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Synthesis of Copper(I) Complexes of N-Heterocyclic Carbene–Phenoxyimine/amine Ligands: Structures of Mononuclear Copper(II), Mixed-Valence Copper(I)/(II), and Copper(II) Cluster Complexes

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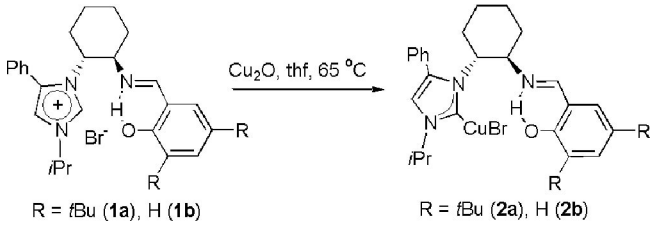
Copper(I) bromide complexes (**2a** and **2b**) of NHC–phenol-imine ligand precursors {3-[(1*R*,2*R*)-2-{[1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)meth-(*E*)-ylidene]amino}cyclohexyl]-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1a**) and 3-[(1*R*,2*R*)-2-{[1-(2-hydroxyphenyl)meth-(*E*)-ylidene]amino}-cyclohexyl]-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1b**), respectively} have been prepared. Complexes **2a** and **2b** exhibit copper coordination only through the carbene carbon atom (*C*) and do not spontaneously eliminate HBr to give additional phenoxyimine (*NO*) bonds, which is attributed to intramolecular hydrogen bonding. Crystallisation of **2a** and **2b** gives **2a′** and **2b′**, respectively, that contain (*C*) copper(I) bromide and $(NO)_2$ copper(II) coordination. Complex **2b′** also exhibits intermolecular Cu^IBr interactions giving a Cu_2Br_2 bridge that links two molecules of **2b′** resulting in an ellipse motif. Reduction of the ligand precursor imine group of **1a** allows synthesis of silver(I) and copper(I) NHC–phenolamine complexes **6** and **7**, respectively, that also retain the phenol hydrogen atom. Attempts to selectively prepare **2a′** gave a copper(II) complex **9** that exhibits an $(NO)_2Cu^{II}$ structure with pendant imidazolium salt groups. Reaction between the silver(I) bromide derivative of **1a** and $CuCl_2{\cdot}2H_2O$ gives a complex derived from a $Cu_6(O)(OH)_4Cl_3$ core and two (*NO*) and one (*CNO*) ligands, respectively. The use of **2a** and **7** as precatalysts for 1,4-conjugate addition to enones and aziridination of alkenes was studied, showing that, whilst both catalysts are active, enantioselectivities are low, which is attributed to the lack of Cu-(*NO*) coordination.

Introduction

The coordination chemistry of N-heterocyclic carbenes (NHCs) of group-11 metals has developed significantly since the isolation[1] and first complexation[2] studies of stable NHCs by Arduengo in the early 1990s. Over subsequent years the synthesis and study of copper, silver and gold NHC complexes has resulted in useful applications, particularly in catalysis. Silver NHC complexes have been of particular interest because of their wide use as ligand-transfer agents[3] to transition metals principally from groups 8–10 and also their biological activity as antimicrobial agents.[4] Copper NHC complexes have now been shown to act as precatalysts for a range of reactions,[5] including conjugate addition,[6] alkylation/arylation,[7] reduction,[8] cycloaddition,[9] carbonylation,[10] hydrosilylation,[11] and more recently boration,[12] aziridination[13] and hydroamination/hydrothiolation.[14] Since 2003 the catalytic application[15] of gold NHC complexes has also come to the fore, encompassing isomerisations,[16] carbene transfer and insertion,[17] cross coupling,[18] hydrofluorination[19] -alkoxylation[20] and -amination[21] reactions and ring-opening polymerisation.[22]

Herein, we describe the synthesis, structures and catalytic studies of copper complexes of a chiral NHC precursor based on an imidazol–phenoxyimine motif (Scheme 1) that we envisaged could have potential application to enantioselective catalysis. Palladium, rhodium and dimetallic iron/silver complexes of **1a** have been reported previously[23] showing tridentate NHC (*C*), imine (*N*), phenoxide (*O*) (*CNO*), NHC only (Rh*C*), or bridging (Ag*C*, Fe*NO*) coordination, respectively. We were also motivated by several



Scheme 1. Synthesis of Cu^I NHC complexes derived from **1a** and **1b**.

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reports describing the catalytic applications of copper NHC complexes, particularly those that incorporate additional oxygen (alkoxide and aryl oxide) coordinating groups in the ligand structure.[6b,7a,7b,7e,7i,24] In addition, there are also many examples of copper(II) complexes of phenoxyimine (Schiff base) ligands principally of the tetradentate $[N_2O_2]^{2-}$ salen type, used as catalysts[25] in a number of enantioselective reactions including alkylation/arylation,[26] cyclopropanation,[27] and aziridination.[28]

Results and Discussion

Initial work focused on the synthesis of copper complexes derived from the imidazolium–phenolimine precursors **1a** and **1b**. Using an analogous route that is commonly used to prepare silver(I) NHC complexes,[3] reaction between **1a** or **1b** and Cu_2O (Scheme 1) gave the complexes **2a** and **2b** in > 90% yield as light green and deep red solids, respectively. The reaction solvent was found to be important, because dichloromethane gave intractable products, in contrast to the excellent yields obtained in tetrahydrofuran.

NMR spectroscopy shows signals consistent with the proposed formulation including one at $\delta \approx 13$ ppm for the phenol O*H* atom and one at $\delta \approx 175$ ppm for the carbene carbon atom in the ^1H and ^{13}C NMR spectra, respectively. The phenol O*H* chemical shift of $\delta \approx 13$ ppm is indicative of hydrogen bonding attributable to an imine–phenol tautomer rather than amine–enone.[29] A similar structural motif has also been observed in reported silver– and rhodium–NHC complexes, where the latter was structurally characterised.[23] The complexes **2a** and **2b** are air-sensitive, giving paramagnetic species as judged by very broad NMR signals on exposure to air. Mass spectrometry showed predominantly copper-containing signals with a copper/ligand ratio of 1:2 that is also commonly observed in NHC–silver(I) halide complexes due to solution or gas-phase/ligand redistribution.

Attempts to grow single crystals of **2a** and **2b** did not give the anticipated molecular structures. Single crystals were grown over a period of two weeks from acetonitrile for **2a** and a mixture of tetrahydrofuran and diethyl ether for **2b**. Approximately 50% by mass of **2a** and **2b** were isolated as dark green and red crystals of **2a′** and **2b′**, respectively. The molecular structures are shown in Figures 1 and 2, and selected geometrical data are given in Tables 1 and 2.

Both structures possess the same 3:2 metal/ligand stoichiometry and exhibit similar structural motifs containing copper(I) NHC bromide and copper(II) phenoxyimine coordination. Presumably, the source of copper(II) ions is from partial decomposition of the parent complexes, although the mechanism is unclear. The structures differ principally in the Cu_2Br_2 interactions observed for **2b′** that support dimerisation of $Cu^I_2Cu^{II}L_2$ units, that are observed for **2a′**. Structure **2a′** exhibits the expected linear coordination of Cu^I atoms, whereas for **2b′** a Cu_2Br_2 parallelogram motif is observed. The Cu–Br bond lengths of **2b′** divide into two

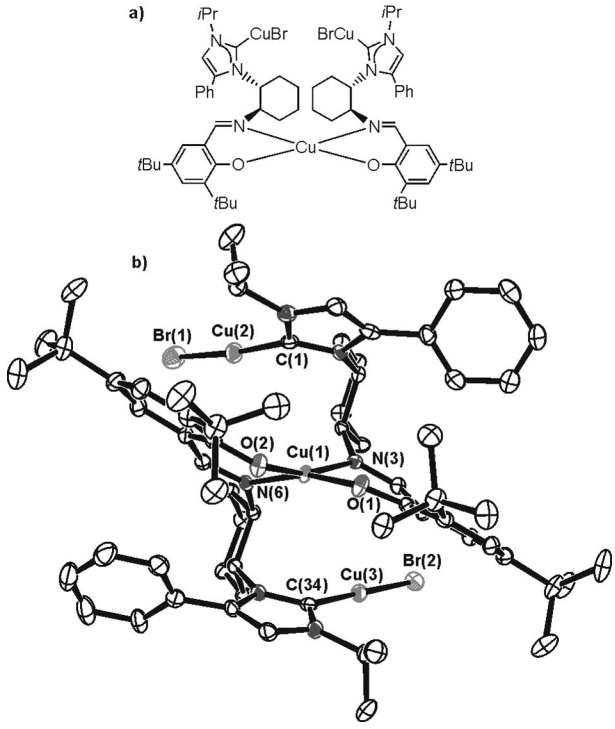


Figure 1. (a) Line drawing of **2a′**. (b) Molecular structure of **2a′**. Hydrogen atoms have been removed for clarity. Displacement ellipsoids at 50% probability level.

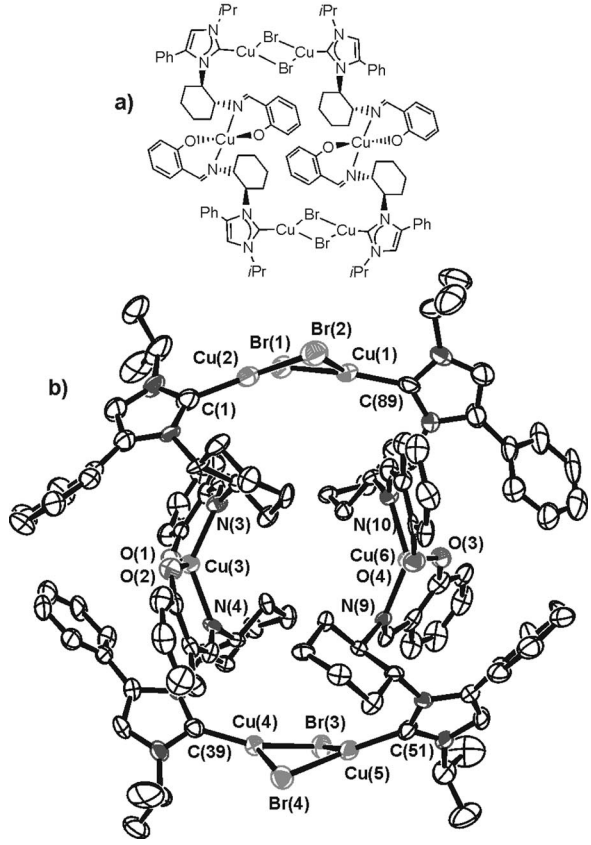


Figure 2. (a) Line drawing of **2b′**. (b) The molecular structure of **2b′**. Hydrogen atoms have been removed for clarity. Displacement ellipsoids at 50% probability level.

Table 1. Selected distances [Å] and angles [°] for complex **2a′**.

Cu(1)–N(3)	1.961(3)	Cu(1)–N(6)	1.987(3)
Cu(1)–O(1)	1.900(3)	Cu(1)–O(2)	1.897(3)
Cu(2)–Br(1)	2.2268(7)	Cu(2)–C(1)	1.917(4)
Cu(3)–Br(2)	2.2344(6)	Cu(3)–C(34)	1.897(4)
N(3)–Cu(1)–N(6)	96.08(13)	O(1)–Cu(1)–O(2)	86.60(11)
Br(1)–Cu(2)–C(1)	173.61(12)	Br(2)–Cu(3)–C(34)	178.63(12)
$O(1)–Cu(1)–N(3)_{plane}$ ∠ $O(2)–Cu(1)–N(6)_{plane}$			22.4(8)

Table 2. Selected distances [Å] and angles [°] for complexes **2b′**.

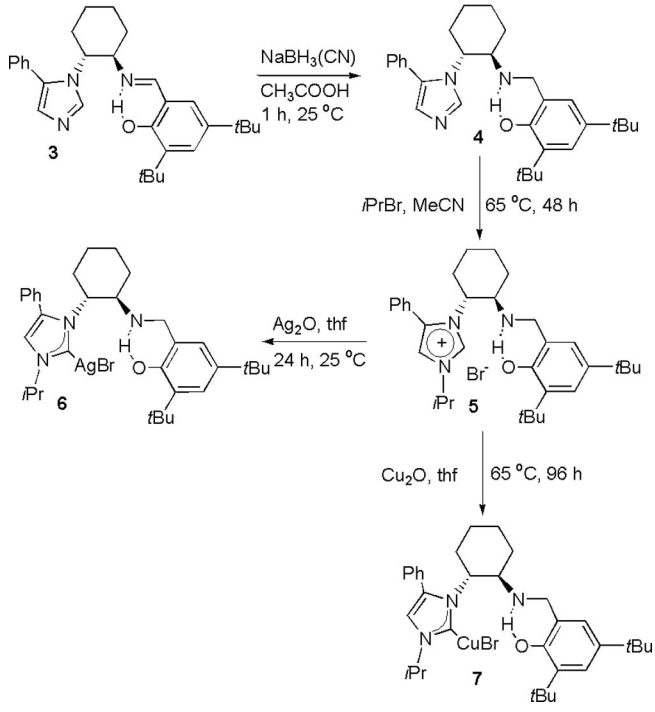
Cu(1)–Br(1)	2.3303(17)	Cu(1)–Br(2)	2.6194(17)
Cu(1)–C(89)	1.922(10)	Cu(2)–Br(1)	2.7093(18)
Cu(2)–Br(2)	2.327(2)	Cu(2)–C(1)	1.931(11)
Cu(4)–Br(3)	2.3561(15)	Cu(4)–Br(4)	2.6100(15)
Cu(4)–C(39)	1.931(9)	Cu(5)–Br(3)	2.5736(14)
Cu(5)–Br(4)	2.3589(15)	Cu(5)–C(51)	1.910(9)
Cu(3)–N(3)	2.002(7)	Cu(3)–N(4)	1.995(7)
Cu(3)–O(1)	1.879(5)	Cu(3)–O(2)	1.880(5)
Cu(6)–N(9)	1.990(7)	Cu(6)–N(10)	1.988(7)
Cu(6)–O(3)	1.894(6)	Cu(6)–O(4)	1.908(6)
Br(1)–Cu(1)–C(89)	147.4(3)	Br(2)–Cu(2)–C(1)	150.8(3)
Br(3)–Cu(4)–C(39)	147.1(3)	Br(4)–Cu(5)–C(51)	144.4(3)
N(3)–Cu(3)–N(4)	135.1(3)	O(1)–Cu(3)–O(2)	145.1(3)
N(9)–Cu(6)–N(10)	139.3(3)	O(3)–Cu(6)–O(4)	143.1(3)
$N(3)–Cu(3)–O(1)_{plane}$ ∠ $N(4)–Cu(3)–O(2)_{plane}$			55.8(7)
$N(9)–Cu(6)–O(3)_{plane}$ ∠ $N(10)–Cu(6)–O(4)_{plane}$			53.6(7)

distinct ranges identifying "intra-" and "inter"-molecular Cu–Br bonding, which is also observed in NHC silver(I) halide complexes that commonly contain $(NHC)_2Ag_2X_2$ units. However, in copper NHC chemistry only one example of an $(NHC)_2Cu_2X_2$ (X = Cl) motif containing bridging halides[30] has been reported, although there are bridging[31] and non-bridging[32] examples containing direct Cu–Cu bonds and terminal halides.

Considering the Cu^{II} coordination of **2a′** and **2b′**, both exhibit distortion from a planar CuO_2N_2 core that is usually observed for complexes of phenoxy–imines containing small substitutents. The most notable difference between the Cu^{II} atoms is the relative disposition of the phenoxy–imine groups. Defining a zero torsion angle between phenoxy–imine planes that exhibit *trans* planar coordination the angle between the planes O(1)–Cu(1)–N(3) and O(2)–Cu(1)–N(6) is 168° for **2a′**, whereas for **2b′** the angles at Cu(3) and Cu(6) are ca. 56 and 54°, respectively. Essentially *cis* coordination of phenoxy–imine groups is observed at Cu(1) of **2a′** and distorted *trans* coordination at both copper atoms of **2b′**. For steric and electronic reasons, the vast majority of the ca. 250 structures[33] of copper phenoxy–imine complexes not constrained by N_2O_2 macrocycles exhibit *trans* coordination as seen for **2b′**. However, for **2a′** molecular models suggest that *trans* coordination would lead to significant non-covalent interactions between *t*Bu and cyclohexyl groups on opposing ligands, therefore directing *cis* coordination. A further consequence is that for **2a′** the CuBr groups are embedded in the hydrocarbyl purlieu, preventing formation of Cu_2Br_2 bonding analogous to **2b′**. The Cu–O and Cu–N bond lengths of **2a′** and **2b′** are very similar to each other and within the range of related structures, indicating there is no apparent strain at the Cu^{II} atoms.

As shown in Figure 2 the copper atoms of complex **2b′** constitute an elliptical structure where the Cu–Cu distances of the major and minor axes are 6.6 [Cu(3)–Cu(6)] and 11.8 Å [Cu(1)–Cu(4)], respectively. Although Figure 2 may suggest there is free volume at the centre of the ellipse, space-filling models show that the cyclohexyl groups fill the inner volume.

Attempts to deprotonate **2a** and **2b** by using a variety of bases (KO*t*Bu, NaH, pyridine) in tetrahydrofuran led to precipitation of green solids that were insoluble in all common organic solvents. Presumably oligomeric materials resulted, and attempts to conproportionate or spontaneously eliminate HBr from **2a** or **2b** by heating were unsuccessful. Given the observation that deprotonation of the phenol O*H* of **1a** and **1b** and resulting complexes **2a** and **2b** does not lead to the synthesis of chelating complexes, a phenol–amine derivative was investigated as shown in Scheme 2. Examination of the Cambridge Structural Database[33] indicates that a hydrogen-bonding interaction between a phenol and an adjacent secondary amine group is weaker in comparison to phenol–imines as judged by the N···O distances and the prevalence of phenol–amines that do not exhibit intramolecular hydrogen bonding. It was therefore hoped that deprotonation of the O*H* group of **5** (Scheme 2) would proceed similarly to non-hydrogen-bonded phenol and naphthol compounds that when incorporated into NHC precursors give transition metal complexes of NHC–aryl oxides.[7a,7j,34]



Scheme 2. Synthesis of NHC–phenolamine precursors and complexes **4**–**7**.

Reaction between **3** and $NaBH_3CN$ gives the imidazole–phenolamine (**4**) that provides access to the imidazolium ligand precursor **5**. Compound **5** shows ^1H and ^{13}C NMR spectra similar to those of **1a** except for the absence of imine signals and additional signals at δ = 3.84 and 53.3 ppm in the ^1H and ^{13}C NMR spectra, respectively, for the new benzylic CH_2 group. The ^1H NMR signal of the O*H* proton is a useful guide to the extent of hydrogen bonding. For compounds **1a** and **1b** a signal at $\delta \approx 13$ ppm is observed in $CDCl_3$,[23] whereas signals of phenols containing similar substituents unable to hydrogen-bond are typically at $\delta \approx 6$ ppm. Compound **5** exhibits a signal at δ = 9.40 ppm indicating that hydrogen bonding is present, and the synthesis of silver(I) (**6**) and copper(I) (**7**) derivatives (Scheme 2) shows that the OH group is retained. For example, reaction between **5** and Cu_2O in tetrahydrofuran gives **7** as a light brown solid, and ^1H NMR spectroscopy shows a signal at δ = 10.05 ppm attributable to the O*H* hydrogen atom. Analogous to **2a** and **2b**, deprotonation attempts did not lead to soluble complexes.

Given the unusual structures of **2a′** and **2b′** obtained in crystallisation attempts of **2a** and **2b**, a short study was undertaken to examine the rational synthesis of related compounds using combinations of **2a**, the analogous silver(I) NHC complex (**8**) (Figure 3)[23] and the copper(II) precursors $Cu(O_3SCF_3)_2$ and $CuCl_2{\cdot}2H_2O$. Although reactions occurred in all cases, single crystals could be grown successfully only from the reaction between **8** and the copper(II) salts $Cu(O_3SCF_3)_2$ and $CuCl_2{\cdot}2H_2O$. The molecular structures of the resulting complexes **9** and **10** are shown in Figures 3 and 4, and selected geometrical data are given in Tables 3 and 4, respectively.

Complex **9** is a pale green solid isolated in 90% yield based on copper, and elemental analysis confirms bulk purity. Complex **9** can be regarded as the imidazolium salt analogue of complex **2a′** resulting from loss of AgBr, which is immediately evident during synthesis as a cream precipitate. A plausible mechanism for the formation of **9** results from the intermediate formation of triflic acid and subsequent protonation of NHC–AgBr units to give imidazolium salt formation. Unfortunately, addition of NEt_3 to the reaction mixture did not prevent the formation of **9**. The molecular structure of **9** is similar to that of **2a′**. The torsion angle between the phenoxy–imine planes, 156° [O(1)–Cu(1)–N(3) and O(2)–Cu(1)–N(6)], is slightly smaller than for **2a′** and suggests that non-covalent interactions of the CuBr groups contribute to the observed *cis* coordination. In addition, the triflate anions do not participate in any hydrogen bonding, and there are no intermolecular interactions that are directional.

Complex **10** (Figure 4) is an intriguing structure that was isolated as dark green air-stable crystals in ca. 5% of the combined mass of starting materials. The core of the molecule contains six copper, five oxygen and three chlorine atoms, coordinated by three ligands derived from **8**. All the ligands exhibit phenoxy–imine-to-copper bonding at Cu(4), Cu(5) and Cu(6), and one also bridges to Cu(3) as an NHC. The remaining two imidazole groups are formulated as

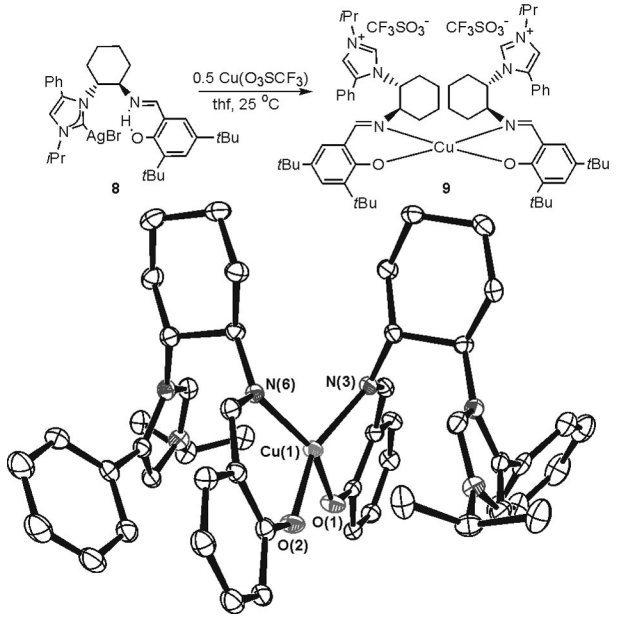


Figure 3. Synthesis and molecular structure of complex **9**. Hydrogen atoms, *t*Bu groups and anions have been removed for clarity. Displacement ellipsoids at 50% probability level.

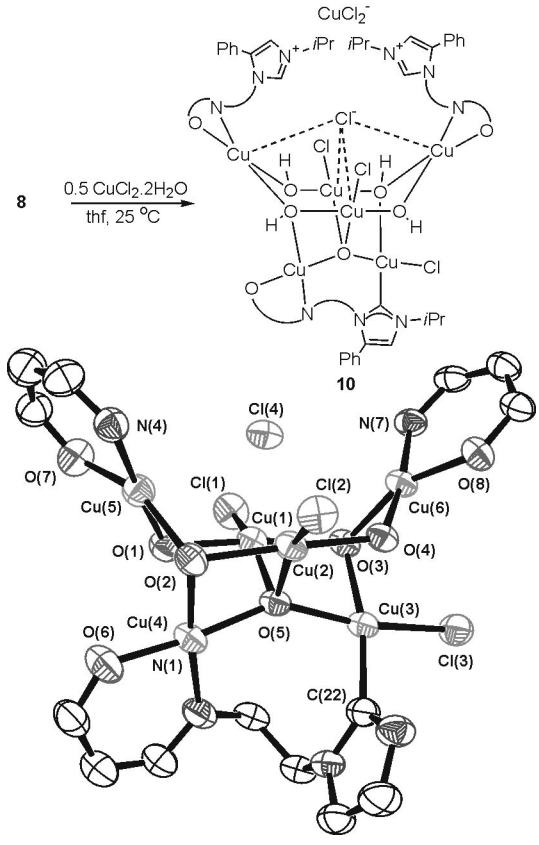


Figure 4. Synthesis and molecular structure of **10**. Hydrogen atoms, aryl, cyclohexyl, *i*Pr, *t*Bu, imidazolium groups and anions have been removed for clarity. Displacement ellipsoids at 50% probability level.

Table 3. Selected distances [Å] and angles [°] for complex **9**.

Cu(1)–N(3)	1.9676(15)	Cu(1)–N(6)	1.9733(16)
Cu(1)–O(1)	1.9036(14)	Cu(1)–O(2)	1.8977(13)
N(3)–Cu(1)–N(6)	98.28(6)	O(1)–Cu(1)–O(2)	86.36(6)
$O(1)–Cu(1)–N(3)_{plane}$ ∠ $O(2)–Cu(1)–N(6)_{plane}$			34.4(7)

Table 4. Selected distances [Å] and angles [°] for complex **10**.

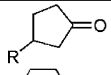
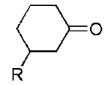
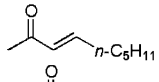
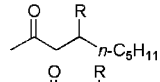
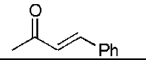
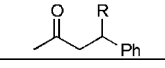
Cu(1)–O(1)	1.934(3)	Cu(1)–O(3)	1.979(3)
Cu(1)–O(5)	1.953(2)	Cu(1)–Cl(1)	2.402(12)
Cu(2)–O(2)	1.997(3)	Cu(2)–O(4)	1.938(2)
Cu(2)–O(5)	1.945(3)	Cu(2)–Cl(2)	2.2509(11)
Cu(3)–O(3)	2.043(3)	Cu(3)–O(5)	1.965(3)
Cu(3)–Cl(3)	2.2644(11)	Cu(3)–C(22)	1.967(4)
Cu(4)–O(2)	2.095(3)	Cu(4)–O(5)	1.916(2)
Cu(4)–O(6)	1.889(3)	Cu(4)–N(1)	1.970(4)
Cu(5)–O(1)	1.951(3)	Cu(5)–O(2)	2.027(3)
Cu(5)–O(7)	1.891(3)	Cu(5)–N(4)	1.986(3)
Cu(6)–O(3)	1.994(2)	Cu(6)–O(4)	1.937(2)
Cu(6)–O(8)	1.896(3)	Cu(6)–N(7)	1.958(3)
Cu(4)–O(1)	2.291(3)	Cu(3)–O(4)	2.334(2)
Cu(1)–Cl(4)	2.6976(10)	Cu(2)–Cl(4)	2.6923(10)
Cu(5)–Cl(4)	2.851(3)	Cu(6)–Cl(4)	3.103(3)
Cu(1)–Cu(2)	3.039(3)		
O(1)–Cu(1)–O(3)	166.65(11)	Cl(1)–Cu(1)–O(5)	156.08(8)
O(2)–Cu(2)–O(4)	167.91(11)	Cl(2)–Cu(2)–O(5)	158.50(8)
Cu(1)–O(5)–Cu(2)	102.489(11)	Cu(3)–O(5)–Cu(4)	144.03(13)
Cu(1)–O(1)–Cu(5)	116.49(13)	Cu(1)–O(3)–Cu(6)	119.30(12)
Cu(2)–O(2)–Cu(5)	112.85(12)	Cu(2)–O(4)–Cu(6)	122.26(13)

imidazolium cations based on the presence of water during the reaction and required charge balance (vide infra). The position of all hydrogen atoms could not be determined unambiguously from difference maps, and therefore definitive assignment of copper oxidation state(s) and the presence of oxide/hydroxide in the core is not possible on this basis. However, there are several features that strongly indicate the proposed formulation shown in Figure 4. All the copper atoms of the core exhibit pseudo-square-planar geometry typical of Cu^{II}, and clearly the oxygen atom O(5) is coordinated to four copper atoms in a pseudo-tetrahedral geometry precluding formulation as hydroxide. Considering all the core copper atoms as copper(II) and collective formal charges attributable to ligands and anions, the four oxygen atoms, O(1)–O(4), require formulation as hydroxide to balance charge. The atoms O(2) and O(3) exhibit trigonal-pyramidal geometry, whereas O(1) and O(4) show two-coordinate bent geometry, providing all with the opportunity to accommodate a hydrogen atom. Excluding the phenoxy–imine ligands, the copper–oxygen bonds range from 1.889(3) [Cu(4)–O(6)] to 2.095(3) Å [Cu(4)–O(2)], whereas the distances Cu(4)–O(1) [2.291(3) Å] and Cu(3)–O(4) [2.334(2) Å] are within the range of copper(II) complexes exhibiting a Jahn–Teller distortion.[33] Therefore, coordination at Cu(3) and Cu(6) may be better formulated as distorted square-pyramidal. Furthermore, the distances between Cu(1) and Cu(2) and the chloride "anion" Cl(4) [Cu(1)–Cl(4) 2.6976(10), Cu(2)–Cl(4) 2.6923(10) Å] also indicate Jahn–Teller-distorted Cu^{II}, where the anion Cl(4) is perhaps best described as bridging Cu(1) and Cu(2) and part of the Cu_6 core. The distance Cu(1)–Cu(2) [3.039 Å] precludes a metal–metal bond. The remaining counteranion is a linear $CuCl_2$ species that is indicative of Cu^{I} and therefore is formulated as monoanionic.

With respect to related structural motifs, there are several examples of clusters based on copper halides that contain a central oxygen atom[35] and also copper–oxygen arrays supported by ligands incorporating phenoxy–imine,[36] alkoxide,[37] oxime[38] and NHC–alkoxide.[39] However, to the best of our knowledge the metal oxide/hydroxide motif exhibited in **10** is unprecedented. Although the chemistry of **10** could potentially be very interesting, clearly a more rational synthesis is required.

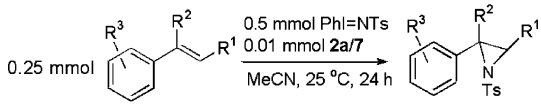
Complexes **2a** and **7** were tested as precatalysts for enantioselective 1,4-conjugate addition and alkene aziridination. Tables 5, 6, and 7 show representative data. Although **2a** and **7** are active, unfortunately significant enantioselectivity was not observed. For conjugate addition reactions comparable activity is observed for **2a** and **7** except for (*E*)-4-phenylbut-3-en-2-one, where **2a** is completely inactive using $ZnEt_2$ as the nucleophile. The lack of enantioselectivity for the 1,4-conjugate addition reaction is perhaps surprising given that mono-NHC copper(I) halide complexes derived from NHC ligands without additional coordinating atoms do generally show a measurable enantioselectivity.[6d,6g] Whilst control experiments using CuI did show that ligand-

Table 5. Catalytic 1,4-conjugate addition reactions between enones and $ZnEt_2$ or PhMgBr using complexes **2a** and **7**.[a]

Precursor	Product	R (yield [%])[b] **2a**	**7**
		Ph (65) Et (90)	Ph (71) Et (91)
		Ph (70) Et (95)	Ph (75) Et (96)
		Ph (73) Et (95)	Ph (77) Et (95)
		Ph (75) Et (0)	Ph (60) Et (56)

[a] Enone (1.00 mmol), RM (1.5 mmol), catalyst (0.04 mmol), diethyl ether, 25 °C, 1 h. [b] Isolated yield after column chromatography.

Table 6. Catalytic aziridination reactions between alkenes and PhI=NTs using complexes **2a** and **7**.

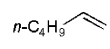
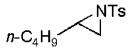
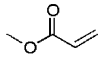
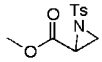
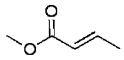
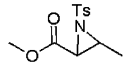
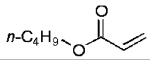
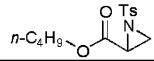


$R^1/R^2/R^3$	Yield (%) **2a**[a]	Yield (%) **7**[a]
H/H/H	70	78
Me/H/H	67	80
H/Me/H	85	86
H/H/4-Cl	85	82
H/H/4-Me	83	86
H/H/3-NO_2	79	79

[a] Isolated yield after column chromatography.

accelerated catalysis is occurring, the acceleration was not very significant, and there is the strong suspicion that complex degradation is at least competitive with catalysis of an NHC complex.

Table 7. Catalytic aziridination reactions between alkenes and PhI=NTs using complexes **2a**.[a]

Precursor	Product	Yield [%][a]
		75
		54
		67
		52
		57
		50

[a] Alkene (0.25 mmol), PhI=NTs (0.5 mmol), catalyst (0.01 mmol), MeCN, 25 °C, 24 h. [b] Isolated yield after column chromatography.

In comparison to conjugate addition reactions, there are very few reports describing copper NHC complex catalysed alkene aziridination,[13] and there are no enantioselective studies based on chiral NHC. Tables 6 and 7 show that **2a** and **7** are active precatalysts giving respectable yields with low catalyst loading, but again no significant enantioselectivity was observed.

Conclusions

Whilst NHC copper(I) complexes of phenoxy–imine hybrid ligands can be prepared, they are prone to decomposition on exposure to air or water. Based on the stability of related copper NHC–aryl oxide compounds, it appears that problematic deprotonation of the phenol to give a chelating or bridging ligand is the primary reason for the observed instability. Presumably, complex instability also accounts for poor catalytic performance with respect to enantioselectivity. However, rich coordination chemistry has been revealed, and particularly complex **10** provides inspiration for the synthesis of new O/OH cluster geometries of copper and other transition metals. It remains to be seen if ligands derived from **1a** or NHC are crucial to their formation.

Experimental Section

General: All manipulations were performed under argon by using standard Schlenk techniques unless stated otherwise. All solvents were dried with the appropriate drying agent and distilled under dinitrogen according to literature methods.[40] Organic reagents were purchased from Aldrich and used as supplied. Ag_2O (Strem, 99+%), Cu_2O (Aldrich, 97%), $CuCl_2{\cdot}2H_2O$ (Aldrich, 99.99%) and $Cu(O_3SCF_3)_2$ (Aldrich 97%) were used as supplied. Compounds **1a**, **1b** and **3** were prepared as reported previously.[23,41,42] NMR spectra were recorded at probe temperature with JEOL 270 (^{1}H, 270 MHz; ^{13}C, 68 MHz), Bruker AV-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz), Bruker AMX-500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) or JEOL 400 (^{1}H, 400 MHz, ^{13}C, 100 MHz) spectrometers. Chemical shifts are described in parts per million downfield from $SiMe_4$ and are reported consecutively as position (δ_H or δ_C), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, dd = doublet of doublets, br. = broad), coupling constant (J [Hz]), relative integral and assignment. ^{1}H NMR spectra were referenced to the chemical shift of residual proton signals ($CHCl_3$: δ = 7.27 ppm; C_6D_5H: δ = 7.16 ppm; C_4D_7HO: δ = 1.73 ppm). ^{13}C NMR spectra were referenced to a ^{13}C resonance of the solvent ($CDCl_3$: δ = 77.2 ppm; C_6D_6: δ = 128.1 ppm; C_4D_8O: δ = 24.4 ppm). ^{13}C HSQC, PENDANT and Gradient HMBC experiments were performed by using standard Bruker pulse sequences. Mass spectra were recorded with VG 70-250E or Kratos MS-50 spectrometers. Electrospray (ES) mass spectra were recorded by using methanol or acetonitrile as the mobile phase. Major fragments were given as percentages of the base peak intensity (100%). Elemental analyses were performed at the University of North London.

{3-[(1*R*,2*R*)-2-{[-(*E*)-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)methylidene]amino}cyclohexyl]-1-isopropyl-4-phenyl-3*H*-imidazol-1-ylidene}copper(I) Bromide (2a): Tetrahydrofuran (30 mL) was added to a Schlenk tube containing a solid mixture of **1a** (500 mg, 0.86 mmol) and copper(I) oxide (82 mg, 0.86 mmol), and the mixture was stirred at 65 °C for 4 d. On cooling, the green mixture was filtered through Celite, and the volatiles were removed from the filtrate under reduced pressure to give **2a** as a light green solid. Yield 515 mg, 93%. ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C): δ = 1.26 [s, 9 H, C(CH_3)$_3$], 1.43 [s, 9 H, C(CH_3)$_3$], 1.49 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.50 [d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH(CH_3)$_2$] 1.29–2.73 (m, 8 H, $^{c\text{-hex}}$CH_2), 4.04 (m, 1 H, $^{c\text{-hex}}$CHN$_{imin}$), 4.42 (m, 1 H, $^{c\text{-hex}}$CHN$_{imid}$), 4.80 (sept, $^3J_{H,H}$ = 6.8 Hz, 1 H, CHCH$_3$), 6.74 (s, 1 H, NCHC), 6.95–7.45 (m, 7 H, ^{Ph}CH), 8.18 (s, 1 H, ^{imin}CH), 13.08 (s, 1 H, OH) ppm. ^{13}C NMR (67.9 MHz, CD_2Cl_2, 25 °C): δ = 23.5 [CH(CH_3)$_2$], 24.1 ($^{c\text{-hex}}$CH_2), 24.2 [CH(CH_3)$_2$], 25.8 ($^{c\text{-hex}}$CH_2), 29.3, 31.3 [C(CH_3)$_3$], 34.0 ($^{c\text{-hex}}$CH_2), 34.0, 34.7 [C(CH$_3$)$_3$], 35.0 ($^{c\text{-hex}}$CH_2), 54.1 [CH(CH$_3$)$_2$], 61.0 ($^{c\text{-hex}}$CHN$_{imid}$), 74.5 ($^{c\text{-hex}}$CHN$_{imin}$), 114.5 (NCHC), 117.7 (*C*$_{ipso}$), 126.3, 127.1 (^{Ph}CH), 127.9 (*C*$_{ipso}$), 128.9, 129.4, 130.2 (^{Ph}CH), 136.4, 136.5, 140.4 (*C*$_{ipso}$) 157.6 (O*C*$_{ipso}$), 166.2 (^{imin}CH), 173.5 (Cu*C*) ppm. MS (ES): *m*/*z* (%) = 501 (100) [M – CuBr]$^+$, 1065 (55) [2 M – 2 Br – Cu]$^+$. $C_{33}H_{45}BrCuN_3O$ (643.18): calcd. C 61.62, H 7.05, N 6.53; found C 61.71, H 7.14, N 6.71.

{3-[(1*R*,2*R*)-2-{[(*E*)-(2-Hydroxyphenyl)methylidene]amino}cyclohexyl]-1-isopropyl-4-phenyl-3*H*-imidazol-1-yildene}copper(I) Bromide (2b): This was prepared by using a procedure analogous to that of **2a** from **1b** (500 mg, 1.07 mmol) and copper(I) oxide (153 mg, 1.07 mmol) to give complex **2b** as a red solid. Yield 550 mg, 96%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.87 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(CH_3)$_2$], 0.92 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH-(CH_3)$_2$], 1.16–1.52 (m, 6 H, $^{c\text{-hex}}$CH_2), 1.89 (m, 1 H, $^{c\text{-hex}}$CH_2), 2.91 (m, 1 H, $^{c\text{-hex}}$CH_2), 4.50 (m, 1 H, $^{c\text{-hex}}$CHN$_{imin}$), 4.51 [sept, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH(CH$_3$)$_2$], 4.67 (m, 1 H, $^{c\text{-hex}}$CHN$_{NHC}$), 5.95 (s, 1 H, NCHC), 6.60 (m, 1 H, ^{Ph}CH), 6.91–7.29 (m, 8 H, ^{Ph}CH), 8.26 (s, 1 H, ^{imin}CH), 12.90 (s, 1 H, OH) ppm. ^{13}C NMR (68 MHz, C_6D_6, 25 °C): δ = 23.3 [CH(CH_3)$_2$], 24.2 ($^{c\text{-hex}}$CH_2), 24.3 [CH-(CH_3)$_2$], 25.9, 34.1, 34.4 ($^{c\text{-hex}}$CH_2), 54.5 [CH(CH$_3$)$_2$], 61.7 ($^{c\text{-hex}}$CHN$_{NHC}$), 74.1 ($^{c\text{-hex}}$CHN$_{imin}$), 114.3, 117.4 (^{Ph}CH), 119.2 (NCHC) 119.6, 126.2 (*C*$_{ipso}$), 129.3, 129.7, 130.8, 132.6, 132.9 (^{Ph}CH), 161.9 (O*C*$_{ipso}$), 166.7 (^{imin}CH), 177.1 (Cu*C*) ppm. MS (ES): *m*/*z* (%) = 388 (100) [M – CuBr]$^+$. $C_{25}H_{29}BrCuN_3O$ (529.09): calcd. C 56.55, H 5.51, N 7.91; found C 56.49, H 5.57, N 7.81.

2,4-Di-*tert*-butyl-6-{[(1*R*,2*R*)-2-(5-phenylimidazol-1-yl)cyclohexylamino]methyl}phenol (4): Sodium cyanoborohydride (103 mg, 1.63 mmol) was added to a Schlenk tube containing a glacial acetic acid (20 mL) solution of **3** (500 mg, 1.09 mmol), and the solution was stirred for 1 h, after which an additional portion of sodium cyanoborohydride (68 mg, 109 mmol) was added and the mixture stirred for a further 30 min. Subsequently, the solution was neutralised by adding it dropwise to an aqueous sodium hydroxide solution (10 M, 50 mL), and the resulting precipitate was extracted with dichloromethane (2 × 50 mL). The dichloromethane extract was washed with a saturated aqueous solution of sodium hydrogen carbonate (3 × 10 mL), dried with magnesium sulfate, filtered, and the volatiles were removed from the filtrate under reduced pressure to give **4** as a pale yellow solid. Yield 450 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.18 [s, 9 H, C(CH_3)$_3$], 1.31 {s, 9 H, [C(CH_3)$_3$]}, 1.17–2.24 (m, 8 H, $^{c\text{-hex}}$CH_2), 2.86 (m, 1 H, $^{c\text{-hex}}$CHN$_{amin}$), 3.45 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, ^{amin}CH_2), 3.70 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H ^{amin}CH_2), 3.73 (m, 1 H, $^{c\text{-hex}}$CHN$_{imid}$), 6.66 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, ^{Ar}CH), 6.97 (s, 1 H, NCHC) 7.15 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, ^{Ar}CH), 7.24–7.63 (m, 6 H, ^{Ph}CH + NCHN) ppm; NH and OH signals not observed. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 24.4, 25.3 ($^{c\text{-hex}}$CH_2), 29.5 [C(CH_3)$_3$], 31.5, 34.8 ($^{c\text{-hex}}$CH_2), 31.6 [C(CH_3)$_3$], 34.1, 34.8 [C(CH$_3$)$_3$], 50.1 (^{amin}CH_2), 58.9 ($^{c\text{-hex}}$CHN$_{imid}$), 61.4 ($^{c\text{-hex}}$CHN$_{amin}$), 122.0 (C_{ipso}), 123.0 (NCHC), 123.1, 128.2, 128.3, 128.8, 129.5 (^{Ph}CH), 129.6 (C_{ipso}), 133.9 (NCHN), 134.1, 136.0, 140.5 (C_{ipso}), 153.9 (OC_{ipso}) ppm. MS (ESI): *m*/*z* (%) = 460 (100) [M + H]$^+$. $C_{30}H_{41}N_3O$ (459.67): calcd. C 78.39, H 8.99, N 9.14; found C 78.49, H 8.93, N 9.00.

3-[(1*R*,2*R*)-2-(3,5-Di-*tert*-butyl-2-hydroxybenzylamino)cyclohexyl]-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium Bromide (5): Compound **4** (1.00 g, 2.18 mmol), 2-bromopropane (1.34 g, 10.9 mmol) and acetonitrile were added to an ampoule sealed with a Teflon stopcock, and the solution was stirred at 65 °C for 48 h. On cooling, the volatiles were removed under reduced pressure, and the resulting yellow solid was recrystallised from dichloromethane (3 mL) and petroleum ether (40–60 °C) (5 mL) to give **5** as a yellow solid. Yield 1.10 g, 87%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.91–2.40 (m, 8 H, $^{c\text{-hex}}$CH_2), 1.18 [s, 9 H, C(CH_3)$_3$], 1.26 [s, 9 H, C(CH_3)$_3$], 1.66 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(CH_3)$_2$], 1.67 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(CH_3)$_2$] 3.75–3.84 (m, 4 H, $^{c\text{-hex}}$CHN$_{amin}$ + $^{c\text{-hex}}$CHN$_{imid}$ + ^{amin}CH_2), 4.90 [sept, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH(CH$_3$)$_2$], 6.72 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, ^{Ar}CH), 7.09 (d, $^4J_{H,H}$ = 1.9 Hz, 1 H, ^{Ar}CH) 7.20–7.43 (m, 6 H, NCHC + ^{Ph}CH), 9.40 (br., 1 H, OH), 11.35 (br., 1 H, NCHN) ppm; NH signal not observed. ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 22.7, 22.8 [CH(CH_3)$_2$], 22.9, 24.6, 28.9, ($^{c\text{-hex}}$CH_2), 29.0 [C(CH_3)$_3$], 31.1 ($^{c\text{-hex}}$CH_2), 31.0 [C(CH_3)$_3$], 33.5, 34.2 [C(CH$_3$)$_3$], 50.4 [CH(CH$_3$)$_2$], 53.3 (^{amin}CH_2), 59.9 ($^{c\text{-hex}}$CHN$_{imid}$), 62.0 ($^{c\text{-hex}}$CHN$_{amin}$), 116.1 (NCHC), 121.4 (C_{ipso}), 122.5, 122.8 (^{Ph}CH), 124.6 (C_{ipso}), 128.5, 129.2, 130.0 (^{Ph}CH), 135.0 (NCHN), 135.3, 135.4, 140.2 (C_{ipso}), 153.4 (OC_{ipso}) ppm. MS (ESI): *m*/*z* (%) = 503 (100) [M – Br]$^+$. $C_{33}H_{48}BrN_3O$ (581.30): calcd. C 68.03, H 8.30, N 7.21; found C 67.90, H 8.10, N 7.32.

{3-[(1*R*,2*R*)-2-(3,5-Di-*tert*-butyl-2-hydroxybenzylamino)cyclohexyl]-1-isopropyl-4-phenyl-3*H*-imidazol-1-ylidene}silver(I) Bromide (6): Dichloromethane (10 mL) was added to a Schlenk tube containing **5** (250 mg, 0.43 mmol) and silver(I) oxide (54 mg, 0.24 mmol) and the mixture stirred for 24 h with the exclusion of light. The resulting mixture was filtered through a Celite plug, and the volatiles were removed from the filtrate under reduced pressure to give **6** as a dark yellow solid. Yield 278 mg, 94%. ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 1.23 [s, 9 H, C(CH_3)$_3$], 1.37 [s, 9 H, C(CH_3)$_3$], 1.07–2.39 (m, 8 H, $^{c\text{-hex}}$CH_2), 1.52 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H CH-(CH_3)$_2$], 1.60 [d, $^3J_{H,H}$ = 6.6 Hz, 3 H CH(CH_3)$_2$], 3.64–3.87 (m, 4 H, $^{c\text{-hex}}$CHN$_{NHC}$ + $^{c\text{-hex}}$CHN$_{amin}$ + ^{amin}CH_2), 5.30 [sept, $^3J_{H,H}$ = 6.6 Hz, 1 H CH(CH$_3$)$_2$], 6.80 (s, 1 H, NCHC), 7.06–7.53 (7 H, m ^{Ph}CH), 9.68 (br., 1 H, OH) ppm; NH signal not observed. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 24.6, 24.6 [CH(CH_3)$_2$], 25.5, 26.3 ($^{c\text{-hex}}$CH_2), 30.0 [C(CH_3)$_3$], 30.2, 32.3 [C(CH_3)$_3$], 32.7 ($^{c\text{-hex}}$CH_2), 34.9 [C(CH$_3$)$_3$], 35.6 ($^{c\text{-hex}}$CH_2), 52.1 (^{amin}CH_2), 56.9 [CH(CH$_3$)$_2$], 62.0 ($^{c\text{-hex}}$CHN$_{NHC}$), 63.3 ($^{c\text{-hex}}$CHN$_{amin}$), 115.8 (NCHC), 123.4 (C_{ipso}), 123.7, 124.2 (^{Ph}CH), 128.8 (C_{ipso}), 129.7, 129.9, 130.9 (^{Ph}CH), 136.6, 137.6, 141.4 (C_{ipso}) 155.1 (OC_{ipso}), 158.2 (AgC) ppm. MS (ES): *m*/*z* (%) = 1109 (100) [2 M – Ag – 2 Br]$^+$. MS (HRES): calcd. for $C_{66}H_{94}AgN_6O_2$ 1109.6484; found 1109.6494. $C_{33}H_{47}AgBrN_3O$ (689.52): calcd. C 57.48, H 6.87, N 6.09; found C 57.61, H 6.81, N 6.19.

{3-[(1*R*,2*R*)-2-(3,5-Di-*tert*-butyl-2-hydroxybenzylamino)cyclohexyl]-1-isopropyl-4-phenyl-3*H*-imidazol-1-ylidene}copper(I) Bromide (7): This was prepared by using a procedure analogous to that for **2a** from **5** (500 mg, 0.86 mmol) and copper(I) oxide (123 mg, 0.86 mmol) to give complex **7** as a light brown solid. Yield 520 mg, 94%. ^{1}H NMR (300 MHz, C_4D_8O, 25 °C): δ = 0.90 (m, 1 H, $^{c\text{-hex}}$CH$_2$), 1.22 [s, 9 H, C(CH_3)$_3$], 1.38 [s, 9 H, C(CH_3)$_3$], 1.55 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(CH_3)$_2$], 1.63 [d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH(CH_3)$_2$], 1.69–1.95 (m, 3 H, $^{c\text{-hex}}$CH_2), 2.15 (m, 2 H, $^{c\text{-hex}}$CH_2) 2.39 (m, 1 H, $^{c\text{-hex}}$CH_2), 2.62 (m, 1 H, $^{c\text{-hex}}$CH_2), 3.60–3.94 (m, 3 H, $^{c\text{-hex}}$CHN$_{amin}$ + ^{amin}CH_2), 4.00 (m, 1 H, $^{c\text{-hex}}$CHN$_{NHC}$), 4.92 [sept, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH(CH$_3$)$_2$], 6.82 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H ^{Ar}CH), 7.11 (d, $^4J_{H,H}$ = 2.3 Hz, 1 H, ^{Ar}CH), 7.38 (s, 1 H, NCHC), 7.42 (m, 5 H, ^{Ph}CH), 10.05 (s, 1 H, OH) ppm; NH signal not observed. ^{13}C NMR (75.5 MHz, C_4D_8O, 25 °C): δ = 24.1, 24.6 [CH(CH_3)$_2$], 25.9, 26.7 ($^{c\text{-hex}}$CH_2), 30.3, 32.3 [C(CH_3)$_3$], 32.7 ($^{c\text{-hex}}$CH_2), 34.9, 35.7 [C(CH$_3$)$_3$], 36.9 ($^{c\text{-hex}}$CH_2), 52.6 (^{amin}CH_2), 55.9 [CH(CH$_3$)$_2$], 62.4 ($^{c\text{-hex}}$CHN$_{NHC}$), 63.9 ($^{c\text{-hex}}$CHN$_{amin}$), 116.4 (NCHC), 123.0, 124.1 (^{Ph}CH), 124.3 (C_{ipso}), 129.8, 130.0, 131.1 (^{Ph}CH), 136.0, 136.9, 140.8 (C_{ipso}), 155.7 (OC_{ipso}), 175.0 (CuC) ppm. MS (ESI): *m*/*z* (%) = 502 (100) [M – CuBr]$^+$, 1065 (55) [2 M – 2 Br – Cu]$^+$.

General Procedure for Copper-Catalysed 1,4-Conjugate Addition Reactions: The organometallic reagent (1.50 mmol) was added to a reaction tube charged with a diethyl ether (3 mL) solution of the copper complex **51** or **53** (0.04 mmol) and the solution stirred for 15 min. Subsequently, the enone (1.00 mmol) was added dropwise to the mixture over a period of 10 min and the mixture stirred for 1 h and then quenched by the addition of $HCl_{(aq.)}$ (1 M, 2 mL). The resulting mixture was stirred until clear, and then the organic phase was extracted with diethyl ether (2 × 1 mL) and dried with $MgSO_4$. The volatiles were removed under reduced pressure to give an off-white solid that was purified by column chromatography on silica gel. Enantioselectivity was determined by HPLC, using Daicel, Chiralpak AD-H and Chiralcel OD columns where appropriate. Typical HPLC conditions: injection volume: 1 μL; pump flow: 0.500 mL/min; oven temperature: 20 °C; wavelength detection: 190–800 nm; mobile phase: hexane/propan-2-ol (98:2).

General Procedure for the Copper-Catalysed Aziridination Reactions Using Iminoiodane PhI=NTs: Acetonitrile (2 mL) was added to a reaction tube charged with alkene (2.5 mmol), iminoiodane (0.5 mmol), and copper complex (0.01 mmol) and the solution stirred at 20 °C for 24 h. Products were isolated and purified by column chromatography on silica gel. Enantioselectivity was determined by HPLC, using Daicel, Chiralpak AD-H and Chiralcel OD columns where appropriate. Typical HPLC conditions: injection volume: 1 μL; pump flow: 0.500 mL/min; oven temperature: 20 °C; wavelength detection: 190–800 nm; mobile phase: hexane/propan-2-ol (98:2).

Table 8. Details of X-ray structure determinations.

Complex	**2a′**	**2b′**	**9**	**10**
Empirical formula	$C_{66}H_{88}Br_2Cu_3N_6O_6$	$C_{100}H_{112}Br_4Cu_6N_{12}O_4$	$C_{68}H_{90}CuF_6N_6O_8S_2$	$C_{110.9}H_{151.6}Cl_6Cu_7N_9O_8$
Formula mass	1347.86	2246.90	1361.12	2396.29
Crystal color	green	orange	blue	green
Crystal size [mm]	$0.19\times0.19\times0.15$	$0.13\times0.05\times0.02$	$0.41\times0.20\times0.10$	$0.24\times0.20\times0.02$
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a [Å]	14.2056(8)	19.2970(8)	14.4517(8)	15.7246(14)
b [Å]	19.6843(11)	21.9449(6)	20.3292(10)	20.1336(17)
c [Å]	23.1741(13)	25.7846(9)	23.9293(13)	19.8969(17)
β [°]	90	90	90	100.387(2)
V [Å^3]	6480.1(6)	10919.0(7)	7030.2(6)	6196.0(9)
Z	4	4	4	2
$d_{calcd.}$ [g cm^{-3}]	1.382	1.367	1.286	1.284
μ [mm^{-1}]	2.255	2.662	0.442	1.360
θ range [°]	1.68–25.03	2.98–25.02	1.65–25.03	2.46–25.53
No. refls. measured	69437	42903	74143	49656
No. independent refls.	11425 (R_{int} = 0.0348)	18434 (R_{int} = 0.0706)	12412 (R_{int} = 0.0348)	24763 (R_{int} = 0.0270)
Restraints/parameters	0/728	1146/1135	0/867	443/1324
Trans. coefficient range	0.661–0.710	0.724–0.949	0.863–0.960	0.735–0.975
$R(F)$ [$I>2\sigma(I)$][a]	0.0357	0.0685	0.0270	0.0415
$R_w(F^2)$ (all data)[b]	0.0959	0.1695	0.0686	0.1162
Goodness of fit (F^2)	1.057	1.051	1.039	1.020
Absolute struct. parameter	0.018(7)	0.162(11)	–0.005(6)	0.046(7)
$\Delta\rho$ (max/min) [e Å^{-3}]	2.552/–0.683	0.512/ –0.567	0.524/–0.181	1.161/–0.528

[a] $R(F) = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$. [b] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

X-ray Crystal Structure Determinations. 2a′: Diffraction data were collected at 110 K with a Bruker SMART APEX diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Diffractometer control, data collection and initial unit-cell determination were performed by using SMART software; frame integration and unit-cell refinement were carried out with SAINT+.[43] Absorption corrections were applied by SADABS.[43] Structures were solved by direct methods using SHELXS-97[44] and refined by full-matrix least squares using SHELXL-97.[44] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined by using a riding model. X-ray structure details are given in Table 8. $C_{66}H_{88}Br_2Cu_3N_6O_6$ (1347.89): calcd. C 58.81, H 6.58, N 6.23; found C 59.01, H 6.66, N 6.18. **2b′:** Diffraction data were collected at 120 K with a Bruker-Nonius APEXII diffractometer at the window of a Bruker-Nonius FR591 rotating anode (Mo-K_α) with the X-ray beam focused by using 10 cm confocal mirrors. Unit-cell determination was carried out in DirAx.[45] The data collection was controlled by COLLECT[46] and processed by DENZO.[47] An absorption correction was applied by using SADABS. The structure was determined with SIR2004[48] and refined by full-matrix least-squares analysis on F^2 in SHELXL-97,[44] both implemented in the program WinGX.[49] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms treated as for **2a′**. There is a large void in the structure filled with highly disordered solvent molecules that cannot be modelled as discrete atoms. The SQUEEZE routine in PLATON[50] was used to treat this disordered solvent. The results of the SQUEEZE routine show that there are probably two molecules of solvent per asymmetric unit (probably one or both of the solvents of crystallisation, diethyl ether and tetrahydrofuran). Several isopropyl groups and phenyl groups exhibit varying degrees of disorder over several positions, which could not be successfully modelled. As a result of this, several of the anisotropic displacement ellipsoids are elongated. X-ray structure details are given in Table 8. **9:** Diffraction data were collected, and the structure solved and refined analogous to that of **2a′** with the exception that disorder present in the *t*Bu group containing C(63)–C(67) was represented by using a two-site model with rotation about the C(48)–C(63) bond. The relative occupancies were refined to 46:54%. X-ray structure details are given in Table 8. $C_{68}H_{90}CuF_6N_6O_8S_2$ (1361.15): calcd. C 60.00, H 6.66, N 6.17; found C 60.11, H 6.72, N 6.17. **10:** Data were collected at 120 K from a weakly diffracting crystal by using synchrotron radiation (λ = 0.6895 Å) and a Bruker APEXII diffractometer. Diffractometer control and data processing were carried out with APEXII.[43] A semi-empirical absorption correction was applied with SADABS. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were positioned geometrically on the basis of sensible oxidation states, observed geometry and overall charge balance, and were refined with a riding model. Disorder was resolved satisfactorily for the $[CuCl_2]^-$ anion and for a *t*Bu group of one ligand, the latter correlated with partial occupancy of a toluene solvent molecule site. Another toluene molecule could also be located and modelled as discrete atoms. Application of the SQUEEZE procedure for identified voids in the structure indicates that there are probably two further, highly disordered, toluene solvent molecules in the asymmetric unit. X-ray structure details are given in Table 8. All four crystal structures are non-centrosymmetric, and gave satisfactory refinement of the "absolute structure" enantiopole parameter for a single handedness with no detected twinning.[51] CCDC-710635 (**2a′**), -710636 (**2b′**), -710737 (**9**) and -710368 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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