4H), 6.66

(t, *J* = 7.6 Hz, 4H), 6.51 (t, *J* = 6.8 Hz, 2H), 6.39 (s, 2H), 5.85 (d, *J* = 8.8 Hz, 2H), 5.67 (br, 2H, NH), 5.25 (d, *J* = 14.8 Hz, 2H, NCH<sub>2</sub>), 4.80 (d, *J* = 15.6 Hz, 2H, NCH<sub>2</sub>), 4.71 (d, *J* = 14.8 Hz, 2H, NCH<sub>2</sub>), 4.62 (d, *J* = 15.2 Hz, 2H, NCH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, MeCN-*d*<sub>3</sub>): δ 191.2 (Cu–C), 163.1, 155.1, 150.1, 143.0, 142.1, 141.8, 140.6, 136.7, 136.4, 135.3, 134.8, 134.2, 133.8, 129.6, 129.5, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.1, 127.9, 126.3, 126.2, 126.1, 124.5, 123.2, 121.6, 113.8, 113.5, 113.1, 54.9, 52.7. Anal. Calcd for  $C_{80}H_{60}Cu_2F_{12}N_{12}O_2P_2$ : C, 58.64; H, 3.69; N, 10.26. Found: C, 58.21; H, 3.81; N, 10.34. ESI-MS (positive ions, MeCN), *m/z* 674.3 [Cu(L3')]<sup>+</sup>. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its MeCN solution at room temperature.

**[Cu<sub>2</sub>(L4)<sub>2</sub>][Cu<sub>2</sub>(μ-l)<sub>2</sub>], 9a.** This complex was synthesized from reaction of [H<sub>2</sub>(L4)]<sub>2</sub> (**4a**) (161 mg, 0.2 mmol) with copper powder (64 mg, 1.0 mmol) for 3 h. Yield: 145 mg (78%), orange crystals. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.33, 8.66 (both d, *J* = 8.8 Hz, each 4H, phen), 8.83, 7.70 (both d, *J* = 1.2 Hz, each 4H, NCHCHN), 8.46 (s, 4H, phen), 5.87 (s, 8H, Mes), 1.89 (s, 12H, Me), 1.17 (s, 24H, Me). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 175.5 (Cu–C), 146.9, 142.7, 138.7, 137.9, 132.9, 131.9, 129.1, 127.7, 127.0, 126.6, 121.0, 117.9, 20.7, 16.3. Anal. Calcd for  $C_{72}H_{64}Cu_4I_4N_{12}$ : C, 46.51; H, 3.47; N, 9.04. Found: C, 46.75; H, 3.42; N, 9.27. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its MeCN solution at room temperature.

**[Cu<sub>3</sub>(L4)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>, 9b.** This complex was synthesized from reaction of [H<sub>2</sub>(L4)](PF<sub>6</sub>)<sub>2</sub> (**4b**) (168 mg, 0.2 mmol) with copper powder (64 mg, 1.0 mmol) for 22 h. Yield: 154 mg (90%), yellow crystals. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.30, 8.64 (both d, *J* = 8.8 Hz, each 4H, phen), 8.82, 7.69 (both d, *J* = 2.0 Hz, each 4H, NCHCHN), 8.45 (s, 4H, phen), 5.87 (s, 8H, Mes), 1.89 (s, 12H, Me), 1.17 (s, 24H, Me). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 175.7 (Cu–C), 147.1, 142.8, 138.9, 138.1, 133.0, 132.1, 129.2, 127.8, 127.1, 126.7, 121.1, 118.0, 20.7, 16.3. Anal. Calcd for  $C_{77}H_{64}Cu_3F_{18}N_{12}P_3$ : C, 50.19; H, 3.74; N, 9.76. Found: C, 49.91; H, 3.70; N, 9.48. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its MeCN solution at room temperature.

**[Cu<sub>3</sub>(L5)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub>, 10a.** This complex was synthesized from reaction of [H<sub>2</sub>(L5)](PF<sub>6</sub>)<sub>2</sub> (**5a**) (158 mg, 0.2 mmol) with copper powder (64 mg, 1.0 mmol) for 24 h. Yield: 118 mg (73%), orange crystals. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.87 (br s, 4H), 8.29 (br s, 4H), 8.21 (br s, 4H), 8.07 (br s, 4H), 7.52 (br s, 4H), 7.48 (t, *J* = 7.6 Hz, 4H, Py), 7.10–7.30 (br, 4H, Py), 6.97 (t, *J* = 6.4 Hz, 4H, Py), 6.39 (br, 4H, Py), 4.26 (s, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 177.9 (Cu–C), 152.9, 148.6, 148.3, 141.1, 138.9, 137.9, 128.5, 126.4, 125.2, 123.4, 120.8, 120.4, 117.1, 52.8. Anal. Calcd for  $C_{60}H_{44}Cu_3F_{18}N_{16}P_3$ : MeCN: C, 44.98; H, 2.86; N, 14.38. Found: C, 45.14; H, 2.73; N, 14.42. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its MeCN solution at room temperature.

**[Cu<sub>4</sub>(L5)<sub>2</sub>(μ-l)<sub>2</sub>](CuI<sub>3</sub>), 10b.** This complex was synthesized from reaction of [H<sub>2</sub>(L5)]<sub>2</sub> (**5b**) (150 mg, 0.20 mmol) with copper powder (64 mg, 1.0 mmol) for 24 h. Yield: 152 mg (78%), red crystals. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.73 (br s, 4H), 8.48 (br, 4H), 8.02 (br s, 4H), 7.92 (m, 8H), 7.78 (m, 6H), 7.64 (br s, 4H), 7.37 (t, *J* = 5.6, 6.4 Hz, 4H), 7.09 (br, 2H), 5.43 (br s, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 179.0 (Cu–C), 154.1, 149.7, 148.6, 140.8, 140.7, 140.2, 138.1, 127.8, 126.3, 124.1, 122.6, 121.5, 120.0, 55.9. Anal. Calcd for  $C_{60}H_{44}Cu_4I_2N_{16}DMF$ : C, 37.56; H, 2.55; N, 11.82. Found: C, 37.74; H, 2.63; N, 11.72. Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether to its DMF solution at room temperature.

## ■ ASSOCIATED CONTENT

### Supporting Information

Synthetic procedure of 2,9-diiodo-1,10-phenanthroline, crystallographic data for **6**, **7**, **8'**, **9a,b**, and **10a,b** in CIF format, CV, UV–vis absorption spectra and emission data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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