Structural Diversity of Copper(I)–N-Heterocyclic Carbene Complexes; Ligand Tuning Facilitates Isolation of the First Structurally Characterised Copper(I)–NHC Containing a Copper(I)–Alkene Interaction

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Abstract: The preparation of a series of imidazolium salts bearing N-allyl substituents, and a range of substituents on the second nitrogen atom that have varying electronic and steric properties, is reported. The ligands have been coordinated to a copper(I) centre and the resulting copper(I)–NHC (NHC=N-heterocyclic carbene) complexes have been thoroughly examined, both in solution and in the solid-state. The solid-state structures are highly diverse and exhibit a range of unusual geometries and cuprophilic interactions. The first structurally characterised copper(I)–NHC complex containing a copper(I)–alkene interaction is reported. An N-pyridyl substituent, which forms a dative bond with the copper(I) centre, stabilises an interaction between the metal centre and the allyl substituent of a neighbouring

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ligand, to form a 1D coordination polymer. The stabilisation is attributed to the pyridyl substituent increasing the electron density at the copper(I) centre, and thus enhancing the metal(d)-to-alkene(π^*) back-bonding. In addition, components other than charge transfer appear to have a role in copper(I)-alkene stabilisation because further increases in the Lewis basicity of the ligand disfavours copper(I)-alkene binding.

Introduction

The binding of alkenes to copper(I) metal centres has been proposed as an important step in a variety of chemical processes, for example, in alkene aziridination and cyclopropanation, and in conjugate additions to α,β -unsaturated ketones.^[1-5] Furthermore, in nature, it is believed that the formation of a copper(I)-ethylene adduct in the ethylene response 1 (ETR 1) plant protein is a key step in the regulation of several aspects of the plant life cycle.^[6] As the bonding is relatively weak, many systems take advantage of the reversible binding nature of copper(I)-alkenes. Other potential applications in which the strength of the copper(I)-alkene bond may play an important role include separation chemistry, in which alkenes are selectively separated from crude organic feedstock,^[7] and in molecular sensing to detect the presence of alkenes.^[8] As metal-carbonyl bonding is similar to metal-alkene bonding, applications such as separation and sensing may also take advantage of the reversible binding of copper(I) carbonyls.

The interaction of alkenes with copper(I) ions has been studied and reported in several papers. Most of the complexes previously examined involve copper(I)–L–ethylene

complexes, in which L is a chelating nitrogen-donor ancillary ligand.^[9-11] Several copper(I)-tris(pyrazolyl)borate-ethylene complexes have been isolated and structurally characterised.^[2,12,13] It has been found that decreasing the Lewis basicity of the ancillary ligand, by introducing fluoroalkyl substituents, decreases the amount of copper—ethylene π backbonding. This decrease can be explained using the Dewar-Chatt-Duncanson model. Surprisingly, the fluorinated complex is an air-stable solid and does not lose ethylene under reduced pressure, whereas its methylated analogue oxidises upon exposure to air.^[2] This finding is counter-intuitive when considering the different levels of π back-bonding in the complexes. Recently, York and co-workers published a DFT study on the impact of ancillary ligand basicity on copper(I)-ethylene binding interactions.^[14] They report that both charge-transfer and components other than chargetransfer are affected by the basicity of the ligand. Although copper—ethylene π back-bonding increases with increasing ligand basicity, polarisation and frozen-density terms simultaneously become less favourable, resulting in little overall binding-energy change with alteration of ligand basicity.

Some reported reactions, in which a copper(I)–alkene interaction is postulated, use copper(I)–N-heterocyclic carbene (NHC) complexes.^[15,16] To the best of our knowledge, interaction of an alkene with a copper(I)–NHC complex has not been previously observed in the solid state. The strong σ -donating property of NHC ligands may result in a low favourable polarisation term and a more repulsive frozen-density term. Understanding the nature of the copper(I)–NHC interaction and its effect on copper(I)–alkene binding is imperative for the development of copper(I)–NHC complexes

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for use in catalytic processes, which rely on alkene coordination to the copper centre. Herein, we report the syntheses and full characterisation of copper(I)–NHC complexes, in which the NHC ligands contain an alkene substituent. The first structurally characterised copper(I)–NHC complex containing a copper(I)–alkene interaction is described.

Results and Discussion

A potential strategy for the stabilisation and examination of a copper(I)–alkene interaction in a copper(I)–NHC complex is to use a hemilabile alkene substituent on the NHC ligand itself. Thus, imidazolium ligand precursors **1a–1e** were prepared using established procedures, and fully characterised (Figure 1) (see the Supporting Information).^[17–19] All of the ligands possess either one or two N-allyl substituents, and have a variety of substituents with different steric and electronic properties on the second nitrogen atom.



Figure 1. Imidazolium ligand precursors **1a–1e**.

Copper(I)–NHC complexes can be synthesised using a range of methods, including: 1) Deprotonation of an imidazolium salt using a strong base, followed by coordination to a metal centre.^[20–22] 2) Transmetalation of the corresponding silver(I)–NHC complex.^[23] 3) Deprotonation of the imidazolium and coordination in situ using a basic metal precursor.^[24] 4) Electrochemical reduction of the imidazolium and coordination to a metal centre.^[25,26]

The reaction of compound **1b** with a base (*t*BuOK) in the presence of CuBr resulted in desired product **2b**, in addition to two allyl rearrangement products (see the Supporting Information).^[27] Therefore, because the allyl substituents appear to be sensitive to strong bases, the coordination of ligands **1a–1e** to a copper(I) centre was achieved through deprotonation and coordination in situ, by using copper oxide (Scheme 1).

Complexes **2a–2e** were fully characterised using NMR spectroscopy, mass spectrometry and elemental analysis, all of which support formation of complexes of the type [Cu-(NHC)Br]. Complexes **2a**, **2b**, **2d** and **2e** were further examined using X-ray crystallography. Complex **2a** crystallises as a centrosymmetric $(\mu$ -Br)₂-bridged dimer (Figure 2). The central (CuBr)₂ core is slightly asymmetric, with Cu–Br



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Scheme 1. Synthesis of copper(I)-NHC complexes 2a-2e.

bond lengths of 2.44 and 2.46 Å. The $(CuBr)_2$ core forms a plane with a torsion angle of approximately 24° with respect to the plane defined by the benzimidazol-2-ylidene rings. The Cu–C bond length, at 1.91 Å, is normal for this type of complex.^[24,25,28]



Figure 2. Molecular structure of 2a. Ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

Complex **2b** crystallises as a dimer with a weak, though unusual, cuprophilic interaction (Cu—Cu 2.74 Å) (Figure 3). These types of interaction are usually observed because of the bidentate nature of a ligand bringing the copper centres into close proximity. Cuprophilic interactions in complexes



Figure 3. Molecular structure of **2b**. Ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

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that lack a bidentate ligand are less common than their argentophilic and aurophilic analogues, although some examples have been described in the literature.^[29–32] It is evident from the solid-state structure that distortion of the C-Cu-Br bond angles (to 169.8° and 167.7°) away from linearity occurs, presumably as a result of the cuprophilic interaction. The Cu–C bond lengths of 1.91 and 1.92 Å are within the usual range for copper(I)–NHC complexes, as are the Cu– Br bond lengths (both 2.28 Å).^[24,25,28] These findings indicate that the cuprophilic interaction does not significantly modify the electronic properties of the copper(I) centres.

Complex **2d** crystallises as a $[Cu(NHC)_2Br]$ -type complex, with a rather unusual distorted-trigonal coordination geometry (Figure 4). This type of complex has only been observed



Figure 4. Molecular structure of 2d. Ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

previously in two other examples.^[21,33] This structure is somewhat unexpected, especially given that elemental analysis gives a ratio of 1:1 NHC/CuBr. Due to the labile nature of copper(I)-NHC complexes, it is possible that transmetalation occurs during crystallisation, providing one mole equivalent of [Cu(NHC)2Br] and one mole equivalent of CuBr. The trigonal geometry is surprising, especially considering the steric bulk of the mesityl wingtip groups. The bulky mesityl groups widen the C-Cu-C bond angle (151.1°), an effect that in turn decreases the C-Cu-Br bond angles (103.3° and 105.6°) and also forces the bromide ion further from the copper(I) centre (Cu-Br 2.62 Å) in order to relieve steric congestion. This Cu-Br bond is rather long compared with those of other complexes described in the literature, and to some extent, may also be caused by the strong σ -donor effect of the two NHC ligands coordinated to the copper(I) centre. The Cu-C bond lengths, at 1.93 and 1.94 Å, are slightly elongated with respect to those of previous complexes; however, these values do compare favourably with those reported previously by Albrecht et al. (1.930(2) Å)^[21] and Lavoie et al. (1.935(3) Å) for [Cu- $(NHC)_2X$] (X = halide) complexes.^[33]

The copper(I) centre in complex 2e is two coordinate with an approximately linear geometry (172.1°, Figure 5). The Cu–C and Cu–Br bond lengths, at 1.92 and 2.28 Å, respectively, are within typical ranges for this type of complex. The 2-methoxyphenyl ring is twisted, with respect to the plane defined by the NHC ring, by approximately 47°. This



Figure 5. Molecular structure of 2e. Ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

twisting would act to prohibit π -overlap between the methoxyphenyl and NHC rings, resulting in the highly π -electron-donating OMe group having little electronic effect on the NHC ligand.

The steric properties of the ligands of 2a-2e have been varied and result in a range of interesting structures that differ significantly around the copper(I) centres. However, these variations did not facilitate any copper(I)–alkene coordination. The ligand precursors described (see below) were therefore appended with 2-pyridyl N-substituents. It was anticipated that this would modulate the electronic properties of the NHC ligand, in addition to providing the opportunity for metal chelation. The complexes formed from these ligands are fascinating in their own right. Moreover, these ligands allowed the isolation of the first example of a structurally characterised copper(I)–NHC complex containing a copper(I)–alkene interaction.

Ligand precursors 1 f-1i (Figure 6) were prepared, and fully characterised using NMR spectroscopy, mass spectrometry and elemental analysis.^[34,35] These ligands offer the pos-



Figure 6. Imidazolium ligand precursors 1 f-1i.

sibility of chelation by binding to the metal centre through both the carbenic carbon and pyridyl nitrogen atoms, with ligand **1i** having two potential NHC donors. In the solidstate structures of imidazolium salts **1f**, **1g** and **1i**, the pyridyl and imidazolium rings lie almost coplanar, which increases π -overlap between the two rings (Figure 7). This significant π -overlap between the two aromatic systems results in a particularly low-field shift of the imidazolium C2 proton

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Figure 7. Molecular structure of imidazolium salts 1 f, 1g and 1i. Ellipsoids are shown at 50% probability level. Hydrogen atoms and solvent molecules (acetonitrile molecules in compound 1g, and a water molecule and an acetonitrile molecule in compound 1i) have been omitted for clarity.

resonances in the ¹H NMR spectra, with that of compound **1g** being observed at $\delta = 12.22$ ppm (300 MHz, CDCl₃). There is a strong anion– π interaction between the N–C–N π -cloud and a neighbouring bromide anion in these ligand precursors, interatomic distances falling well below the sum of the van der Waals radii (3.36 Å in **1f**, 3.31 Å and 3.32 Å in **1g** and 3.29 Å in **1i**). Anion– π interactions are much less common than cation– π interactions; this interaction is facilitated by the particularly electron-poor (and positively charged) N–C–N moiety of the imidazolium owing to the effect of the electron-withdrawing pyridyl substituents on the imidazolium ring. The presence of anion– π interactions in these structures may facilitate the use of imidazolium salts as anion binders.^[36,37]

The reaction of Cu_2O with ligand precursors 1a-1e led to the formation of analytically pure copper(I)-NHC com-

plexes **2a–2e**. However, reaction of **1f** with Cu₂O at reflux in dichloromethane, in the presence of 4 Å molecular sieves, led to the isolation of an intractable green oil. Therefore, another approach for the synthesis of desired [Cu-(NHC)Br]-type complex, **2f**, was followed. Complex **1f** was treated with one equivalent of CuBr in the presence of an excess of Cs₂CO₃ in anhydrous acetonitrile at 50 °C. Cs₂CO₃ is too weak a base to cause allylic-rearrangement reactions to occur, but is strong enough so that deprotonation of **1f** can occur. After workup, a yellow solid was obtained (**2f**'), which was fully characterised by ¹H and ¹³C{¹H} NMR spec-

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troscopy, high-resolution mass spectrometry and elemental analysis. ¹H NMR spectroscopy revealed the complete loss of the low-field imidazolium proton resonance, and the presence of a broad low-field resonance at $\delta = 183.7$ ppm (126 MHz, CD₃CN) in the ¹³C{¹H} NMR spectrum strongly suggested the formation of a copper(I)–NHC complex. Elemental analysis shows that, instead of a [Cu(NHC)Br] complex, **2**f' was a bis-NHC complex ([Cu(NHC)₂Br], Figure 8).

The formation of a bis-NHC complex is also implied in the high-resolution mass spectrum, in which the dominant molecular ion corresponds to [Cu- $(NHC)_2$]⁺. However, great care should be taken when interpreting the ESI mass spectra of copper(I)–NHC complexes because their labile nature can



Figure 8. Suggested structure of complex **2 f**'.

lead to ligand scrambling, resulting in the appearance of bis-NHC species in samples of pure mono-NHC compounds. This ligand-scrambling behaviour is well-documented for silver(I)–NHC complexes.^[38] Complex **2 f**' is proposed to be an ionic complex on the basis of its poor solubility in common organic solvents (e.g. dichloromethane, chloroform and tetrahydrofuran), and slightly better solubility in more polar acetonitrile.

A different method was required to synthesise the [Cu-(NHC)Br] complex of ligand precursor **1f**. Reaction of an excess of Ag_2O with **1f** in anhydrous dichloromethane, in the presence of 4 Å molecular sieves, led to the formation of a dark suspension that after filtration, removal of the solvent and recrystallisation, yielded silver(I)–NHC complex **Ag-2 f** (Scheme 2).

Characterisation of **Ag-2f** by ¹H NMR spectroscopy indicated the loss of the imidazolium proton resonance, and formation of the silver(I)–NHC complex was confirmed by the ¹³C{¹H} NMR spectrum, which showed a low-field resonance at δ =181.6 ppm (75 MHz, CDCl₃). **Ag-2f** crystallises as [Ag(NHC)₂]⁺AgBr₂⁻, in which the C–Ag bonds lie almost perpendicular to the Br–Ag bonds. The two silver centres are linked by a weak argentophilic interaction (see the Supporting Information). Despite the decomposition observed during the reaction of **1f** with Cu₂O, transmetalation from **Ag-2f** was performed successfully, under strictly inert conditions (Scheme 2).

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Scheme 2. Synthesis of silver(I)–NHC complex Ag-2f and transmetalation to give copper(I)–NHC complex 2f.

Complex **2 f** was characterised by ¹H NMR spectroscopy, high-resolution mass spectrometry and elemental analysis. The ¹H NMR spectrum showed that the resonances of many of the ligand protons were broadened considerably in comparison with **Ag-2 f** and **2 f**'. The protons most affected by the spectral broadening included all but one of the pyridyl protons, the backbone NHC protons and the allylic methylene protons. One of the pyridyl protons and the alkenic protons retain reasonably sharp resonances (Figure 9).



Figure 9. ¹H NMR spectrum (4.4–8.8 ppm region) of complex 2f (300 MHz, CDCl₃).

A similar observation was made previously for a related complex by Danopoulos.^[24] The spectral broadening is attributed to non-rigidity in solution, although it is suggested that an equilibrium involving mono- and bis-NHC complexes could contribute to the broadening. It is notable that the protons with the most broadened resonances are those in closest proximity to the metal (that is, nearest the carbenic carbon and pyridyl nitrogen atoms). On this basis, it is proposed that the spectral broadening is caused by coordinative lability at the copper(I) centre. This lability may lead to the formation of mono- and bis-NHC complexes along with mono-NHC dimers. Indeed, from a slightly different ligand, Danopoulos and co-workers were able to characterise two different complexes (a dimer and a polymer) in the

solid-state that could be formed selectively by varying the crystallisation conditions.

Elemental analysis on a sample of 2f strongly indicated that the target complex, [Cu(NHC)Br], had been successfully formed. To confirm this, single crystals suitable for X-ray diffraction analysis were grown from a dilute solution of the product in a mixture of dichloromethane and pentane (1:2). Complex 2f crystallised as a one-dimensional polymer, propagated by coordination of the copper(I) centre of one unit to the alkene of a neighbouring unit (Figure 10). This result is the first example of alkene coordination to a copper(I)-NHC complex. Interestingly, although alkene coordination to the copper(I) centre is observed in the solid state, noticeable shifts in the resonances of the alkenic ¹H nuclei were not observed in the ¹H NMR spectrum at room temperature, thus indicating that alkene coordination to the metal centre is highly labile. The coordination geometry around the copper centre is best described as distorted trigonal pyramidal, with the alkene (considered as a monodentate ligand with regards to geometry), carbenic carbon and bromide atoms occupying the basal positions (bond angles of 130.74°, 115.30° and 112.60°) and the pyridyl nitrogen atom occupying the apical position. Significant distortion of an idealised trigonal-pyramidal geometry occurs, in part, because of the geometric restriction imposed by the 5-membered chelate ring, which has a bite angle of 74.9° as defined by the C-Cu-N angle. The chelate ring itself is essentially planar. Notably, long bonds are observed between the NHC ligand and copper centre (1.97 Å) and between the pyridyl nitrogen atom and copper centre (2.50 Å), possibly as a consequence of the copper centre trying to optimise orbital overlap with both donors. The Cu-Br bond, at 2.44 Å, is relatively long with respect to the terminal Cu-Br bonds described for complexes 2b and 2e (2.28/2.28 and 2.28 Å) but compares well with the bridging Cu-Br bonds of 2a (2.44 and 2.46 Å). This lengthening may result from a need to reduce steric clashing around the four-coordinate copper(I) centre, and also from the possible increase in electron density at the copper(I) centre, caused by having three other donor moieties bound to the metal.

Alkene coordination in complex 2f results in a pronounced lengthening of the alkenic C=C bond from 1.33 Å (1 f) to 1.37 Å (2 f). The coordination of the alkene to the metal centre appears to have been facilitated by the addition of the pyridyl group to the NHC ligand. The pyridyl group acts as both an ancillary donor and also as a modifier of the electronic properties of the NHC donor. With this in mind, it is unsurprising that many of the structurally characterised copper(I)-alkene complexes reported thus far contain chelating N-donor ligands such as tris(pyrazolyl)borate.^[2,39] However, the exact role of the pyridyl ring in enabling alkene coordination to the metal centre in this case is unclear; the pyridyl ring may be altering the properties of the copper(I) centre directly, by coordination to it, or it may be indirectly affecting the copper(I) centre by modifying the donor ability of the NHC ligand (decreasing the energy of the LUMO).

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Figure 10. Molecular structure of 2f (top) and one-dimensional polymer propagated by coordination of the copper(I) centre of one unit to the alkene of a neighbouring unit (bottom). Ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

Slight modification of 1 f, by the addition of a nitro group to the pyridyl ring, gave 1g. The intermediate silver(I)-NHC complex Ag-2g was found to be less soluble than Ag-**2 f**; despite the poor solubility, analysis by ¹H NMR spectroscopy indicated loss of the imidazolium proton resonance. Complex Ag-2g was used to synthesise the corresponding copper(I)-NHC complex without further purification or analysis. Full characterisation of 2g by ¹H and ¹³C{¹H} NMR spectroscopy, high-resolution mass spectrometry and elemental analysis indicated the presence of analytically pure [Cu(NHC)Br]. Broadening of certain resonances was observed in the ¹H NMR spectrum of 2g. However, it should be noted that the resonance broadening is not nearly as pronounced as that for 2 f, possibly indicating that 2g is a much less labile complex. Single crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of 2g in acetonitrile (Figure 11).

Complex **2g** crystallised as a monomer, with the coordination environment around the copper(I) centre best described as distorted T-shaped. A similar coordination environment has been reported previously by Danopoulos et al.^[24] The extended structure of **2g** shows that alkene coordination is switched off by addition of the nitro group, with the closest approach of an alkene to the copper(I) centre occurring at a distance of 5.23 Å. The alkenic C=C bond at 1.32 Å is shorter than in complex **2f** (1.37 Å), and is closer in length to the ligand precursor **1g** (1.33 Å). The Cu–C and Cu–Br distances, at 1.91 and 2.29 Å, respectively, are within the range expected for a linear [Cu(NHC)Br] complex, as is



Figure 11. Molecular structure of 2g. Ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

the C-Cu-Br bond angle (176.8°). The Cu–N bond length on the other hand is extremely long (2.56 Å), implying the presence of a weak interaction between the pyridyl nitrogen and copper(I) centre. The fact that this bond is lengthened with respect to the Cu–N bond of 2f (2.50 Å), despite the lower coordination number of 2g, suggests that the primary effect of adding the nitro group has been to inductively withdraw electron density away from the pyridyl nitrogen atom, making it a poorer donor to the metal centre.

Ligand **1h**, which contains an electron-donating *para*methoxy substituent (with respect to the pyridyl nitrogen atom), was prepared and coordinated to the copper centre using the same route as outlined in Scheme 2. The resulting copper(I)–NHC complex (**2h**) was characterised by ¹H NMR spectroscopy, high-resolution mass spectrometry

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and elemental analysis. The ¹H NMR spectrum shows significant resonance broadening, similar to the ¹H NMR of complex **2 f**. Single crystals suitable for X-ray diffraction analysis were obtained from a solution of the complex in CH_2Cl_2/n -hexane (1:3) (Figure 12).



Figure 12. Molecular structure of **2h**. Ellipsoids are shown at 50% probability level. Hydrogen atoms have been omitted for clarity.

Complex 2h was found to crystallise as a monomer, analogous to complex 2g, with the coordination environment around the copper(I) centre being distorted T-shaped. The Cu-C (1.91 Å) and Cu-Br (2.27 Å) distances are comparable to those found in complex 2g, whereas the Cu-N distance is markedly shortened in complex 2h (2.31 Å) compared with 2g (2.56 Å), and indeed, 2f (2.50 Å). This indicates that the ability of the pyridyl moiety to act as a σ donor is significantly enhanced as a result of the para-methoxy group, leading to a much stronger interaction between the pyridyl nitrogen atom and copper(I) centre. Surprisingly, the extended structure of 2g does not show any interaction between the copper(I) centre and an alkene, with the closest approach occurring at a distance of 4.09 Å. The short Cu-N distance is likely to destabilise the filled frontier orbital at the copper(I) centre, thus, stabilisation of copper(I)-alkene

coordination through increased copper(I)—ethylene π backbonding would be expected. The absence of alkene coordination in this complex indicates that components other than charge transfer may be playing a role, with polarisation and frozen-density terms becoming less favourable with increased electron density on the metal centre.

To examine the effect of an extra NHC donor on copper(I) coordination, a symmetrical bis-NHC analogue of **1f** was synthesised (**1i**). Complexation of **1i** to a copper(I) centre was at-

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tempted using the procedure described for the synthesis of 1 f', instead of the procedure involving the silver(I)-NHC complex because bis-imidazolium salts are known to require more forcing conditions when reacting with Ag₂O.^[40] The solubility of the product was reasonably poor, although ¹H and ¹³C¹H NMR spectra with good signal-to-noise ratios could be obtained at elevated temperatures (333.6 K) with a large number of scans. The ¹H NMR spectrum illustrates the presence of only one ligand environment and also the loss of the imidazolium proton. Unlike the spectra for complexes 2 f-2h, the spectrum of the product is sharp, perhaps indicating that this complex is less labile than complexes 2 f-2h. The ¹³C{¹H} NMR spectrum shows a characteristic low-field resonance at $\delta = 181.9 \text{ ppm}$ (126 MHz, CD₃CN, 333.6 K), indicating the formation of a copper(I)-NHC complex. The high-resolution mass spectrum was dominated by a peak at m/z 354.08, which was found to correspond to a $[Cu_2L_2]^{2+}$ fragment. Single crystals suitable for X-ray diffraction analysis were obtained by cooling a saturated solution of the product from 333 K to ambient temperature in anhydrous acetonitrile. The solid-state structure shows a formulation of [Cu₃(NHC)₂Br₃] for **2i** (Figure 13).

Complex 2i was found to crystallise as a ligand-supported cuprophilic trimer. Cuprophilic trimers that have similarities to 2i have been described previously in the literature,^[41] although many of these occur as C_3 -symmetric triangular copper(I) clusters.^[42–44] The geometries (excluding possible cuprophilic interactions) about all three of the copper(I) centres are best described as distorted linear, with bond angles of 171.0°, 164.6° and 156.9°. The Cu-C and Cu-Br bond lengths, in complex 2i, are within typical ranges for copper(I)-NHC complexes. The distances between the three copper(I) centres are 2.87 Å and 2.78 Å, and thus, possibly represent weak cuprophilic interactions. It is notable that pyridyl coordination does not occur; the closest copper(I)pyridyl interaction occurs between Cu(3) and N(8) at a distance of 2.64 Å. This lack of coordination presumably results from the conformational restriction imposed by the ligand on the positions of the copper(I) centres (i.e. away from the



Figure 13. Molecular structure of **2i** (left) and **2i'** (right). Ellipsoids are shown at 50% probability level. Hydrogen atoms and bromide anions in **2i'** have been omitted for clarity.

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pyridyl nitrogen atoms), but may also result from the withdrawal of electron density from the pyridyl nitrogen atoms by the NHC rings, making the pyridyl rings poorer donors. Twisting of the NHC rings, with respect to the pyridyl rings, occurs to varying degrees (torsion angles between 10.3° and 31.8°); this twisting acts to decrease π -overlap between the NHC and pyridyl rings. Possibly as a result of the lack of coordination of the pyridyl rings to the copper(I) centre in **2i**, no alkene coordination is observed; it appears that all three copper(I) centres are coordinatively saturated in complex **2i**.

An explanation for the dominant ion in the high-resolution mass spectrum being a [Cu₂L₂]²⁺ fragment, and an explanation for the highly symmetric NMR data, was found by serendipitous crystallisation. Complex 2i' crystallised during the slow evaporation of a sample of 2i exposed to air and moisture (Figure 13). It is evident that exposure of samples of 2i to air and moisture results in the formation of helicate 2i'. The highly symmetric NMR data indicates that helicate 2i' is the dominant species in the NMR solvent (with concomitant release of CuBr from 2i). Elemental analytical data is indicative of a 3:1 mixture of 2i/2i' in the final product. The stability of 2i' is a somewhat surprising result, especially given the tendency of copper(I)-NHC complexes bearing non-bulky N-substituents (i.e. allyl) to decompose, reforming imidazolium salts and unidentifiable copper(II)containing detritus. The formation of a copper(I)-NHC complex over any other species suggests that the 16-membered metallacycle contained within 2i' is highly stable, even after prolonged exposure to air and moisture. The remarkable stability of 2i' makes it an interesting candidate for use in catalysis.

Conclusion

A series of copper(I)-NHC complexes with N-allyl substituents and varying steric and electronic properties have been described. The complexes exhibit a range of fascinating structures; copper(I)-alkene coordination in the solid state being observed in one of the complexes (complex 2 f). There are two possible explanations for this observation: 1) The co-planar pyridyl group withdraws electron density from the carbonic carbon atom, thus reducing electron density on the copper(I) centre and increasing polarisation effects between the metal and the alkene. 2) The co-planar structure naturally enforces the pyridyl-N atom towards the copper(I) centre to form a dative bond. This dative bond, although weak, increases the electron density of the copper(I) centre, thus increasing the affinity of the copper(I) centre for the alkene through its enhanced metal(d)-to-alkene(π^*) back-bonding ability.

The addition of a nitro group to the pyridyl substituent significantly increases the pyridyl Cu–N bond length in complex 2g (compared with 2f). This increase in bond length switches off the interaction between the copper(I) centre and the alkene, suggesting that metal(d)-to-alkene(π^*)

back-bonding is the dominant effect in these complexes, and that increasing the electron density of the metal centre serves to stabilise copper(I)-alkene coordination. However, increasing the electron density of the metal centre even further, through the addition of a methoxy group to the pyridyl moiety (complex **2h**), does not result in a copper(I)-alkene interaction. This observation is interesting considering the relatively short Cu–N bond. This indicates that effects other than charge transfer cannot be ruled out, and that low favourable polarisation and repulsive frozen-density terms have come into effect.

The coordination of pyridyl, NHC and alkene moieties of one ligand to the same copper(I) centre would result in high angular strain, hence the metal centre instead bonds to a nearby alkene to form a 1D coordination polymer. Complex 2f is an extremely interesting candidate for catalytic processes, in which binding of alkenes to the copper(I) centre is proposed. Furthermore, applications such as separation chemistry, gas purification or sensing, which all rely on the reversible nature of a copper(I)-alkene interaction (or a copper(I)-carbonyl interaction), could make use of this ligand system. These binding interactions are clearly more complex than simply increasing the basicity of the ligand to stabilise alkene coordination, with both chargetransfer and non-charge-transfer components requiring consideration. This is in agreement with recent studies of York et al. on copper(I)-alkene binding using DFT calculations.[14]

Experimental Section

General: Where stated, manipulations were performed under an atmosphere of dry argon by means of standard Schlenk line or glovebox techniques. The gas was dried by it passing through a twin-column drying apparatus containing molecular sieves (4 Å) and P_2O_5 . Anhydrous solvents were prepared by passing the solvent over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water by using the Dow–Grubbs solvent system. Deuterated chloroform, acetonitrile and DMSO were dried over CaH_2 , cannula filtered or distilled, and then degassed using freeze-pump-thaw cycles prior to use. All other reagents and solvents were used as supplied.

¹H and ¹³C¹H NMR spectra were recorded on either a Bruker DPX300 or a Bruker AV500 spectrometer. The values of chemical shifts are given in ppm and values for coupling constants (J) in Hz. Assignment of some ¹H NMR spectra was aided by the use of 2D ¹H-¹H COSY experiments and the assignment of some ¹³C{¹H} NMR spectra was aided by ¹³C{¹H} dept 135 experiments. Mass spectra were collected on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. Microanalyses were performed using a Carlo Erba Elemental Analyser MOD 1106 spectrometer. X-ray diffraction data were collected on either a Bruker Nonius X8 diffractometer fitted with an Apex II detector with Mo-K_{α} radiation ($\lambda = 0.71073$ Å), or an Agilent SuperNova diffractometer fitted with an Atlas CCD detector with Mo-K_{α} radiation ($\lambda = 0.71073$ Å). Crystals were mounted under oil on glass or nylon fibres. Data sets were corrected for absorption using a multiscan method, and the structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F2 using SHELXL-97, interfaced through the program X-Seed. Molecular graphics for all structures were generated using POV-RAY in the X-Seed program.

1,3-Diallylbenzimidazol-2-ylidene copper(I) bromide (2a): A Schlenk flask was charged with 1,3-diallylbenzimidazolium bromide (0.42 g,

1.5 mmol), Cu₂O (0.43 g, 3.0 mmol) and 4 Å molecular sieves. The contents of the flask were dried and degassed thoroughly in vacuo. Anhydrous dichloromethane (30 mL) was added through a cannula and the mixture was stirred at reflux for 24 h. After this time, the mixture was allowed to cool and was filtered under inert conditions. The solvent was removed from the filtrate in vacuo to give the product as a white solid. Yield: 0.30 g, 0.88 mmol, 59%. Single crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of the product in chloroform. ¹H NMR (500 MHz, CDCl₃): $\delta = 7.46$ -7.42 (m, 2H, bimH), 7.41-7.36 (m, 2H, bimH), 6.04 (ddt, J=17.0, 10.3, 5.7 Hz, 2 H, CH=CH₂), 5.36 (dd, J=10.3, 0.8 Hz, 2 H, HC=CHH_(cis)), 5.29 (dd, J=17.0, 0.8 Hz, 2 H, HC=CHH_{(trans}), 5.06 ppm (d, J=5.7 Hz, 4 H, NCH₂); ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃): $\delta = 186.1$, 133.8, 131.9, 124.1, 119.5, 111.82, 51.5 ppm; HRMS (ESI+): m/z calcd for $[M-Br]^+$: 261.0448; found: 261.0440; elemental analysis calcd (%) for C13H14BrCuN2: C 45.69, H 4.13, N 8.20; found: C 45.40, H 4.30, N 7.90.

1-Allyl-3-methylimidazol-2-ylidene copper(I) bromide (2b): A Schlenk flask was charged with 1-allyl-3-methylimidazolium bromide (0.60 g, 3.0 mmol), Cu₂O (0.85 g, 5.9 mmol) and 4 Å molecular sieves. The contents of the flask were dried and degassed thoroughly in vacuo. Anhydrous dichloromethane (40 mL) was added through a cannula and the mixture was stirred at reflux for 80 h. After this time, the mixture was allowed to cool and was filtered under inert conditions. The solvent was removed from the filtrate in vacuo to give the product as a white solid. Yield: 0.39 g, 1.5 mmol, 50%. Single crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of the product in dichloromethane. ¹H NMR (300 MHz, CDCl₃): $\delta =$ 6.91 (s. 1H, imH), 6.91 (s. 1H, imH), 5.94 (ddt, J=16.3, 10.2, 6.0 Hz, 1H, CH=CH₂), 5.36-5.20 (m, 2H, HC=CH₂), 4.72 (d, J=6.0 Hz, 2H, NCH₂), 3.83 ppm (s, 3H, CH₃); ${}^{13}C{}^{1}H$ NMR (75 MHz, CDCl₃): $\delta = 178.1$, 132.6, 122.0, 120.7, 119.8, 53.8, 38.4 ppm; HRMS (ESI+): m/z calcd for $[M-Br]^+$: 185.0135; found: 185.0145; elemental analysis calcd (%) for C₇H₁₀BrCuN₂: C 31.65, H 3.79, N 10.55; found: C 31.30, H 3.80, N 10.10.

1,3-Diallylimidazol-2-ylidene copper(I) bromide (2c): A Schlenk flask was charged with 1,3-allylimidazolium bromide (0.54 g, 2.4 mmol), Cu₂O (0.67 g, 4.7 mmol) and 4 Å molecular sieves. The contents of the flask were dried and degassed thoroughly in vacuo. Anhydrous dichloromethane (35 mL) was added through a cannula and the mixture was stirred at reflux for 24 h. After this time, the mixture was allowed to cool and was filtered under inert conditions. The solvent was removed from the filtrate in vacuo to give the product as a pale yellow oil. Yield: 0.35 g, 1.2 mmol, 51 %. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.93$ (s, 2H, imH), 5.95 (ddt, J = 16.6, 10.2, 6.0 Hz, 2H, $CH=CH_2$), 5.31 (dd, J = 10.2, 0.9 Hz, 2H, $HC=CHH_{(cas)}$), 5.26 (dd, J = 16.6, 0.9 Hz, 2H, $HC=CHH_{(cras)}$), 4.73 ppm (d, J = 6.0 Hz, 4H, NCH₂); ¹³C[¹H] NMR (75 MHz, CDCl₃): $\delta = 177.8, 132.6, 120.8, 120.0, 54.0$ ppm; HRMS (ESI +): m/z calcd for $[M-Br]^+$: 211.0291; found: 211.0280; elemental analysis calcd (%) for C₉H₁₂BrCuN₂: C 37.35, H 4.20, N 9.70; found: C 37.06, H 4.15, N 9.61.

1-Allyl-3-mesitylimidazol-2-ylidene copper(I) bromide (2d): A Schlenk flask was charged with 1-allyl-3-mesitylimidazolium bromide (0.32 g, 1.0 mmol), Cu₂O (0.30 g, 2.1 mmol) and 4 Å molecular sieves. The contents of the flask were dried and degassed thoroughly in vacuo. Anhydrous dichloromethane (20 mL) was added through a cannula and the mixture was stirred at reflux for 60 h. After this time, the mixture was allowed to cool and was filtered under inert conditions. The solvent was removed from the filtrate in vacuo to give the product as a clear oil, which slowly crystallised on standing. Yield: 0.24 g, 0.64 mmol, 62%. Single crystals suitable for X-ray diffraction analysis were grown by the vapour diffusion of pentane in to a concentrated solution of the product in dichloromethane. The X-ray crystal structure showed a complex of the type [Cu(NHC)₂Br]. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.10$ (d, J = 1.7 Hz, 1H, imH), 6.95 (s, 2H, ArH), 6.87 (d, J=1.7 Hz, 1H, imH), 6.03 (ddt, J= 15.8, 10.2, 5.8 Hz, 1 H, CH=CH₂), 5.35 (dd, J=10.2, 0.7 Hz, 1 H, HC= CHH_(cis)), 5.26 (d, J=15.8 Hz, 1H, HC=CHH_{(trans})), 4.85 (d, J=5.8 Hz, 2H, NCH₂), 2.31 (s, 3H, *p*-CH₃), 2.00 ppm (s, 6H, *o*-CH₃); ¹³C{¹H} NMR $(75 \text{ MHz}, \text{CDCl}_3)$: $\delta = 179.0, 139.5, 135.2, 134.7, 132.7, 129.5, 122.5, 120.7,$ 119.7, 53.9, 21.2, 17.9 ppm; HRMS (ESI+): m/z calcd for [M-Br+ MeCN]⁺: 330.1026; found: 330.1024; elemental analysis calcd (%) for $C_{15}H_{18}BrCuN_{2}.^{2}\!/_{3}CH_{2}Cl_{2}{:}$ C 44.13, H 4.57, N 6.57; found: C 44.60, H 5.00, N 6.10.

1-Allyl-3-(2-methoxybenzene)imidazol-2-ylidene copper(I) bromide (2e): A Schlenk flask was charged with 1-allyl-3-(2-methoxybenzene)imidazolium bromide (0.58 g, 2.0 mmol), Cu2O (0.57 g, 4.0 mmol) and 4 Å molecular sieves. The contents of the flask were dried and degassed thoroughly in vacuo. Anhydrous dichloromethane (30 mL) was added through a cannula and the mixture was stirred at reflux for 74 h. After this time, the mixture was allowed to cool and was filtered under inert conditions. The solvent was removed from the filtrate in vacuo to give the product as a vellow oil, which slowly crystallised on standing. Yield: 0.41 g, 1.2 mmol, 58%. Single crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of the product in dichloromethane. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.51$ (dd, J=8.0, 1.4 Hz, 1H, ArH), 7.41 (td, J=8.0, 1.4 Hz, 1H, ArH), 7.18 (d, J= 1.7 Hz, 1H, imH), 7.06 (t, J=8.0 Hz, 2H, ArH), 7.01 (d, J=1.7 Hz, 1H, imH), 6.04 (ddt, J=16.5, 10.3, 6.0 Hz, 1 H, CH=CH₂), 5.42–5.30 (m, 2 H, HC=C H_2), 4.85 (d, J = 6.0 Hz, 2H, NC H_2), 3.85 ppm (s, 3H, OC H_3); ¹³C{¹H} NMR (75 MHz, CDCl₃): $\delta = 178.6$, 153.1, 132.5, 130.4, 128.4, 127.5, 123.4, 121.2, 120.0, 119.8, 112.5, 56.0, 54.2 ppm; HRMS (ESI+): m/z calcd for $[M-Br]^+$: 277.0397; found: 277.0360; elemental analysis calcd (%) for C13H14BrCuN2O: C 43.65, H 3.94, N 7.83; found: C 44.00, H 4.40, N 7.35.

1-Allyl-3-(2-pyridyl)imidazol-2-ylidene copper(I) bromide (2 f): 1-Allyl-3-(2-pyridyl)imidazolium bromide (0.23 g, 0.85 mmol) and Ag_2O (0.13 g, 0.55 mmol) were added to a Schlenk flask along with 4 Å molecular sieves. Anhydrous dichloromethane (30 mL) was added and the dark suspension was stirred overnight in the absence of light. After this time, the dark suspension was filtered and the solvent removed in vacuo to yield Ag-2 f as a white oily solid, which was used without further purification. In a glovebox, Ag-2f was dissolved in dichloromethane (35 mL). With stirring, solid CuBr was added (0.13 g, 0.93 mmol). Immediately, the solution began to turn yellow with the concomitant formation of a pale yellow precipitate (AgBr). The suspension was stirred for 2 h and then filtered to remove the insoluble AgBr/CuBr. The solid was washed with dichloromethane until the filtrate ran clear. The solvent was removed from the filtrate in vacuo to yield the product as a yellow crystalline powder. Yield: 0.20 g, 0.62 mmol, 73 %. Single crystals suitable for X-ray diffraction analysis were grown on standing of a dilute solution of the product in dichloromethane/pentane (1:2). ¹H NMR (300 MHz, CDCl₃): $\delta = 8.55$ (br s, 1 H), 8.08 (br s, 1 H), 7.91 (t, J = 7.7 Hz, 1 H), 7.80 (br s, 1H), 7.37 (br s, 1H), 7.10 (br s, 1H), 6.12-5.94 (m, 1H, CH=CH₂), 5.39 (d, J = 10.0 Hz, 1H, CH=CH $H_{(cis)}$), 5.36 (d, J = 17.0 Hz, 1H, CH= CHH_(trans)), 4.88 ppm (br s, 2H, NCH₂), definite assignment of the aromatic resonances to either pyridyl or backbone imidazolylidene protons is hampered because of spectral broadening; HRMS (ESI+): m/z calcd for [M-Br+MeCN]⁺: 289.0509; found: 289.0517; elemental analysis calcd (%) for C₁₁H₁₁BrCuN₃: C 40.20, H 3.37, N 12.78; found: C 39.90, H 3.30, N 12.50.

1-Allyl-3-(2-(5-nitro)pyridyl)imidazol-2-ylidene copper(I) bromide (2g): 1-Allyl-3-(2-(5-nitropyridyl)imidazolium bromide (0.31 g, 1.0 mmol) and Ag₂O (0.19 g, 0.82 mmol) were added to a Schlenk flask along with 4 Å molecular sieves. Anhydrous dichloromethane (30 mL) was added and the mixture was stirred in the absence of light at ambient temperature for 72 h. After this time, the mixture was filtered through Celite and the solid washed with copious dichloromethane. The combined filtrate was collected and reduced in volume to 30 mL. Addition of diethyl ether (100 mL) led to the precipitation of the Ag-NHC complex as white needles. The Ag-NHC complex (0.082 g, 0.20 mmol) and CuBr (0.056 g, 0.39 mmol) were added to a Schlenk flask in a glovebox. Anhydrous dichloromethane (25 mL) was added and the resulting suspension was stirred at ambient temperature in the absence of light for 3.5 h. After this time, the suspension was filtered to remove AgBr/CuBr and the pale orange filtrate collected. Anhydrous pentane (40 mL) was added to the stirring filtrate and a crystalline red solid formed, collected by filtration and dried in vacuo. Yield: 0.046 g, 0.12 mmol, 63 %. Single crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated acetonitrile solution of the product. ¹H NMR (300 MHz,

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CDCl₃): δ = 9.38 (br s, 1 H, pyH), 8.72 (dd, *J* = 8.8, 2.6 Hz, 1 H, pyH), 8.59 (br d, *J* = 8.8 Hz, 1 H, pyH), 7.97 (br s, 1 H, imH), 7.16 (br s, 1 H, imH), 6.05 (ddt, *J* = 16.3, 10.2, 6.1 Hz, 1 H, CH=CH₂), 5.50–5.38 (m, 2 H, CH=CH₂), 4.92 ppm (d, *J* = 6.1 Hz, 2 H, NCH₂); ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 145.2, 135.1, 131.5, 121.4, 119.8, 114.4, 55.4 ppm (some of the ¹³C resonances are not observed due to broadening); HRMS (ESI+): *m*/*z* calcd for [*M*-Br+MeCN]⁺: 334.0360; found: 334.0371; elemental analysis calcd (%) for C₁₁H₁₀BrCuN₄O₂: C 35.36, H 2.70, N 14.99; found: C 35.45, H 2.65, N 14.75.

1-Allyl-3-(2-(4-methoxy)pyridyl)imidazol-2-ylidene copper(I) bromide (2h): 1-Allyl-3-(2-(4-methoxy)imidazolium bromide (0.16 g, 0.54 mmol) and Ag₂O (0.081 g, 0.35 mmol) were added to a Schlenk flask along with freshly-activated 4 Å molecular sieves. Anhydrous dichloromethane (25 mL) was added, and the mixture was stirred in the absence of light at room temperature for 2.5 h. After this time, the mixture was filtered through Celite and the solvent removed in vacuo to yield the crude product as an off-white oily solid. Recrystallisation from acetone/pentane gave Ag-2h as a white solid. Yield=0.17 g, 0.43 mmol, 80%. Ag-2h (0.15 g, 0.37 mmol) and CuBr (0.059 g, 0.41 mmol) were added to a small Schlenk flask in a glovebox. Anhydrous dichloromethane (25 mL) was added and the suspension formed was stirred at room temperature in the absence of light for 16 h. After this time, the suspension was filtered to remove AgBr/CuBr and the yellow filtrate collected. The solvent was removed in vacuo to give the product as a yellow crystalline solid. Yield: 0.11 g, 0.31 mmol, 84 %. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.31$ (br s, 1 H), 7.82 (br s, 1 H), 7.78 (br s, 1 H), 7.07 (br s, 1 H), 6.88 (br s, 1 H), 6.14–5.94 (m, 1H, CH=CH₂), 5.45-5.32 (m, 2H, CH=CH₂), 4.86 (br s, 2H, NCH₂), 4.02 ppm (s, 2H, OCH₃); HRMS (ESI⁺): m/z calcd (%) for [M-Br+MeCN]+: 319.0615; found: 319.0615.

2,6-Bis(3-allylimidazol-2-ylidene)pyridyl copper(I) bromide (2i): An ampoule was charged with 1,1'-(2,6-pyridyl)-bis(3-allylimidazolium) bromide (0.15 g, 0.33 mmol), CuBr (0.10 g, 0.66 mmol) and Cs₂CO₃ (1.1 g, 0.10 g)3.3 mmol). The contents of the ampoule were dried and degassed thoroughly in vacuo. Anhydrous acetonitrile (15 mL) was added and the suspension was heated at 50 °C for 1.5 h. After this time, the mixture was allowed to cool to ambient temperature, filtered and the solvent removed in vacuo to give the crude product as a yellow solid. The product was recrystallised from acetonitrile/diethyl ether. Yield: 0.10 g, 0.10 mmol, 60%. Single crystals of 2i suitable for X-ray diffraction analysis were grown by cooling a saturated solution of the product from 333 K to ambient temperature in anhydrous acetonitrile ([Cu₃Br₂L₂]Br·MeCN). Single crystals of 2i' suitable for X-ray diffraction analysis were grown by the slow evaporation of a concentrated solution of the product in wet acetonitrile ([Cu₂L₂]2Br·2H₂O). ¹H NMR (500 MHz, CD₃CN, 333.6 K): $\delta =$ 8.28 (t, J=8.0 Hz, 2 H, pyH), 7.81 (d, J=2.0 Hz, 4 H, imH), 7.73 (d, J= 8.0 Hz, 4H, pyH), 7.23 (d, J=2.0 Hz, 4H, imH), 5.72-5.61 (m, 4H, CH= CH₂), 5.02 (d, J = 10.3 Hz, 4H, HC=CH $H_{(cis)}$), 4.93 (d, J = 16.5 Hz, 4H, HC=CH $H_{(trans)}$), 4.40 ppm (d, J=4.5 Hz, 8H, NCH₂); ¹³C{¹H} NMR $(126 \text{ MHz}, \text{ CD}_3\text{CN}, 333.6 \text{ K}): \delta = 181.9, 150.6, 145.1, 134.0, 124.5, 120.0,$ 119.9, 114.7, 55.4 ppm; HRMS (ESI+): *m*/*z* calcd for [Cu₂L₂]²⁺: 354.0774; found: 354.0787; elemental analysis calcd (%) for $C_{136}H_{136}Br_{11}Cu_{11}N_{40}$ (3:1 2i/2i'): C 41.79, H 3.51, N 14.33; found: C 41.60, H 3.45, N 13.85.

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