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Silver(I) and Copper(I) Complexes with Bis-NHC Ligands: Dinuclear Complexes, Cubanes and Coordination Polymers

Valentine Charra,^a Pierre de Frémont,^a Pierre-Alain R. Breuil,^b Hélène Olivier-Bourbigou^b
and Pierre Braunstein*^a

Abstract: Silver(I) and copper(I) complexes containing neutral bis(N-heterocyclic carbene) (NHC) ligands and coordinated or non-coordinated chloride, bromide, iodide, or tetrafluoroborate anions, were synthesised. The nature of the anions impacts deeply the structural features of the complexes in the solid-state and neutral cubane-, neutral coordination polymer-, or dicationic bridged-type architectures have been characterized. The structures of (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)disilver(I) dichloride (2a), bis(μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene- κ -C)tetra- μ_3 -bromotetrasilver(I) (2b), bis(1,3-bis(3'-butylimidazol-2'-ylidene)benzene)disilver(I) tetrafluoroborate (2d) in 2d·CH₂Cl₂, (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)dicopper(I) dichloride (3a) and (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)dicopper(I) dibromide (3b) were established by X-ray diffraction.

Keywords

NHC ligands – Copper – Silver – Dinuclear Complexes – Cubanes – Coordination Polymers – Transmetalation - X-ray diffraction.

1. Introduction

Since the first stable free *N*-heterocyclic carbene (NHC) was isolated by Arduengo in 1991 [1], this class of ligands has found numerous applications in organometallic chemistry in particular for the preparation of new metal-based catalysts [2-7]. The first NHC silver(I) complex was prepared by Arduengo *et al.* by reaction between a free carbene and silver(I) triflate [8]. Today, the reaction of imidazol(in)ium salts with a variety of silver(I) precursors such as Ag₂O [9], Ag(OAc) [10, 11], Ag₂CO₃ [12] or AgCl [13], with K₂CO₃ or Na₂CO₃ as

external base, allows for the formation of Ag(I)-NHC complexes in high yields. Ag(I)-NHC complexes are stable towards air and moisture. The reaction of Ag₂O with halide imidazol(in)ium salts, first described in 1998 by Lin, is particularly efficient to synthesize halide Ag(I)-NHC complexes under mild conditions, without having to handle free NHCs [9]. The second product formed following Lin's protocol being water, non-distilled solvents can be employed, which renders this approach very convenient and popular [9]. Ag(I)-NHC complexes are potent catalysts for e.g. the cycloaddition of CO₂ to terminal epoxides [14] and C–N coupling reactions [15]. During pharmacological studies, they proved to release *in vivo* slowly and steadily free silver cations acting as tumour cells killers or suppressants of infections [16-19]. Ag(I)-NHCs are mostly employed as transmetalating agents to access late transition metal NHC complexes, without the need to handle unwieldy free carbenes. They are indeed known to transmetalate efficiently their NHC ligand(s) to Cu [20], Ni [21, 22], Pd [21, 23], Pt [23] and Au [24] precursors. The coordination geometry around the Ag(I) centre tends to be linear. When the associated anion (X⁻) is a halide, the formation of polynuclear complexes or clusters with X–Ag–X bridge(s) can lead to a broad structural diversity in the solid-state. In Ag(I)-NHC clusters complexes, d¹⁰-d¹⁰ interactions are often encountered [25, 26], while the coordination geometry around the Ag(I) cations may deviate from linear to trigonal or even tetrahedral. Tetranuclear Ag(I) complexes do not always form cubanes [27, 28] but can lead to planar structures [29, 30].

Copper is the cheapest coinage metal, and despite the spectacular recent achievements in organogold chemistry [31-34], the development of organocopper chemistry appears most desirable from an economic point of view. The first reported Cu(I)-NHC complex was also prepared by Arduengo, by reaction of a free carbene with copper(I) triflate [8]. Owing to the strong σ -donor properties of NHCs, the resulting complexes are often robust against air and moisture. Several methods are known to access Cu(I)-NHC complexes, such as the use of Ag(I)-NHCs as transmetalating reagents, the reaction of free carbenes with Cu(I) halides, or of imidazolium salts with Cu(I) oxide [5, 35]. Recently, Cu(I) bis- or multidentate-NHC complexes have attracted much attention [36] because of their luminescence properties [37, 38], their ability to transmetalate their NHC ligand(s) to Ru [39], Rh [40], Pd [41, 42], Ag [43], and Ni [44] precursors, or their catalytic properties (Sonogashira reaction [45], nitrene and carbene transfer reactions [46]). Moreover, the nature of the metal-carbene bond in Cu(I)-NHC complexes has been the subject of theoretical studies [47, 48] while copper belongs to the very few metals able to form clusters with bridging imidazolydenes [44]. The coordination geometry around the Cu(I) centre tends to be linear but in the presence of bidentate donor

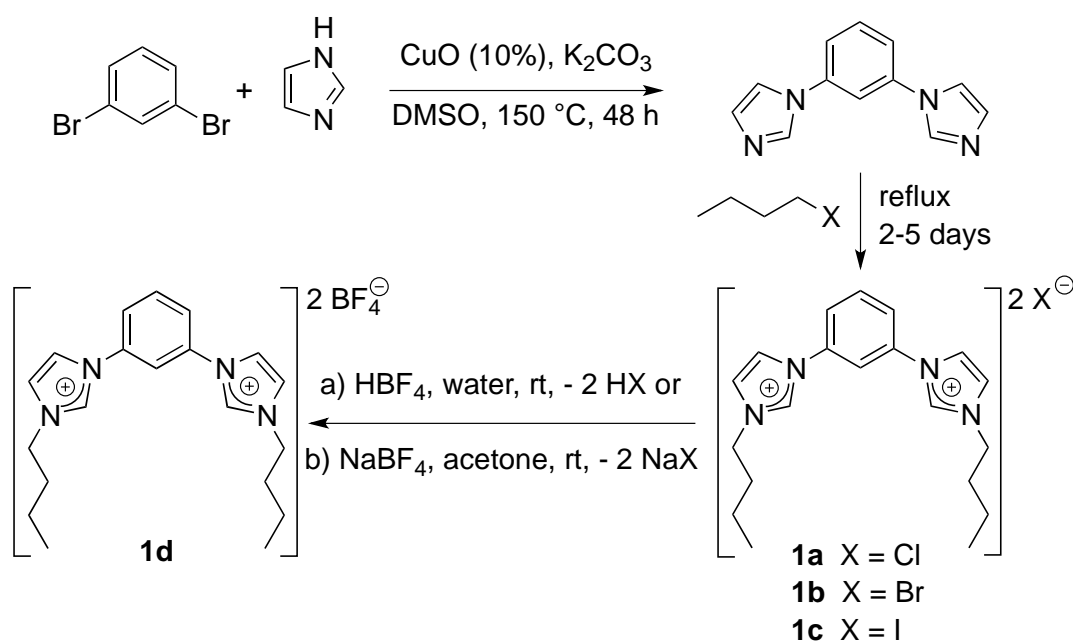
ligands and halide, “T-shaped” trigonal planar or tetrahedral coordination geometries readily arise [30, 49]. By contrast with the case of silver, polymeric Cu(I)-NHC complexes are scarce.

In this paper, we report the synthesis and the characterisation of a series of discrete and polymeric bis-NHC Ag(I) and Cu(I) complexes, and discuss their various structural features in the solid-state.

2. Results and discussion

2.1. Synthesis of the imidazolium salts

The imidazolium salts 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) chloride (ImidBuCl, **1a**), 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) bromide (ImidBuBr, **1b**) and 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) iodide (ImidBuI, **1c**) were prepared in two steps: i) synthesis of 1,3-bis(imidazolyl)benzene via Cu(II)-catalyzed aryl amination [50], ii) *N,N*-quaternizations with alkyl halides (Scheme 1). For the first step, the literature work-up was modified to avoid purification by flash chromatography on silica: a simple filtration of a dichloromethane solution through Celite[®], followed by precipitation with pentane was sufficient.



Scheme 1. Synthesis of the imidazolium salts **1a-d**

During the second step of the synthesis, the reaction of 2 equiv. of 1-chlorobutane, 1-bromobutane, or 1-iodobutane with 1,3-bis(imidazolyl)benzene yielded respectively **1a** (65%), **1b** (63%), or **1c** (68%). The different reaction conditions were adjusted according to the type of haloalkanes [51] (Scheme 1). The formation of **1a** required a temperature around 130 °C, in refluxing chlorobenzene. Lowering the temperature to 100 °C resulted in poor conversion (5%), even after 3 days. By contrast, the syntheses of **1b,c** were successful in refluxing THF but long reaction times (at least 72 h for **1b**, 48 h for **1c**) were still required to avoid the formation of mono-alkylated (intermediate) products. The reported synthesis of **1c** (77%), in 8 h, at 150 °C, in toluene, in a sealed tube [52] was not retained in this work due to its lack of practicality. The ¹H NMR spectra of the salts **1a-c** in CD₂Cl₂ display the characteristic resonance of the NCHN proton between 11.2 and 11.7 ppm [51, 52].

The salt 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) tetrafluoroborate (ImidBuBF₄, **1d**) was first obtained in low yield (15%) by anion metathesis using **1b** and tetrafluoroboric acid in distilled water. A second attempt, with sodium tetrafluoroborate in acetone, afforded **1d** as an off-white powder in excellent yield (98%). The successful anion metathesis reaction was confirmed by ¹H NMR, where the significant shift from 11.5 to 9.7 ppm between the imidazolium NCHN signal of **1b** and **1d**, is due to the nature of the associated anion.

2.2. Synthesis of the silver(I) complexes

The reaction of the imidazolium salts **1a,b** with 1.5 equivalent of Ag(I) oxide was carried and monitored by ¹H and ¹³C{¹H} NMR spectroscopy. The disappearance of the characteristic azolium proton signals of **1a,b**, and the appearance of typical downfield carbon signals for Ag(I)-bound carbenes at 179.2 ppm and 182.6 ppm, confirmed the formation of the Ag(I) NHC complexes **2a** and **2b**, which were isolated in yields of 61% and 65%, respectively. The signals of the butyl chains remain unchanged, in both ¹H and ¹³C{¹H} NMR spectra, when going from the imidazolium salts **1a,b** to the Ag(I) complexes **2a,b**. In the ¹H NMR spectra, the CH^{imidazole} and CH^{aryl} signals of **2b** in the aromatic region are shifted by 1.30 ppm and 1.16 ppm. The signals of the aryl groups and of the imidazole backbones of **2a,b** are found between 7.00 and 8.00 ppm. Elemental analyses confirmed the clean formation of [L+2Ag+2X]_n - type products. However, they did not allow to discriminate between neutral bridge- [X-Ag-NHC- \wedge -NHC-AgX], cationic chelate- [(\wedge (NHC-Ag-NHC)⁺ \wedge)₂][AgX₂⁻]₂, or even

neutral cubane- $[\wedge(X\wedge Ag-NHC\wedge NHC-Ag\wedge X)_2\wedge]$ type of complexes. The ESI mass spectra of **2a,b** display respectively the following signals for m/z (L = ligand): $[L+2Ag+Cl]^+ = 572.99$, $[L+Ag+Cl+H]^+ = 467.10$, $[L+H]^+ = 323.22$, and $[2L+4Ag+3Br]^+ = 1314.18$, $[2L+3Ag+3Br+H]^+ = 1208.88$, $[2L+3Ag+2Br]^+ = 1126.96$, $[2L+2Ag+Br]^+ = 939.15$, $[L+2Ag+Br]^+ = 616.94$, $[L+Ag+Br+H]^+ = 511.06$, $[2L+2Ag]^{2+} = 430.12$. They hint at the likely formation of neutral dinuclear $[L+2Ag+2X]$ or neutral tetranuclear $[2L+4Ag+4X]$ complexes even though molecular fragmentation may have occurred during the analyses. To remove any doubt concerning the structures of these Ag(I) NHC halide complexes, a single crystal X-ray diffraction analysis of their colourless crystals, grown by slow evaporation of solutions of a mixture of dichloromethane and octane, was undertaken.

The complex μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene)dichlorodisilver(I) (ImidBuAg₂Cl₂, **2a**) is an organometallic coordination polymer, which crystallizes in the monoclinic system and the $P2_1/c$ space group (Figure 1). Adjacent monomeric units [ImidBuAg₂Cl₂] are held together by a bridging chloride Cl1. There is one carbene donor per metal and halogen, in agreement with a $[L+2Ag+2X]_{n=\infty}$ -type complex. The Ag1–C1 and Ag2–C14 bond distances are equal to 2.081(6) and 2.102(6) Å, and the Ag1–Cl1, Ag2–Cl2 and Ag2–Cl1 distances to 2.3340(16), 2.3802(15) and 2.8878(15) Å, respectively. These values are similar to those found in other Ag(I) NHC complexes [53, 54]. The silver cation Ag1 has a distorted linear coordination geometry with a C1–Ag1–Cl1 angle of 169.3(2)°, whereas the second silver cation Ag2 is in a distorted trigonal planar coordination environment with Cl2–Ag2–Cl1, C14–Ag2–Cl1 and C14–Ag2–Cl2 bond angles of 97.97(5), 108.2(2) and 152.6(2)°, respectively. Each imidazole ring from the same ligand is oriented head to tail with a torsion angle of 173.3°.

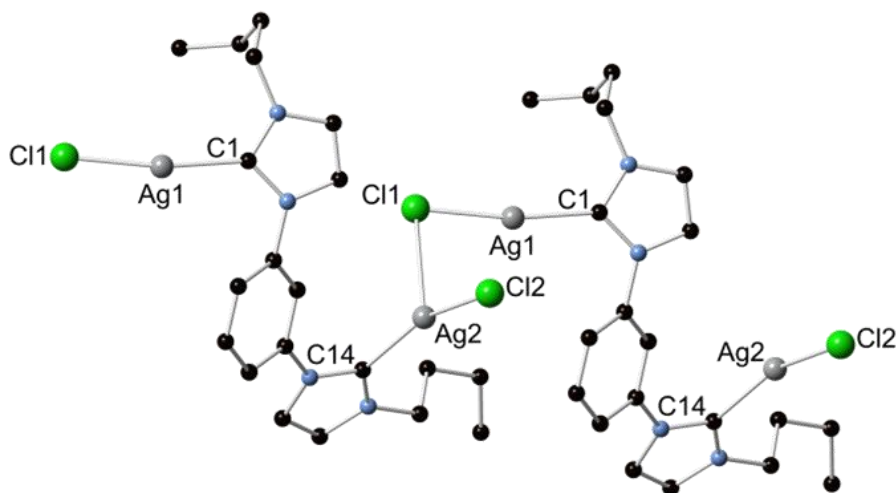


Figure 1. Ball and stick representation of the molecular structure of two dinuclear, monomeric units [ImidBuAg₂Cl₂] forming the polymer chains of **2a** in the solid-state. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1–C1 2.081(6), Ag2–C14 2.102(6), Ag1–Cl1 2.3340(16), Ag2–Cl2 2.3802(15), Ag2–Cl1 2.8878(15); C1–Ag1–Cl1 169.39(17), C14–Ag2–Cl2 152.60(16), C14–Ag2–Cl1 108.20(15), Cl1–Ag2–Cl2 97.97(5).

The complex bis(μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene)- κ -C)tetra- μ -3-bromotetrasilver(I) (ImidBu₂Ag₄Br₄, **2b**) crystallizes in the monoclinic system with the *P*2₁/*c* space group and has a cubane-type structure (Figure 2). There is one carbene functionality per metal and halogen, in agreement with a [2L+4Ag+4X]_{n=1}-type complex. Two of the Ag–Ag distances (Ag1–Ag2 = 3.137(1) Å and Ag3–Ag4 = 3.159(1) Å) are shorter than the sum of the van der Waals radii (3.44 Å) and may be diagnostic of d¹⁰-d¹⁰ “argentophilic” interactions [25, 26, 55, 56], whereas the other two Ag–Ag separations are much longer (Ag2–Ag3 = 3.945(1) Å, Ag1–Ag4 = 3.547(1) Å). The ratio of 0.799 between the average Ag–Ag distances (3.44 Å) and the average Br–Br distances (3.31 Å) is intermediate between those for an ideal cubane (1.00) and stella quadrangular (0.667) geometries [57]. Hence, the structure of ImidBu₂Ag₄Br₄ (**2b**) forms a distorted cubane, a geometry well documented in the literature for other NHC or phosphine Ag(I) complexes [58-67]. The Ag–C and Ag–Br bond lengths fall in the range 2.140(4) - 2.161(4) Å and 2.6850(5) - 2.8567(6) Å, respectively. These values are in agreement with those found in other NHC silver halide cubane complexes [68].

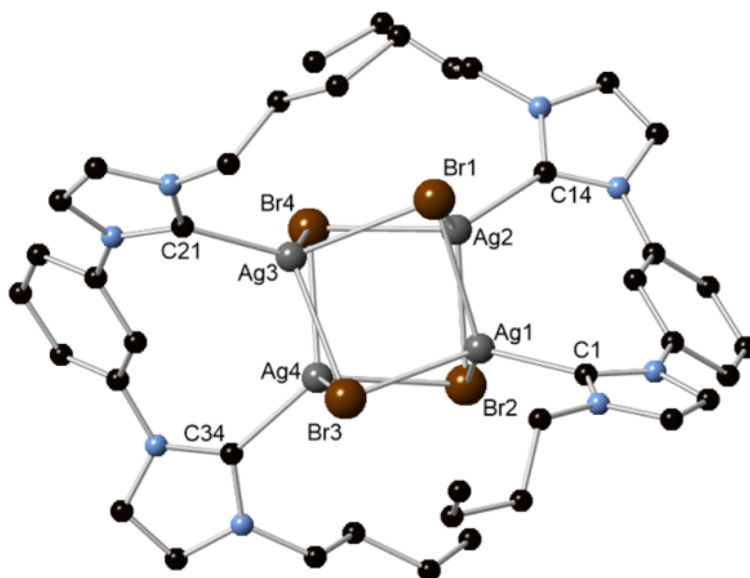


Figure 2. Ball and stick representation of the cubane-type structure of [ImidBu₂Ag₄Br₄] (**2b**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–Ag1 2.143(4), C14–Ag2 2.140(4), C21–Ag3 2.161(4), C34–Ag4 2.148(5), Ag1–Br1 2.8567(6), Ag1–Br2 2.7999(6), Ag1–Br3 2.7048(6), Ag2–Br1 2.8410(6), Ag2–Br2 2.8564(6), Ag2–Br4 2.6850(5), Ag3–Br1 2.8050(6), Ag3–Br3 2.8071(6), Ag3–Br4 2.8456(6), Ag4–Br2 2.7869(6), Ag4–Br3 2.8493(6), Ag4–Br4 2.7593(6), Ag1–Ag2 3.1375(5), Ag3–Ag4 3.1586(5); C1–Ag1–Br1 112.91(11), C1–Ag1–Br2 113.23(13), C1–Ag1–Br3 127.72(13), C14–Ag2–Br1 116.85(11), C14–Ag2–Br2 111.14(11), C14–Ag2–Br4 134.11(11), C21–Ag3–Br1 136.21(12), C21–Ag3–Br3 118.69(11), C21–Ag3–Br4 112.94(12), C34–Ag4–Br2 126.62(12), C34–Ag4–Br3 106.29(12), C34–Ag4–Br4 122.57(12).

In order to explore further the role played by the halide in Ag(I) chemistry, the reactivity of **2a** was assessed toward anion metathesis with AgBr or LiBr, in dry acetone. ¹H NMR spectroscopy evidenced the quantitative conversion of **2a** into **2b** within 16 h. Complex **2b** was isolated in 98% yield, and its purity confirmed by elemental analysis. The depolymerisation of **2a** to rebuild a cubane-structure is a clear illustration of the great affinity of group 11 metals toward soft halide ligands (I>Br>Cl), as well as the propensity of soft halides to form higher order bridges in polynuclear complexes with late transition metals. Interestingly, in wet acetone no conversion was monitored after 24 h.

During the course of our work, Hollis *et al.* reported the Ag(I)-NHC complex bis(μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene)- κ -C)tetra- μ_3 -iodotetrasilver(I) (ImidBu₂Ag₄I₄, **2c**), obtained in 67% yield as a white powder by reaction of the pro-ligand ImidBuI (**1c**) with Ag(I) oxide [68]. Similar to **2b**, this complex has a distorted cubane structure with a [Ag₄I₄]

core. We also prepared and characterized **2c** using the Hollis's approach and a slightly modified purification step. Hollis reported the filtration of a CH₂Cl₂ solution of **2c** and its direct precipitation/washing with diethyl ether, whereas prior to precipitation, we added an additional step, without lowering the yield (75%), by extracting with water most of the impurities present, including possible traces of unreacted **1c**.

The replacement of the halogen bound to silver by the non-coordinating anion BF₄⁻, should have an impact on the complex structure owing to the loss of the silver-halide bonds. The reaction of the imidazolium salt **1d** with Ag(I) oxide, following the protocols described for **2a-c**, failed to give complex **2d**. This is probably due to the insufficient difference of relative acid-base strengths between **1d** and Ag₂O (The pK_a difference between ([NHC-H⁺][BF₄⁻]/[NHC]) and ([Ag₂OH⁺]/[Ag₂O]) which is the driving force to initiate the reaction when Ag₂O is used as the silver(I) source) [69]. We thus attempted the reaction of **2b** or **2c** with 2.0 equivalents of AgBF₄ in dichloromethane, at room temperature for 18 h. Formation of AgX was observed and complete conversion to complex **2d** was supported by the shift of the aromatic signals in the ¹H NMR spectra and of the characteristic signal of the carbenic carbons from 182.6 ppm (**2b**) or 184.8 ppm (**2c**) to 179.6 ppm. Elemental analysis supported the clean formation of a [2L+2Ag+2(BF₄)]_n-type complex. Consistently, the ESI mass spectrum contained a major signal for *m/z* (L = ligand): [2L+2Ag]²⁺ = 430.12. Colourless single crystals suitable for X-ray diffraction analysis were obtained by stratification with pentane of a dichloromethane solution of **2d**. The complex bis-(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene)disilver(I) ditetrafluoroborate ([ImidBuAg]BF₄)₂, **2d** has a centrosymmetric dinuclear structure with Ag(I) ions bridged by two bis-NHC ligands binding in a C,C' mode. The ratio NHC/Ag has thus changed from 1:1 in **2a,b** to 2:1 in **2d**. The latter crystallizes with one molecule of dichloromethane, in the triclinic system and the *P*-1 space group (Figure 3). The structure of **2d** is typical for bis-NHC dinuclear complexes of the type {[NHC)Ag(NHC)⁺]₂, 2[X⁻]} where X⁻ represents a non-coordinating anion [70-73]. There are two carbene donors and one tetrafluoroborate anion per silver, in agreement with a [2L+2Ag+2(BF₄)]_{n=1}-type complex. The C1–Ag1 and C14–Ag1 bond distances are equal to 2.083(3) and 2.085(3) Å, respectively. The Ag(I) cations adopt a quasi-linear coordination geometry in **2d** (C1–Ag–C14 angle of 174.28(1)°). Bonds distances and angles are similar to those reported for other cationic bis-(NHC) Ag(I) complexes [74]. The planes defined by the NHC rings bound to silver form an angle of 45.6(1)°. The planes of the NHC rings belonging to the same ligand form an angle of -138.7(3) and 133.5(3)° with the aryl ring. The planes of the bridging-phenylene spacers are parallel to each other and mutually distant from 4.4 Å,

which rules out any π - π stacking interaction (usually observed between 3.3 and 3.9 Å) in the solid state [75]. There is no interaction between the Ag(I) centres and the BF_4^- anions. The complexes **2a-d** are stable towards moisture in ambient day light (Scheme 2).

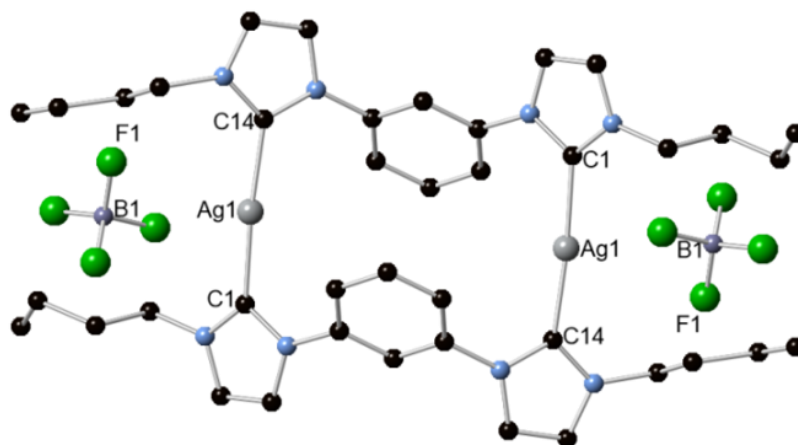
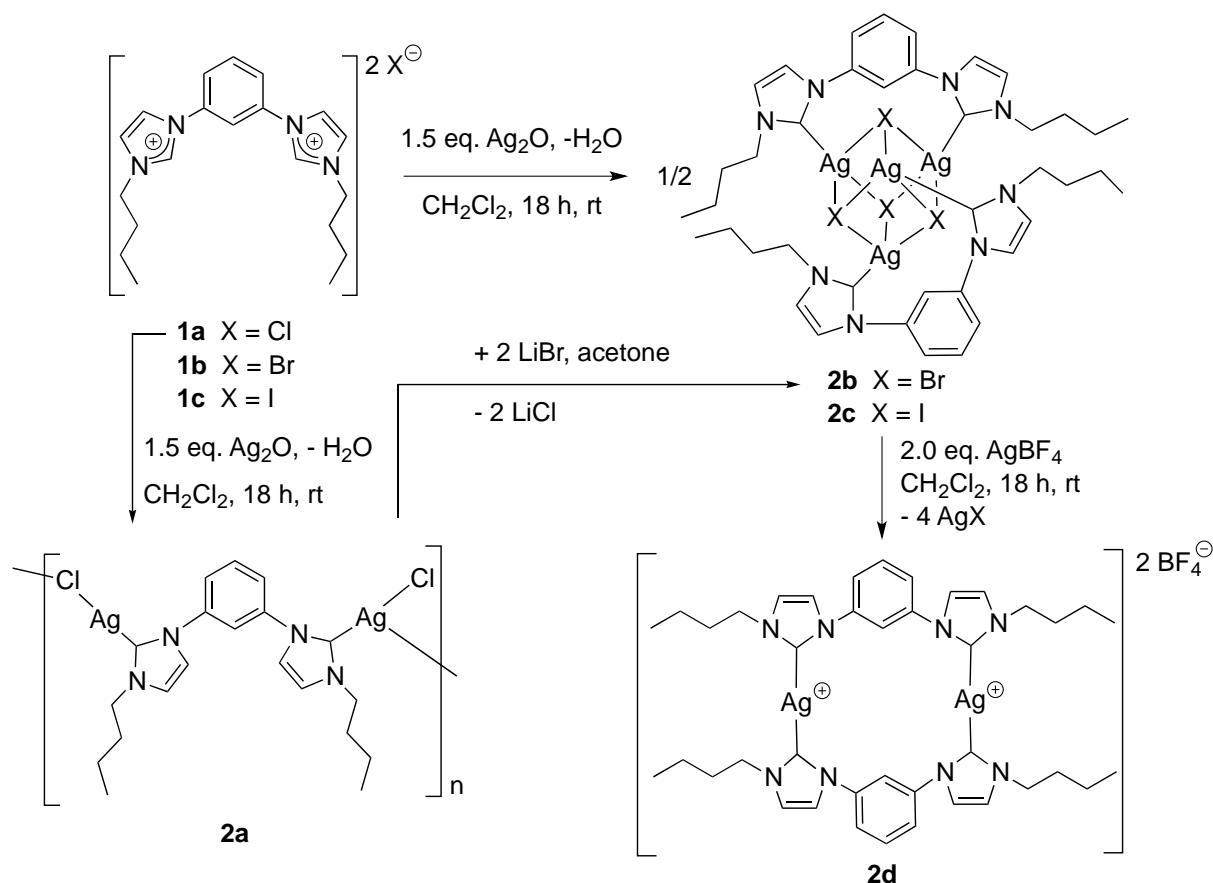


Figure 3. Ball and stick representation of the structure of $[(\text{ImidBu})\text{Ag}]\text{BF}_4$ (**2d**) in $2\mathbf{d}\cdot\text{CH}_2\text{Cl}_2$. Hydrogen atoms and a molecule of dichloromethane have been omitted for clarity. Selected bond lengths (Å) and angle (°): C1–Ag1 2.083(3), C14–Ag1 2.085(3); C1–Ag1–C14 174.28(11).



Scheme 2. Summary of the diverse solid-state structures encountered in the Ag(I) complexes **2a-d** and their transformations.

2.3. Synthesis of the copper(I) complexes

The reactions of the imidazolium salts **1a-c** with 2 equivalents of Cu[N(SiMe₃)₂] [76] were carried and monitored by ¹H and ¹³C{¹H} NMR spectroscopy. The disappearance of the characteristic azolium proton signals of **1a-c**, and the appearance of typical downfield carbon signals for Cu(I)-bound carbenes at 176.6, 177.8, and 184.2 ppm, confirmed the formation of three complexes **3a-c** which were isolated in 98%, 98% and 86% yield, respectively. The exact nature of **3a,b** was established by X-ray diffraction (see below). Converting **1a-c** to **3a-c** does not induce any visible change for the butyl chains signals in the ¹H and ¹³C{¹H} NMR spectra. The aryl signals are slightly affected, with variations smaller than 1.0 and 4.5 ppm in the ¹H NMR or ¹³C{¹H} NMR spectra, respectively. Elemental analyses of **3a,b** confirmed the clean formation of [L+2Cu+2X]_n-type complexes. Similarly to the Ag(I) chemistry, these data are not sufficient to provide an insight into the structural features of the complexes (e.g.

neutral bridge-, cationic chelate-, neutral cubane-, coordination polymer-types). For **3c**, despite numerous purification steps, no satisfactory analyses were obtained. The ESI mass spectra of complexes **3a-c** display respectively the following signals for m/z (L = ligand): $[L+Cu+Cl+H]^+ = 421.12$, $[L+H]^+ = 323.22$; $[L+2Cu+2Br+H]^+ = 610.92$, $[L+2Cu+Br]^+ = 528.99$, $[L+Cu+Br+H]^+ = 467.07$, $[L+H]^+ = 323.22$, and $[2L+5Cu+4I]^+ = 1468.70$, $[2L+4Cu+4I+H]^+ = 1406.77$, $[2L+4Cu+3I]^+ = 1278.86$, $[2L+3Cu+3I+H]^+ = 1216.94$, $[2L+3Cu+2I]^+ = 1089.03$, $[2L+2Cu+I]^+ = 897.19$, $[L+2Cu+I+H]^+ = 702.89$, $[L+2Cu+I]^+ = 574.98$. Despite extensive molecular fragmentations during the analyses, these data strongly suggest the formation of neutral dinuclear $[L+2Cu+2X]$ complexes for **3a** and **3b**, and of a neutral tetranuclear complex $[2L+4Cu+4I]$ for **3c**. To establish their structures by X-ray diffraction, X-ray diffraction analyses of **3a-c** were desirable. Colourless crystals of **3a** and **3b** were obtained by slow evaporation of solutions of a mixture of THF and octane. Unfortunately, attempts to crystallize **3c** from various couples of solvents (THF-pentane, THF-Et₂O, THF-octane, CH₂Cl₂-pentane and CH₂Cl₂-octane), at different temperatures (rt, 4 °C and -20 °C) resulted ultimately in amorphous solids.

The complex μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene)dichlorodicopper(I) (ImidBuCu₂Cl₂, **3a**) is an organometallic coordination polymer, which crystallizes in the monoclinic system and the $P2_1/c$ space group (Figure 4). There is one carbene donor group per copper and chloride, in agreement with a $[2L+2Cu+2X]_{n=\infty}$ -type complex. The neutral dinuclear, monomeric units [ImidBuCu₂Cl₂] are held together by a bridging chloride to form a coordination polymer. The Cu1–C1, Cu1–Cl1, Cu2–C14, Cu2–Cl2 and Cu2–Cl4 bond distances are equal to 1.882(5), 2.115(1), 1.901(5), 2.1835(13) and 2.607(1) Å, respectively. The copper centre Cu1 exhibits a slightly distorted linear coordination geometry, with a C1–Cu1–Cl1 angle of 169.5(2)° whereas Cu2 is in a quasi-trigonal planar environment with C14–Cu1–Cl1, C14–Cu2–Cl2 and Cl1–Cu1–Cl2 angles of 142.2(2)°, 116.4(2)° and 101.05(4)°, respectively. The bridging Cl1 ligand is bound to Cu2 via a long-range interaction (2.6073(14) Å) and to Cu1 via a shorter (covalent) bond (2.115(1) Å). The imidazole rings from the same ligand are oriented in almost opposite directions, which make the ligand an excellent bridge for coordination polymers, and the angle between their planes is equal to 171.5°.

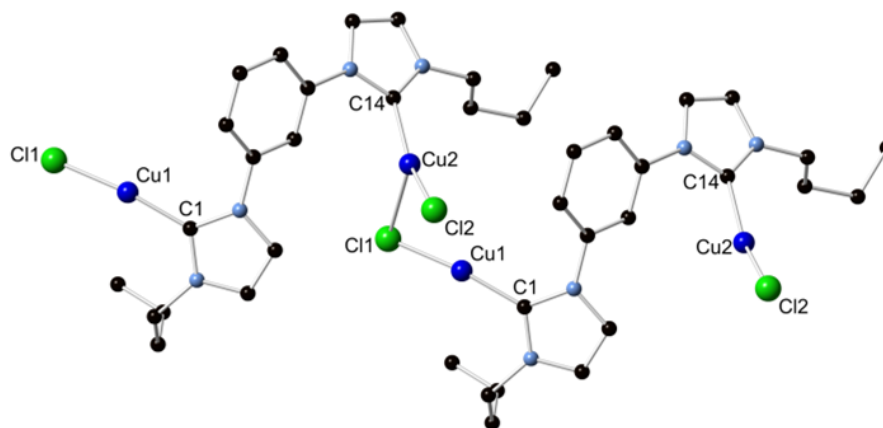


Figure 4. Ball and stick representation of two dinuclear, monomeric units $[\text{ImidBuCu}_2\text{Cl}_2]$ which are held together by Cl1 and form the polymer chain of **3a** in the solid-state. Hydrogen atoms have been omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): C1–Cu1 1.882(5), C14–Cu2 1.901(5), Cu1–Cl1 2.1152(14), Cu2–Cl2 2.1835(13), Cu2–Cl1 2.6073(14); C1–Cu1–Cl1 171.34(15), C14–Cu2–Cl2 147.35(15), C14–Cu2–Cl1 113.34(14), Cu1–Cl1–Cu2 89.79(5), Cl1–Cu2–Cl2 98.96(5).

The complex μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene)dibromodicopper(I) ($\text{ImidBuCu}_2\text{Br}_2$, **3b**) has a structure very similar to that of **3a**, with bromides replacing chlorides. This organometallic coordination polymer crystallizes in the monoclinic system and the $P2_1/c$ space group (Figure 5). There is one carbene donor per copper and bromide with the bis-carbene ligand acting as a bridge between two Cu centres, in agreement with a $[2\text{L}+2\text{Cu}+2\text{X}]_{n=\infty}$ -type complex. Two neutral dinuclear units $[\text{ImidBuCu}_2\text{Br}_2]$ constitute a monomeric entity and are held together by a bridging bromide. The Cu2–C14, Cu2–Br2, Cu1–C1, Cu1–Br1 and Cu1–Br2 bond distances are equal to 1.893(7), 2.245(1), 1.904(6), 2.330(1) and 2.647(1) \AA , respectively. The copper centre Cu2 exhibits a slightly distorted linear coordination geometry, with an C14–Cu2–Br2 angle equal to $171.3(2)^\circ$, whereas Cu1 is in a quasi-trigonal planar environment with C1–Cu1–Br1, C1–Cu1–Br2 and Br2–Cu1–Br1 angles of $147.3(2)^\circ$, $113.3(2)^\circ$ and $98.79(5)^\circ$, respectively. The bridging bromide Br2 is bound to Cu1 via a long-range interaction (2.647(1) \AA) and to Cu2 via a shorter (covalent) bond (2.245 (1) \AA). Like in **3a**, the imidazole rings from the same ligand are oriented in almost opposite directions and the angle between their planes is equal to 168.0° .

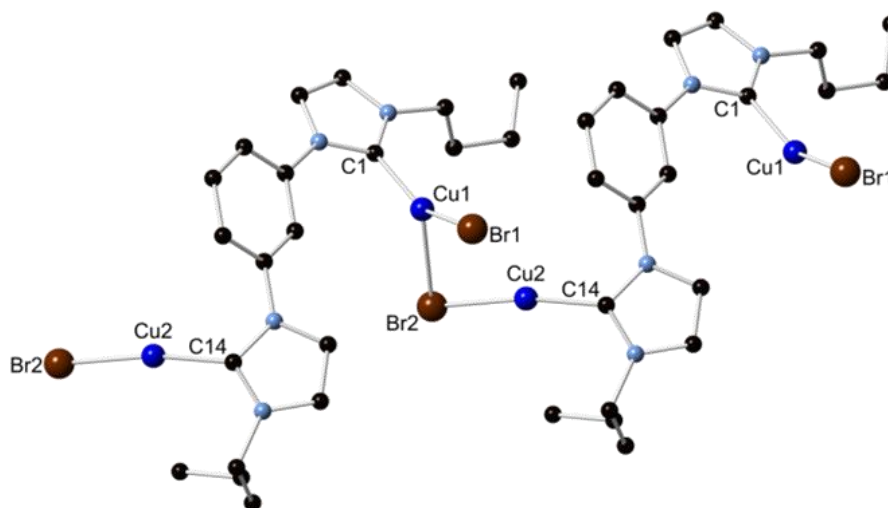
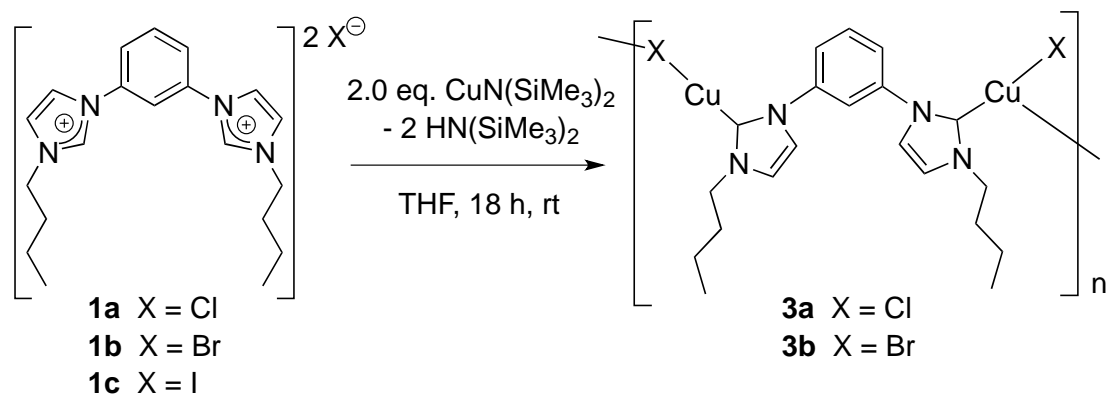


Figure 5. Ball and stick representation of two dinuclear, monomeric units [ImidBuCu₂Br₂] which are held together by Br₂ and form the polymer chain of **3b** in the solid-state. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1–Cu1 1.904(6), C14–Cu2 1.893(7), Cu1–Br1 2.3300(12), Cu2–Br2 2.2451(12), Cu1–Br2 2.6473(12); C1–Cu1–Br1 142.2(2), C14–Cu2–Br2 169.5(2), C1–Cu1–Br2 116.4(2), Br1–Cu1–Br2 101.05(4), Cu1–Br2–Cu2 87.07(4).

The Cu–C bond distances in the complexes **3a,b** are comparable to those reported for other neutral Cu(I) NHC complexes [46, 77–80]. The bis-NHC moiety acts as a bridging bidentate ligand which favours the formation of 1D-polymers in the presence of suitable anionic ligands. Furthermore, long-range halogen-copper interactions also play a key role in the formation of coordination polymers in preference to cubanes. To the best of our knowledge, only three Cu(I)-NHC organometallic coordination polymers have been characterized in the solid-state [77, 79, 80]. Two of them feature pyridine- or oxazoline-functionalized NHC ligands (acting as bidentate donors) and are of the $[-N\curvearrowright\text{NHC}-(\text{CuBr})-]_n$ type, in which each copper is ligated by two carbenes belonging to different ligands, and a bromide [79, 80]. The third example contains bis-NHC ligands and is of the $(-\text{NHC}-\text{Cu}-(\mu\text{-Br})_2-\text{Cu}-\text{NHC}-)_n$ type in which each copper is connected by two bridging bromides [77]. In **3a,b**, the connection between the monomers is different: each copper(I) centre is connected to a carbene and a halide to form a neutral complex. These units are held together by van der Waals interactions to give a $(-\text{NHC}-(\text{CuBr})-(\mu\text{-Br})-\text{Cu}-\text{NHC}-)_n$ -type polymer (Scheme 3).



Scheme 3. Synthesis of the copper(I) complexes **3a** and **3b**.

Unfortunately, we could not obtain single crystals for **3c** suitable for X-ray diffraction and this prevented its unambiguous characterization. However, in this case the formation of a neutral $[\text{Cu}(\text{NHC})_2]_2$ cubane-type structure is strongly supported by NMR and MS-ESI data. Furthermore, a survey of the CSD database clearly points out that the $[\text{Cu}_4\text{I}_8]$ cubane core is often encountered (159 hits) in association with various ligands including phosphines, arsines, amines, pyridines, acetonitrile, water, thiols... [81-85].

Finally for the sake of comparison, three other well-known synthetic pathways to access NHC Cu(I) complexes were assessed. First, the imidazolium salt **1c** was reacted with 1.3 eq. of Cu(I) oxide in distilled and degassed water or in toluene under reflux [86]. After 24 h no reaction had occurred. Second, **1c** and 1.3 eq. of Cu(I) oxide were heated in THF at 110 °C in a sealed tube, under microwave irradiation. After 1 h, the starting materials were recovered [87]. Third, Ag(I)-NHC complexes being efficient at transmetalating their carbene ligand(s) to copper(I), **2c** was placed in presence of CuI, in dichloromethane, at room temperature for 18 h [37, 88]. The ^1H NMR analysis of the crude mixture showed that the transmetalation only partially occurred but increasing the temperature to 40 °C resulted in the quantitative formation of **3c**.

3. Conclusion

A series of bis-(NHC) Ag(I) and Cu(I) complexes was obtained in good yields. Their structures strongly depend on the nature of the associated anions, and range from classic dicationic (**2d**), to cubane-type (**2b**) to coordination polymers (**2a** and **3a,b**). The complexes **3a,b** constitute new additions to the still rare examples of copper-NHC coordination polymers. Overall, such a structural diversity emphasizes the need to characterize thoroughly

any Ag(I) or Cu(I) NHC-based catalytic systems prior to use, in order to establish the true nature of the precatalysts. In this regard, studies exploring the relative stability/activity of the aforementioned silver and copper complexes for coupling reactions are ongoing in our laboratories.

4. Experimental

4.1. General information

Only those reactions with Cu(I) reagents were carried out under inert atmosphere using standard Schlenk techniques. The compound Cu[N(SiMe₃)₂] was synthesized according to a published procedure [89]. All reagents were used as received from commercial suppliers. Solvents were purified and dried under argon by conventional methods. Proton (¹H), carbon (¹³C{¹H}) and fluorine (¹⁹F{¹H}) nuclear magnetic resonance (NMR) spectra were recorded on the following instruments: Bruker AVANCE I – 300 MHz spectrometer and Bruker AVANCE I – 500 MHz spectrometer. The chemical shifts are given in parts per million (ppm). Data are presented as following: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept. = septet, m = multiplet, b = broad), coupling constants (*J*/Hz) and integration. Assignments were determined either on the basis of unambiguous chemical shifts or coupling patterns. The residual solvent proton (¹H) or carbon (¹³C{¹H}) resonance, or the BF₄⁻ anion signals (¹⁹F{¹H}) were used as reference values. For ¹H NMR: CDCl₃ = δ 7.26 ppm, CD₂Cl₂ = δ 5.32 ppm and DMSO-*d*₆ = δ 2.50. For ¹³C NMR: CDCl₃ = δ 77.1 ppm, CD₂Cl₂ = δ 53.8 and DMSO-*d*₆ = δ 39.5 ppm. For ¹⁹F NMR: BF₄⁻ = δ -150.6 ppm. IR and FIR spectra were recorded in the region 4000-200 cm⁻¹ on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the “Service de Microanalyses”, Université de Strasbourg. Mass spectrometry analyses (ESI-MS) were performed by the “Service de Spectrométrie de Masse”, Université de Strasbourg. For X-ray diffraction studies, the intensity data were collected at 173(2) K on a Kappa CCD diffractometer 88 (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on *F*², SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms [90]. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined riding on the corresponding parent atoms.

4.2. Synthetic procedures

4.2.1. Synthesis of 1,3-di(imidazol-1-yl)benzene. To a solution of 1,3-dibromobenzene (25.00 mL, 0.21 mol) in DMSO (200 mL) were added 1H-imidazole (35.00 g, 0.51 mol), potassium carbonate (72 g, 0.52 mol) and Cu(II) oxide (2.00 g, 25.20 mmol). After 48 h at 150 °C, the solvent was removed by distillation. The crude solid was dissolved in dichloromethane (inorganic salts were insoluble) and the solution was filtered through Celite® and concentrated. The product was precipitated from pentane as pale yellow powder (38.30 g, 0.18 mol). Yield: 88%. ¹H NMR (300 MHz, CDCl₃): δ 7.95 (s, 2H, NCHN), 7.63 (m, 1H, CH^{aryl}), 7.51 (t, *J* = 2.0 Hz, 1H, CH^{aryl}), 7.45 (d, *J* = 2.1 Hz, 1H, CH^{aryl}), 7.42 (d, *J* = 1.8 Hz, 1H, CH^{aryl}), 7.39 (t, *J* = 1.3 Hz, 2H, CH^{imidazole}), 7.25 (s, 1H, CH^{imidazole}). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 138.5 (NCHN), 135.4 (C^{aryl}), 131.3 (CH^{imidazole}), 130.8 (CH^{imidazole}), 119.8 (CH^{aryl}), 117.9 (CH^{aryl}), 114.2 (CH^{aryl}).

4.2.2. Synthesis of 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) chloride (1a). 1,3-di(imidazol-1-yl)benzene (4.00 g, 19.04 mmol) and *n*-butyl chloride (10.20 mL, 98.07 mmol) were stirred, in refluxing chlorobenzene, for 72 h. After evaporation under reduced pressure, the crude solid was dissolved in dichloromethane containing few drops of methanol. An off-white powder was obtained after precipitation from Et₂O (4.89 g, 12.38 mmol). Yield: 65%. ¹H NMR (500 MHz, CD₂Cl₂): δ 11.76 (s, 2H, NCHN), 9.27 (s, 2H, CH^{imidazole}), 9.11 (s, 1H, CH^{aryl}), 8.27 (dd, *J* = 8.2, 1.9 Hz, 2H, CH^{aryl}), 7.80 (s, 2H, CH^{imidazole}), 7.54 (t, *J* = 8.3 Hz, 1H, CH^{aryl}), 4.43 (t, *J* = 7.3 Hz, 4H, NCH₂^{Bu}), 2.04 – 1.92 (m, 4H, CH₂^{Bu}), 1.44 – 1.32 (m, 4H, CH₂^{Bu}), 0.93 (t, *J* = 7.4 Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 137.0 (C^{aryl}), 136.4 (CH^{aryl}), 132.5 (CH^{aryl}), 123.5 (CH^{imidazole}), 122.3 (CH^{aryl}), 122.0 (CH^{imidazole}), 114.7 (CH^{aryl}), 50.6 (NCH₂^{Bu}), 32.3 (CH₂^{Bu}), 19.9 (CH₂^{Bu}), 13.7 (CH₃^{Bu}).

4.2.3. Synthesis of 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) bromide (1b). A procedure similar to that used for compound **1a** with 1,3-di(imidazol-1-yl)benzene (4.00 g, 19.04 mmol) and *n*-butyl bromide (9.70 mL, 87.61 mmol), in refluxing THF, for 72 h, gave **1b**, as an off-white powder (5.78 g, 12.00 mmol). Yield: 63%. ¹H NMR (300 MHz, CD₂Cl₂): δ 11.56 (s, 2H, NCHN), 9.04 (t, *J* = 2.0 Hz, 1H, CH^{imidazole}), 8.91 (t, *J* = 1.7 Hz, 2H), 8.24 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.72 (t, *J* = 8.3 Hz, 1H), 7.60 (s, 2H, CH^{imidazole}), 4.45 (t, *J* = 7.3 Hz, 4H, NCH₂^{Bu}), 2.02 (dd, *J* = 14.9, 7.5 Hz, 4H, CH₂^{Bu}), 1.43 (dt, *J* = 14.7, 7.4 Hz, 4H, CH₂^{Bu}), 1.00

(t, $J = 7.3$ Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 137.0 (C^{aryl}), 136.5 (NCHN), 133.0 (CH^{aryl}), 123.4 (CH^{imidazole}), 122.8 (CH^{aryl}), 122.4 (CH^{imidazole}), 115.5 (CH^{aryl}), 51.0 (NCH₂^{Bu}), 32.4 (CH₂^{Bu}), 20.1 (CH₂^{Bu}), 13.8 (CH₃^{Bu}).

4.2.4. Synthesis of 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) iodide (1c). A procedure similar to that used for compound **1a** with 1,3-di(imidazol-1-yl)benzene (4.00 g, 19.04 mmol) and *n*-butyl iodide (10.00 mL, 87.87 mmol), in refluxing THF, for 48 h, gave **1c**, as an off-white powder (7.48 g, 12.93 mmol). Yield: 68%. ¹H NMR (300 MHz, CD₂Cl₂): δ 11.25 (t, $J = 1.7$ Hz, 2H, NCHN), 8.97 (t, $J = 2.1$ Hz, 1H, CH^{aryl}), 8.48 (t, $J = 1.9$ Hz, 2H, CH^{imidazole}), 8.14 (dd, $J = 8.1, 2.2$ Hz, 2H, CH^{aryl}), 7.91 – 7.84 (m, 1H, CH^{aryl}), 7.51 (t, 2H, CH^{imidazole}), 4.46 (t, $J = 7.4$ Hz, 4H, NCH₂^{Bu}), 2.11 – 2.00 (m, 4H, CH₂^{Bu}), 1.47 (dq, $J = 14.7, 7.3$ Hz, 4H, CH₂^{Bu}), 1.02 (t, $J = 7.3$ Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ 136.6 (NCHN), 136.3 (C^{aryl}), 133.3 (CH^{aryl}), 123.5 (CH^{imidazole}), 123.4 (CH^{aryl}), 122.3 (CH^{imidazole}), 116.5 (CH^{aryl}), 51.1 (NCH₂^{Bu}), 32.4 (CH₂^{Bu}), 20.0 (CH₂^{Bu}), 13.7 (CH₃^{Bu}).

4.2.5. Synthesis of 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) tetrafluoroborate (1d). To a solution of 1,3-bis(3'-butylimidazol-1-yl)benzene dibromide (**1b**) (0.100 g, 0.24 mmol) in acetone was added an excess of NaBF₄ (0.263 g, 2.40 mmol). The mixture was stirred at room temperature overnight. NaBr was removed by filtration through Celite[®] and the filtrate was precipitated with pentane, yielding a clean product (0.117 g, 0.23 mmol). Yield: 98%. ¹H NMR (500 MHz, CD₂Cl₂): δ 9.69 (s, 2H, NCHN), 8.26 (t, $J = 2.1$ Hz, 1H, CH^{aryl}), 8.09 (t, $J = 1.9$ Hz, 2H, CH^{imidazole}), 7.88 (dd, $J = 8.2, 2.0$ Hz, 2H, CH^{aryl}), 7.78 – 7.71 (m, 1H, CH^{aryl}), 7.59 – 7.54 (m, 2H, CH^{imidazole}), 4.32 (t, $J = 7.4$ Hz, 4H, NCH₂^{Bu}), 1.98 – 1.91 (m, 4H, CH₂^{Bu}), 1.40 (dt, $J = 14.8, 7.4$ Hz, 4H, CH₂^{Bu}), 0.96 (t, $J = 7.4$ Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 136.4 (NCHN), 135.5 (C^{aryl}), 133.2 (CH^{aryl}), 123.9 (CH^{imidazole}), 123.6 (CH^{aryl}), 122.2 (CH^{imidazole}), 116.5 (CH^{aryl}), 51.1 (NCH₂^{Bu}), 32.2 (CH₂^{Bu}), 19.9 (CH₂^{Bu}), 13.6 (CH₃^{Bu}). ¹⁹F NMR (282 MHz, CD₂Cl₂): δ -149.3 (s, BF₄⁻).

4.2.6. Synthesis of (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)disilver(I) dichloride (2a). 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) chloride (**1a**) (0.68 g, 1.72 mmol) and Ag₂O (0.60 g, 2.58 mmol), molecular sieves (3 Å beads), and CH₂Cl₂ were combined, protected from light and stirred for 18 h under argon at room temperature. The solution was filtered through Celite[®], evaporated under reduced pressure and the solid was washed three times with distilled water. The organic phase was dried over MgSO₄ and filtered. Upon

precipitation with pentane, the complex was cleanly recovered (2.05 g, 1.29 mmol). Yield: 65%. Crystals suitable for X-ray analysis were grown by slow evaporation from a solution mixture of **2a**/CH₂Cl₂/octane. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.98 (s, 1H, CH^{aryl}), 7.71 (d, *J* = 1.6 Hz, 3H, CH^{aryl}), 7.66 (d, *J* = 1.9 Hz, 2H, CH^{imidazole}), 7.23 (d, *J* = 1.9 Hz, 2H, CH^{imidazole}), 4.22 (t, *J* = 7.3 Hz, 4H, NCH₂^{Bu}), 1.94 – 1.83 (m, 4H, CH₂^{Bu}), 1.41 (dq, *J* = 14.7, 7.3 Hz, 4H, CH₂^{Bu}), 0.99 (t, *J* = 7.3 Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 179.2 (C^{carbene}), 141.0 (C^{aryl}), 131.8 (CH^{aryl}), 124.4 (CH^{aryl}), 122.4 (CH^{imidazole}), 122.3 (CH^{imidazole}), 120.2 (CH^{aryl}), 52.6 (NCH₂^{Bu}), 33.5 (CH₂^{Bu}), 19.9 (CH₂^{Bu}), 13.8 (CH₃^{Bu}). Anal. Calc. for C₂₀H₂₆N₄Ag₂Cl₂: C, 39.44; H, 4.30; N, 9.20. Found: C, 39.35; H, 4.48; N, 9.01. ESI MS (*m/z*) (L = Ligand): 572.99 [L+2Ag+Cl]⁺, 467.10 [L+Ag+Cl+H]⁺, 323.22 [L+H]⁺. IR: ν_{max}(solid)/cm⁻¹: 3087w, 2984w, 2929w, 2867w, 1605m, 1560w, 1497m, 1458m, 1412m, 1369m, 1258m, 1228m, 1196, 1110m, 1002w, 948w, 871w, 732s, 692s, 511w, 434w, 409w, 294w, 259w, 236w, 218w, 162w, 154w.

4.2.7. Synthesis of bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-μ₃-bromotetrasilver(I) (2b). A procedure similar to that used for compound **2a** with **1b** (1.66 g, 3.44 mmol) and Ag₂O (1.19 g, 5.16 mmol) gave **2b**, as a white powder (1.47 g, 1.05 mmol). Yield: 61%. Crystals suitable for X-ray analysis were grown by slow evaporation from a solution mixture of **2b**/CH₂Cl₂/octane. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.88 (s, 1H, CH^{aryl}), 7.62 (t, *J* = 1.7 Hz, 2H, CH^{imidazole}), 7.59 (d, *J* = 2.0 Hz, 2H, CH^{aryl}), 7.45 (dd, *J* = 8.6, 7.4 Hz, 1H, CH^{aryl}), 7.26 (d, *J* = 1.9 Hz, 2H, CH^{imidazole}), 4.22 (t, *J* = 7.3 Hz, 4H, NCH₂^{Bu}), 1.96 – 1.84 (m, 4H, CH₂^{Bu}), 1.42 (dq, *J* = 14.7, 7.4 Hz, 4H, CH₂^{Bu}), 0.99 (t, *J* = 7.3 Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 182.7 (C^{carbene}), 141.5 (C^{aryl}), 131.4 (CH^{aryl}), 124.1 (CH^{aryl}), 122.6 (C^{imidazole}), 122.4 (C^{imidazole}), 120.5 (CH^{aryl}), 52.7 (NCH₂^{Bu}), 33.9 (CH₂^{Bu}), 20.3 (CH₂^{Bu}), 14.0 (CH₃^{Bu}). Anal. Calc. for C₂₀H₂₆N₄Ag₂Br₂: C, 34.42; H, 3.75; N, 8.03. Found: C, 35.02; H, 3.76; N, 8.41. ESI MS (*m/z*) (L = Ligand): 1314.18 [2L+4Ag+3Br]⁺, 1208.88 [2L+3Ag+3Br+H]⁺, 1126.96 [2L+3Ag+2Br]⁺, 939.15 [2L+2Ag+Br]⁺, 616.94 [L+2Ag+Br]⁺, 511.06 [L+Ag+Br+H]⁺, 430.12 [L+2Ag]²⁺. IR: ν_{max}(solid)/cm⁻¹: 3088w br, 2928m br, 2867w, 1604m, 1561m, 1497m, 1460m, 1411m, 1369m, 1257m, 1227m, 1196m, 1108m, 1059m, 1001w, 948w, 872m, 729s, 692s, 507w, 435w, 303w, 280w, 247w, 150w, 118w.

4.2.8. Formation of 2b from (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)disilver(I) dichloride (2a). The complex **2a** (0.66 g, 1.09 mmol), LiBr (0.19 g, 2.19 mmol) and dry acetone were combined and stirred for 18 h under inert atmosphere. The solvent was

evaporated and the solid was dissolved in CH₂Cl₂. The solution was filtered through Celite[®] and concentrated under reduced pressure. The complex **2b** was isolated (0.75 g, 0.54 mmol) upon precipitation with pentane. Yield: 98%.

4.2.9. Synthesis of bis(μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene- κ -C)tetra- μ -3-iodotetrasilver(I) (2c**).** A procedure similar to that used for compound **2a** with **1c** (1.00 g, 1.73 mmol) and Ag₂O (0.60 g, 2.59 mmol) gave **2c**, as a white powder 2.05 g, 1.29 mmol). Yield: 75%. ¹H NMR (300 MHz, CD₂Cl₂): δ 8.38 (t, J = 1.8 Hz, 1H, CH^{aryl}), 7.58 – 7.47 (m, 2H, CH^{aryl}), 7.47 – 7.36 (m, 3H, CH^{aryl} + CH^{imidazole}), 7.17 (d, J = 1.5 Hz, 2H, CH^{imidazole}), 4.25 (t, J = 7.1 Hz, 4H, NCH₂^{Bu}), 1.83 (dt, J = 14.9, 7.5 Hz, 4H, CH₂^{Bu}), 1.35 (dq, J = 14.6, 7.3 Hz, 4H, CH₂^{Bu}), 0.90 (t, J = 7.3 Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ 184.8 (C^{carbene}), 141.0 (C^{aryl}), 130.4 (CH^{aryl}), 123.2 (CH^{imidazole}), 121.9 (CH^{aryl}), 121.5 (CH^{aryl}), 121.0 (CH^{imidazole}), 52.0 (NCH₂^{Bu}), 33.5 (CH₂^{Bu}), 19.9 (CH₂^{Bu}), 13.7 (CH₃^{Bu}). Anal. Calc. for C₄₀H₅₂N₈Ag₄I₄: C, 30.33; H, 3.31; N, 7.07. Found: C, 30.01; H, 3.38; N, 6.88. ESI MS (m/z) (L = Ligand): 1584.68 [2L+4Ag+4I+H]⁺, 1456.76 [2L+4Ag+3I]⁺, 1348.86 [2L+3Ag+3I+H]⁺, 1222.94 [2L+3Ag+2I]⁺, 1115.05 [2L+2Ag+2I+H]⁺, 987.14 [2L+2Ag+I]⁺, 664.92 [L+2Ag+I]⁺, 559.03 [L+Ag+I+H]⁺, 430.12 [2L+2Ag]⁺. IR: ν_{\max} (solid)/cm⁻¹: 3158w, 3104w, 3050w, 2954w, 2928w, 2869w, 1604w, 1541w, 1491m, 1463m, 1404m, 1378w, 1343w, 1266w, 1251w, 1221w, 1192w, 1097m, 1072w, 1001w, 946w, 883w, 850w, 821w, 792m, 763w, 721s, 696m, 631w, 505m, 452m, 379w, 307w, 238w, 156w.

4.2.10. Synthesis of bis(1,3-bis(3'-butylimidazol-2'-ylidene)benzene)disilver(I) tetrafluoroborate (2d**).** Bis(μ -1,3-bis(3'-butylimidazol-2'-ylidene)benzene- κ -C)tetra- μ -3-bromotetrasilver(I) (**2b**) (0.53 g, 0.45 mmol), AgBF₄ (0.18 g, 0.90 mmol) and CH₂Cl₂ were combined and stirred for 18 h. The solution was filtered through Celite[®] and concentrated under reduced pressure. Upon precipitation with pentane, the complex was isolated (0.46 g, 0.44 mmol). Yield: 98%. Crystals suitable for X-ray analysis were grown by slow evaporation of a solution mixture of **2d**/CH₂Cl₂/octane. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.64 (s, 2H, CH^{imidazole}), 7.56 (dd, J = 8.0, 2.0 Hz, 2H, CH^{aryl}), 7.50 (s, 1H, CH^{aryl}), 7.33 (d, J = 1.7 Hz, 3H, CH^{aryl+imidazole}), 4.26 (t, J = 7.2 Hz, 4H, NCH₂^{Bu}), 2.01 – 1.89 (m, 4H, CH₂^{Bu}), 1.46 (dq, J = 14.6, 7.3 Hz, 4H, CH₂^{Bu}), 1.02 (t, J = 7.4 Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 179.6 (d, ¹ J (¹³C-¹⁰⁷Ag) = 184 Hz, ¹ J (¹³C-¹⁰⁹Ag) = 213 Hz, C^{carbene}), 141.6 (C^{aryl}), 131.2 (CH^{aryl}), 124.8 (CH^{aryl}), 124.6 (CH^{imidazole}), 123.1 (CH^{imidazole}), 120.3 (CH^{aryl}), 52.8 (NCH₂^{Bu}), 34.0 (CH₂^{Bu}), 20.4 (CH₂^{Bu}), 13.9 (CH₃^{Bu}). ¹⁹F{¹H} NMR (282 MHz, CD₂Cl₂) δ -

150.6 (s, BF₄⁻). Anal. Calc. for C₄₀H₅₂N₈Ag₂B₂F₈•CH₂Cl₂: C, 41.89; H, 4.69; N, 9.31. Found: C, 41.74; H, 4.62; N, 9.99. ESI MS (*m/z*) (L = Ligand): 430.12 [2L+2Ag]²⁺. IR: $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3134w, 2956w, 2162w, 1606w, 1497m, 1463w, 1415m, 1369w, 1281w, 1261w, 1229w, 1048s br, 950w, 874w, 735m br, 693m, 519m, 419w, 397w, 375w, 352w, 303w, 290w, 279w, 247w, 227w, 202w, 195w, 170w, 151w, 121w.

4.2.11. Synthesis of (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)dicopper(I) dichloride

(3a). 1,1'-(1,3-phenylene)bis(3-butyl-1H-imidazol-3-ium) chloride (**1a**) (0.34 g, 0.86 mmol), Cu[N(SiMe₃)₂] (0.38 g, 1.73 mmol), and THF were combined and stirred for 18 h under argon. The solution was filtered through Celite[®]. Upon precipitation with pentane, the complex was cleanly isolated (1.04 g, 0.74 mmol). Yield: 98%. Crystals suitable for X-ray analysis were grown from a solution mixture **3c**/THF/pentane. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.17 (s, 1H, CH^{aryl}), 7.76 (dd, *J* = 7.2, 1.8 Hz, 2H, CH^{aryl}), 7.70 (dd, *J* = 8.9, 7.0 Hz, 1H, CH^{aryl}), 7.65 (d, *J* = 1.9 Hz, 2H, CH^{imidazole}), 7.16 (d, *J* = 1.9 Hz, 2H, CH^{imidazole}), 4.24 (t, *J* = 7.2 Hz, 4H, NCH₂^{Bu}), 1.90 (dq, *J* = 12.8, 7.5 Hz, 4H, CH₂^{Bu}), 1.47 – 1.37 (m, 4H, CH₂^{Bu}), 0.99 (t, *J* = 7.4 Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 176.6 (C^{carbene}), 141.2 (C^{aryl}), 131.6 (CH^{aryl}), 123.6 (CH^{aryl}), 122.3 (CH^{imidazole}), 121.7 (CH^{imidazole}), 119.6 (CH^{aryl}), 52.3 (CH₂^{Bu}), 33.8 (CH₂^{Bu}), 20.2 (CH₂^{Bu}), 13.9 (CH₃^{Bu}). Anal. Calc. for C₂₀H₂₆N₄Cu₂Cl₂: C, 46.16; H, 5.04; N, 10.77. Found: C, 46.37; H, 4.89; N, 10.12. ESI MS (*m/z*) (L = Ligand): 421.12 [L+2Cu+Cl]⁺, 323.22 [L+H]⁺. IR: $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 2952w, 2865w, 2362w, 2160w, 1978w, 1684w, 1601m, 1559w, 1541w, 191m, 1458m, 1412m, 1371w, 1342w, 1318w, 1278m, 1256m, 1231m, 1194w, 1163w, 1104w, 1081w, 1063w, 884w, 799m, 773m, 748s, 719s, 696s, 670m, 645w, 635w, 513w, 491w, 477w, 457w, 414w, 373w, 317w, 251w, 218w, 205w, 198w, 174w, 144w.

4.2.12. Synthesis of (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)dicopper(I) dibromide

(3b). A procedure similar to that used for **3a** with **1b** (0.41 g, 0.86 mmol), Cu[N(SiMe₃)₂] (0.38 g, 1.73 mmol) gave **3b**, as a white powder (0.51 g, 0.84 mmol). Yield: 98%. Crystals suitable for X-ray analysis were grown from a solution mixture of **3b**/THF/pentane. ¹H NMR (300 MHz, CD₂Cl₂): δ 8.24 (s, 1H, CH^{aryl}), 7.78-7.71 (m, 2H, CH^{aryl}), 7.72-7.67 (m, 1H, CH^{aryl}), 7.64 (d, *J* = 1.7 Hz, 2H, CH^{imidazole}), 7.16 (d, *J* = 1.7 Hz, 2H, CH^{imidazole}), 4.24 (t, *J* = 7.2 Hz, 4H, CH₂^{Bu}), 1.98 – 1.84 (m, 4H, CH₂^{Bu}), 1.40 (dt, *J* = 14.6, 7.4 Hz, 4H, C), 0.99 (t, *J* = 7.3 Hz, 6H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 177.8 (C^{carbene}), 141.2 (C^{aryl}), 131.6 (CH^{aryl}), 123.5 (CH^{aryl}), 122.2 (CH^{imidazole}), 121.6 (CH^{imidazole}), 119.6 (CH^{aryl}), 52.4

(NCH₂^{Bu}), 33.8 (CH₂^{Bu}), 20.2 (CH₂^{Bu}), 14.0 (CH₃^{Bu}). Anal. Calc. for C₂₀H₂₆N₄Cu₂Br₂: C, 39.42; H, 4.30; N, 9.19. Found: C, 39.89; H, 4.33; N, 9.82. ESI MS (*m/z*) (L = Ligand): 610.92 [L+2Cu+2Br+H]⁺, 528.99 [L+2Cu+Br]⁺, 467.07 [L+Cu+Br+H]⁺, 323.22 [L+H]⁺. IR: $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3111w br, 2959w, 2931w br, 2866w br, 1601m, 1492m, 1470w, 1459m, 1412m, 1393w, 1371w, 1343w, 1319w, 1279m, 1256m, 1232m, 1195w, 1164w, 1105w, 1081w, 1029w, 1001w, 945w, 885m, 799m, 773m, 748s, 719s, 696s, 670m, 645m, 635sw, 611w, 513w, 491w, 477w, 458w, 418w, 374w, 315w, 278w, 266w, 249w, 227w, 202w, 189w, 175w, 153w, 148w, 141w, 134w, 128w, 120w, 106w.

4.2.13. Synthesis of (1,3-bis(3'-butylimidazol-2'-ylidene)benzene)copper(I) iodide (3c). A procedure similar to that used for **3a** with **1c** (0.50 g, 0.86 mmol), Cu[N(SiMe₃)₂] (0.38 g, 1.73 mmol) gave **3c**, as a white powder (0.51 g, 0.84 mmol). Yield: 86%. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.77 (t, *J* = 2.1 Hz, 1H, CH^{aryl}), 7.62 (t, *J* = 8.0 Hz, 1H, CH^{aryl}), 7.44 (dd, *J* = 8.0, 2.1 Hz, 2H, CH^{aryl}), 7.39 (d, *J* = 1.9 Hz, 2H, CH^{imidazole}), 7.10 (d, *J* = 1.9 Hz, 2H, CH^{imidazole}), 4.21 (t, *J* = 7.3 Hz, 4H, NCH₂^{Bu}), 1.96 – 1.88 (m, 4H, CH₂^{Bu}), 1.43 (dq, *J* = 14.9, 7.4 Hz, 4H, CH₂^{Bu}), 0.99 (t, *J* = 6 Hz, 7H, CH₃^{Bu}). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 184.2 (C^{carbene}), 141.1 (C^{aryl}), 131.0 (CH^{aryl}), 121.8 (CH^{imidazole}), 121.4 (CH^{imidazole}), 119.9 (CH^{aryl}), 118.5 (CH^{aryl}), 52.1 (NCH₂^{Bu}), 33.6 (CH₂^{Bu}), 20.4 (CH₂^{Bu}), 14.1 (CH₃^{Bu}). Anal. Calc. for C₂₀H₂₆N₄Cu₂I₂: C, 34.15; H, 3.73; N, 7.97. Despite numerous attempts to purify the product by fractional precipitations or crystallizations, no satisfactory analyses were obtained. ESI MS (*m/z*) (L = Ligand): 1468.70 [2L+5Cu+4I]⁺, 1406.77 [2L+4CuI+H]⁺, 1216.94 [2L+3Cu+3I+H]⁺, 1089.03 [2L+3Cu+2I]⁺, 897.19 [2L+2Cu+I]⁺, 702.89 [L+2Cu+2I+H]⁺, 574.98 [L+2Cu+I]⁺. IR: $\nu_{\max}(\text{solid})/\text{cm}^{-1}$: 3087w, 2984w, 2929w, 2867w, 1605m, 1560w, 1497m, 1458m, 1412m, 1369m, 1258m, 1228m, 1196, 1110m, 1002w, 948w, 871w, 732s, 691s, 511w, 434w, 409w, 294w, 259w, 236w, 218w, 162w, 154w.

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