Sterically Demanding Ag⁺ and Cu⁺ N-Heterocyclic Carbone Complexes: Synthesis, Structures, Steric Parameters, and Catalytic Activity

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Abstract: The synthesis and full characterization of new air-stable Ag⁺ and Cu⁺ complexes bearing structurally bulky expanded-ring N-heterocyclic carbene (erNHC) ligands is presented. The condensation of protonated NHC salts with Ag₂O afforded a collection of Ag⁺ complexes, and their first use as ligand transfer reagents led to novel isostructural Cu⁺ or Au⁺ complexes. In situ deprotonation of the NHC salts in the presence of a copper(I) source, provides a library of new Cu⁺ complexes. The solid-state structures feature large N=C=N angles (118–128°) and almost identical angles between the aryl groups on the nitrogen atoms and the plane of the N-C-N unit of the carbene (i.e. torsion angles close to 0°). Among the steric parameters, the percent buried volume (%V₈₄₀) values span easily in the 50–57% range, and that one of (9-Dipp)CuBr complex (%V₈₄₀ = 57.5) overcomes to other known erNHC-metal complexes reported to date. Preliminary catalytic experiments in the copper-catalyzed coupling between N-tosylhydrazone and phenylacetylene, afforded 76–93 % product at the 0.5–2.5 mol% catalyst loading, proving the stability of Cu⁺ erNHC complexes at elevated temperatures (100°C).

Introduction

Pioneering work of by Wanzlick in the early 60’s inaugurated the era of N-heterocyclic carbenes (NHCs) as ligands for metals.[1] Thereafter, new breakthroughs achieved by Ardengo, Bertrand, and Herrmann, led to the application of NHCs in organometallic chemistry and catalysis.[2−4] Since then, NHC ligands are considered excellent candidates for the stabilization of a wide range of metal complexes,[5] and particularly for the ubiquitous coinage metals (Ag, Cu, Au),[6] thanks to their strong o-donating ability and steric properties.[7]

N-heterocyclic carbenes based on expanded-ring backbone[8] have emerged as outstanding ligands for transition-metal complexes,[9] as a result of the enlarged N=C=N angle that pushes the N-substituent closer to the carbene carbon providing sterically protection around the metal center and consequently, enhancing the final catalytic activity of the complex.[10−11] Furthermore, the trend to increase the steric demand of the ligand, has strongly influenced the field of catalyst design.[7,8,10] For instance, by tuning the substituent on the N-atom in the tether[12] or the backbone of the NHC skeleton,[13] a unique class of structurally imposing metal complexes has arisen (%V₈₄₀ > 52).[14]

For several years, Ag¹ NHC complexes have been fruitfully explored in medicinal chemistry as biologically active organometallic complexes,[15] joining a swift application in catalysis.[16] Owing to the low thermodynamic stability of the carbene carbon-silver bond, Ag¹ NHC complexes are also useful synthetic reagents in ligand transfer reactions,[17] becoming a convenient entry point into other NHC-metal compounds.[13c,16] On the other hand, many NHC-stabilized Cu⁺ complexes are key catalysts of synthetically relevant transformations,[19] and during the last decade, became a „hot topic” thanks to their photophysical properties.[20]

Although manifold examples of Ag⁺ and Cu⁺ complexes bearing erNHC ligands have been developed,[18b,21] their structural diversity is limited by a flexible alkyl-chain design, which lead to a poor prediction of their structural features, as the ring geometry affects the NHC complex sterics and electronics.[19,9,13a] The steric bulkiness of several erNHC metal complexes generally overcomes that of the imidazoylidene-containing ligands (i.e. IPr) albeit rarely surpass the „latest generation” five-membered NHCs such as IPr** or IPr⁺⁺ (Figure 1).
Results and Discussion

Protonated BF$_4^-$ (1a) and PF$_6^-$ (1b) salts shown in Figure 2, served as ligand source for the synthesis of Ag$^+$ and Cu$^+$ enNHC complexes. Ligands 9-Dipp, 9-Mes, 9-Dietph, 9-Xyl, 10-Dipp, 10-Mes, 10-Dietph and 10-Xyl are relatively unexplored in metal complex synthesis so far.$^{[14]}$

The BF$_4^-$ salts 1aa–1ah were easily accessible by our previously reported procedure.$^{[14]}$ The reaction of enNHCHBr precursors with NH$_4$PF$_6$ in MeOH at room temperature, originated their hexafluorophosphate analogues 1ba–1bh. Anion exchange was confirmed via $^1$H, $^{31}$P and $^{19}$F NMR analysis. The amidinium protons were evidenced in the $^1$H NMR spectra by the characteristic singlet signal at $\delta$ 7.5–8.0 ppm, while the $^{31}$P NMR displayed a septet signal at ca. $\delta$–144 ppm, in the typical range for hexafluorophosphate derivatives. The structure of PF$_6^-$ salt 1ba was unambiguously confirmed by a single crystal X-ray diffraction analysis (Figure S2, see the Supporting Information).$^{[22]}$

Ag$^+$ and Cu$^+$ NHC complexes

The reaction of protonated NHC salts and Ag$_2$O to enNHC-AgX complexes has been studied in great detail.$^{[17, 23]}$ This reaction proceeds better with weakly coordinating anions (e.g. BF$_4^-$ or PF$_6^-$) rather than halides (e.g. Br$^-$, Cl$^-$, I$^-$), presumably due to the halide counter anion is being able to form an hydrogen bond with the C2-H amidinium proton.$^{[56, 21c]}$ Hence, the optimization experiments employing the enNHC salts of bulky ligands 9-Dipp and 10-Dipp were conducted (Table 1). Satisfyingly, the formation of Ag$^+$ enNHC complexes was observed in all cases.

The screening in CH$_2$Cl$_2$ at room temperature (Entries 1 and 2) led to the expected products in poor yields (17 and 21%, respectively) after 24 h. The total consumption of the substrate required a longer reaction time (ca. 3 days) yielding < 50% product. The reaction also was effective in CH$_3$CN under heating conditions (Entries 3 and 4), where the yields raised up to 54%. By using THF as the solvent and higher temperature (68$^\circ$C), the yields enhanced notably (> 70%, Entries 5 and 6) as...
a result of a better solubility of substrate and Ag₂O, leading to a full consumption (revealed by TLC, CH₂Cl₂, 100%). Interestingly, the use of salt 1ba under same reaction conditions, diminished the yield to a half, and most substrate remained unreacted (Entry 7).

While attempting the synthesis of 4 from 1ac and Ag₂O in THF at reflux for 3 days, organic material was isolated as the main product and further identified as the ring opened NHC 1ac (formed presumably as a result of hydrolysis with water catalyzed by heating). A sample of this material crystallized from a toluene solution after several days and the X-ray diffraction analysis of a single crystal confirmed its composition and structure (1ac, Figure S3, see the Supporting Information).

Finally, the reaction of various BF₄⁻ salts with Ag₂O and NaBr in THF under reflux for 24 h, provides a collection of Ag⁺ enNHC complexes in acceptable to good yields (51–80%, Figure 3). Complexes 2–7 are air- and moisture-stable, colorless solids and after recrystallization from a CH₃Cl₂-pentane mixture, high purity crystalline solids can be obtained.

Unfortunately, the isolation of Ag⁺ complexes bearing 10-Mes or 10-Xyl ligands was unsuccessful. Under these reaction conditions, decomposition material was observed instead.

Spectroscopic characterization of Ag⁺ enNHC complexes 2–7 by ¹³C([¹H]) NMR reveals the typical carbene carbon (C_{C–N}) signals of two doublets displaced in high chemical shifts with coupling constants of ¹J_{C–Ag}² = 224–227 Hz, and ¹J_{C–Ag}₁₀ = 260–263 Hz, in agreement with the spin–spin interaction between ¹⁰Ag (spin ¹/₂, 51.8%) and ¹⁰⁹Ag (spin ¹/₂, 48.2%) isotopes with the singlet C_{NHC}¹. The ratio of these constants reflects approximately the gyromagnetic ratio γ for the two silver nuclei involved that is γ(¹⁰⁹Ag)/γ(¹⁰⁹Ag) = 1.15.

These observed couplings indicate a relatively strong C_{NHC}–Ag bond as a result of no or slow exchange of the enNHC ligands between the Ag atoms at the NMR scale and confirms that complexes 2–7 do not exhibit a fluxional behavior in the C_{NHC}–Ag bond, characterized by the lack of C_{NHC}–Ag couplings.

Mass spectrometry analyses (MALDI, ESI⁻+) proved the [[enNHC-Ag₂]Br]⁺, [[enNHC₂]₂Ag⁺]⁻ and [[enNHC-Ag₂]⁺]²⁻ fragments but commonly, the most prominent peak in the spectra is that of the [NHC-Ag⁺]⁻ fragment that denotes the molecular structure of type enNHC-AgX which could be further confirmed by X-ray diffraction analysis of selected examples (Figures 6 and 9).

Next, the synthesis of Cu⁺ enNHC complexes, following literature protocols, was explored (Scheme 1). For example, by attempting the condensation of enNHC salts and a Cu' source (i.e. Cu₂O, Cu₂O, CuBr) most starting material was recovered and only traces of byproduct were isolated, presumably formed upon oxidation of the C_{NHC} under heating in open-air conditions (Pathway B). At the latter, the synthesis of Cu⁺ enNHC complexes was accomplished by the free carbene strategy, involving the in situ protonation of the enNHC salts (1a) in presence of (SMe₂)CuBr (Pathway C).

Gratifyingly, most of the enNHC salts underwent deprotonation under these conditions and complexes 8–15 were successfully obtained (Figure 4). All of the Cu⁺ enNHC complexes adopt a neutral, mononuclear enNHC-Cu-Br conformation as judged in the ¹³C-NMR spectra which remained identical to those of Ag⁺ enNHC complexes and the previously reported Au⁺ enNHC ones.

The carbene carbon signals in the ¹³C([¹H]) NMR spectra show a singlet at around δ = 223 ppm for the nine-membered NHCs (9-enNHC), and at around δ = 214 ppm for the ten-membered NHC (10-enNHC). This implies that the C_{NHC} in the 9-enNHC is significantly less shielded (by ca. 9 ppm) than the respective one of the 10-enNHC. In general, the carbencic carbon of Cu⁺ enNHC complexes is highfield shifted by ca. 10 ppm than their Ag⁺ enNHC congeners. HRMS spectra (ESI⁻+) of Cu⁺ enNHC complexes reflect the peak of the [NHC-Cu⁺]⁻ fragment at the highest intensity nevertheless, the [NHC₂Cu⁺]⁻ species was also found in a minor ratio.

Interestingly, the mass spectrometry analyses of complexes 11 and 15, bearing less bulky ligands, namely 9-Xyl and

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**Table 1. Optimization of the synthesis of Ag⁺ enNHC complexes.**

| Entry | Substrate | Conditions | Product | Yield [%] |
|-------|-----------|------------|---------|-----------|
| 1     | 1aa       | CH₂Cl₂, rt. | 2       | 17        |
| 2     | 1ae       | CH₂Cl₂, 50 °C | 6 | 21        |
| 3     | 1aa       | CH₂Cl₂, 50 °C | 2 | 48        |
| 4     | 1ae       | CH₂Cl₂, 50 °C | 6 | 54        |
| 5     | 1aa       | THF, 68 °C  | 2       | 75        |
| 6     | 1aa       | THF, 68 °C  | 6       | 80        |
| 7     | 1ba       | THF, 68 °C  | 2       | 41        |

[a] Reaction conditions: NHC-HBF₄ (0.1 mmol, 1.0 equiv), Ag₂O (0.1 mmol, 1.0 equiv), NaBr (0.6 mmol, 6.0 equiv), absolute solvent (3 mL), in dark, 24 h. (b) Isolated yields as an average of two runs.

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**Figure 3. Ag⁺ complexes 2–7 bearing enNHC ligands.**
10-Xyl, exhibit peaks of the [(enHNC-Cu)₂Br]⁺ and [(enHNC-Cu)₂Br]³⁺ fragments, which might suggest that the linear enHNC-Cu-Br complex is in equilibrium with the bromide-bridged [(enHNC)₂Cu(μ-Br)]Br species and the neutral tri-coordinate (enHNC)₂CuBr (Scheme 2).

The equilibrium is displaced towards the formation of neutral mononuclear Cu⁺ enHNC complex and to support this hypothesis, the structure of 15 was unequivocally established by single-crystal X-ray analysis (Figure 9, right). Although two molecules were found in the unit cell, no evidence of a metallic Cu···Cu interaction or a bromide-bridged species was observed.

The carbene transfer ability of selected Ag⁺ compounds in the presence of (SMe₂)AuCl or (SMe₂)CuBr as metal sources was further investigated (Scheme 3). The reaction of 2 or 5 conducted to novel enHNC-AuBr complexes 16 (31 % yield) and 17 (53 % yield), respectively. These complexes retained the Br⁻ instead of the Cl⁻, contrary to the stability of the insoluble halide salts which increases in the order AgCl < AgBr < AgI and precipitation of AgBr is more favorable than that of AgCl. The structure of complex (9-Xyl)AuBr 17 was confirmed by X-ray diffraction analysis of a single crystal (Figure 5).

By employing the complexes 2 and 6 bearing Dipp ligands, in the presence of (SMe₂)CuBr, the expected Cu⁺ compounds 8 and 12 were obtained in acceptable yields (40–46 %). These results underline the carbene transfer ability of the bulky Ag⁺ enHNC complexes, in contrast to other sterically demanding NHC systems which were unsuccessful in the transfer of ligand to other metals.

Finally, the Cu⁺ enHNC complexes 8 and 12 were mixed with (SMe₂)AuCl in the typical conditions for the transfer of ligand (CH₂Cl₂, r.t., light exclusion) Nonetheless, the reaction failed to afford the desired Au⁺ enHNC complexes and led to the deposition of a gold mirror.

Scheme 1. Synthetic approaches to Cu⁺ enHNC complexes.

Figure 4. Synthesized Cu⁺ complexes 8–15 bearing enHNC ligands.
Structural studies and steric parameters

A single crystal of complex 17\(^{22}\) was grown from a CHCl\(_3\)/pentane mixture. This complex crystallized with a CHCl\(_3\) molecule from the solvent (Figure 5).

Comparatively, the Au–Br bond length (2.4036(5) Å) is longer than that of Au–Cl found in 9-NHC-Au\(^+\) complexes (2.29–2.35 Å).\(^{14}\) The C\(_{\text{NHC}}\)-Au length is 2.006(4) Å and the N–C\(_{\text{NHC}}\)-N is 119.6(4)\(^\circ\). X-ray quality single crystals of complexes 2, 4, 6, 7, 8, 13 and 15,\(^{22}\) were grown by slow diffusion of pentane into a saturated solution of the complex in CH\(_2\)Cl\(_2\) or CHCl\(_3\) followed by evaporation of solvents at room temperature. Table 2 summarizes relevant geometrical parameters of Ag\(^+\) enHNC complexes 2, 4, 6 and 7, and other related examples selected from literature.

Focusing on the 9-NHCs 2 and 4, the C\(_{\text{NHC}}\)-Ag bond lengths are 2.110(4) Å and 2.119(3) Å, respectively. Bond lengths Ag–Br lie between 2.43–2.44 Å and are within the range of the previously reported Ag\(^+\) NHC complexes of small ring size (2.38–2.57 Å) but slightly larger than those of the corresponding five-membered compounds (2.11–2.32 Å). The N–C\(_{\text{NHC}}\)-N angles (118.2–119.1\(^\circ\)) are smaller than those of the eight-membered NHCs (123.2–123.3\(^\circ\)), and similar to the six- and seven-membered NHCs (6-Mes)AgCl, (6-Dipp)AgBr and (7-Mes)AgBr (118.3–118.9\(^\circ\)). C\(_{\text{NHC}}\)-Cu and Cu–Br bond lengths in Cu\(^+\) complex 8 are 1.904(4) Å and 2.230(8) Å, respectively (Figure 7).
and in the overall arrangement of the erNHC

and are marginally longer

Molecular structures of (9-Dipp)AgBr (Figure 6, top) and (9-Dietph)AgBr (4, bottom) in the solid state. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. For 4 only one of the two symmetry-independent molecules is shown.

The N-C_NHC-N angle found in 8 is 119.0°. Complexes 2 and 4 adopted nearly linear erNHC-Ag-Br angles around 176° while complex 8 appeared considerably out of linearity (\(\angle_{N-C_NHC-N} = 174.7(15)^\circ\)).

The torsion angles (\(\alpha\)) found in these complexes are 48.4°, 37.9° and 28.4°, respectively.\(^{[30]}\) The latter values confirm the twisting of the aryls, with respect to the NHC plane, observed in the solid-state structures of the complexes (see (a) in Figure 8). While a sharp twisting is perceived in Ag\(^\dagger\) complex 2 (top, Figure 6; \(\alpha = 48.4^\circ\)), a significantly smaller twisting is observed in the isostructural Cu\(^\dagger\) congener 8 (Figure 7, \(\alpha = 28.4^\circ\)).

Moving to the X-ray structures of the 10-erNHC complexes of Ag\(^\dagger\) and Cu\(^\dagger\) from a front view (top, Figure 9), is easy to disclose their wide N-C_NHC-N angles (126°–128°). Cu\(^\dagger\) complex 13 exhibit the widest N-C_NHC-N angle of this series (128.6°) followed by complexes 6, 7 and 15 (around 126°). To the best of our knowledge these are the widest N-C_NHC-N angles of any erNHC-metal complex in current literature. C_NHC-Ag bond lengths of 6 and 7 lie around 2.14 Å and are marginally longer than those of six- to eight-membered NHCs, while the Ag–X bond distances are within the same range 2.42–2.44 Å (Table 2).

The C_NHC-Cu bond distances found in Cu\(^\dagger\) complexes 13 and 15 are 1.924(12) Å and 1.915(4) Å, respectively. To our surprise, torsion angles of these 10-erNHC complexes lie between 0° and 4.5°, which implies that the two aryl planes are essentially in coplanarity with the NHC plane.

This implies that the geometry of the diphenylether moiety exerts a domino effect in the overall arrangement of the erNHC complex, which ends up in diminished torsions of the N-Aryls. The folding (see (b) in Figure 8) of the diphenylether moiety influences the arrangement of the methylene groups, which adopt a nearly tetrahedral arrangement with N-CH\_2-C\_aryl angles \(b = 112.7°–118.9°\) (see (c) in Figure 8). Along with the non-trivial presence of hydrogen atoms in these methylene groups, the folding limit the twisting of the N-Aryls as their ortho-substituents are equally pushed down and consequently, the N-aryl planes reach the more stable geometry (the coplanarity relative to the NHC plane). The molecular structures from side-views presented in Figure S1 showcase the folding of the back-
bone ring and the twisting of the N-aryls (see Supporting Information).

For the quantification of the steric profiles of AgI and CuI erNHC complexes, the buried volume values (%V_{bur})\(^{[29]}\) and topographic steric maps\(^{[31]}\) were derived using SambVca 2.0 package.\(^{[32]}\) The typical settings for the calculation (\(r = 3.5\) Å (radius of the sphere around the metal center), \(d = 2.0\) Å (bond length C-NHC-metal), Bondi radii scaled by 1.17 and a mesh spacing of 0.10 Å) were used to scan the sphere of the buried voxels.\(^{[29]}\) The steric distribution around the first coordination sphere of the metal (upper hemisphere), is represented by isocontour lines visualized from a bottom point. In addition, the colour scale help to identify the less-to-more buried (occupied) zones. Figure 10, features illustrations that resemble the coordination sphere in whose center the metal lies (Ag or Cu) and the reference axes (X, Y) partition the hemisphere, giving the steric component for each quadrant.

The %V_{bur} values of AgI erNHC complexes given in the Table 2, are in the range 50.3–56.6 % and are comparatively higher than those of the six- to eight-membered NHCs counterparts (\%V_{bur} up to 49.5). Noteworthy, AgI complex 6 surpass the %V_{bur} value of the extremely hindered (IPr*)AgCl reported by Markó et al. (\%V_{bur} = 53.5)\(^{[27a]}\) and beside to (IPr* (2/Np))AgCl (\%V_{bur} = 57.4),\(^{[28h]}\) these represent the structurally more imposing NHC–AgI complexes in current literature.

The steric maps of the 10-erNHC complexes are presented in Figure 9 (bottom). In complex 6 (%V_{bur} = 56.6), the ortho-isopropyl substituents of the N2- and N5-Aryl substituents prevent the rotation around the N-Aryl bond effectively, by limiting the twisting of the Dipp substituents, which results in a homogeneous steric delivery. Although the top-left quadrant is less bulky (46.4 %), the steric impact of the ligand lies on the three bulkier quadrants (59–63% buried volume). Similarly, complex 7 (%V_{bur} = 50.3) two quadrants exert lower steric impact (42–45%) than the top-left quadrant which overcomes 60% buried volume.

The %V_{bur} value calculated for CuI complex 13 (52.1 %), is marginally larger than that of 15 (51.9 %) as their structures differ only in the presence of para-methyl groups at the N-aryls. The torsion angles (0° and 3.3°, respectively), best describe a slight, but still relevant influence of these para-methyl substituents, into the steric distribution of the complex, through the stabilization of the NHC skeleton. We might better illustrate this with the imprint of one para-methyl substituent visible in the steric map of 13 (see the blue area), whereas in analogous zone of 15, there is no trace of covered field as its para position is vacant (Figure 9).

Since a direct comparison between two NHC complexes possessing different metals might be meaningless,\(^{[7e]}\) a few interesting observations, regarding the steric impact of 9-Dipp...
ligand on these erNHC complexes can be pointed out. The steric maps of Ag complex 2 and Cu complex 8, are shown in Figure 10. The steric contribution of the 9-Dipp ligand in Cu complex 8 (bottom) is notably higher than that of its Ag congeners 2 (top). The top-left quadrant of 2 (45.3%) is less hindered than the analogous quadrant of 8 (55.4%) and a similar asymmetry can be appreciated in the corresponding right tail quadrants (51.1% and 59.1%, respectively). The overall buried volume of complex 2 (51.9%) is still outstanding within the family of Ag erNHC complexes, while complex 8, possess the most sterically encumbered structure within the Cu erNHC family, displaying an impressive %V_{bur} = 57.5%.

The size of the metal ion and somehow, the halogen size, are also factors governing the spatial arrangement of the ligand around the metal itself. Given that the ionic radius of Cu^+ is just much smaller than that of Ag^+, the large silver ion may affect the steric distribution by pushing the substituents away from the first coordination sphere, causing a diminished %V_{bur} value.

**Catalytic applications of NHC–MX complexes**

Our previous study on Au erNHC complexes, shed light upon the strong effect that the steric distribution of the erNHC complex exerts on the catalyst performance.[14] For example, we found that (9-Mes)AuCl (%V_{bur} = 43.6, α = 39.3'), promoted the cyclization of a propargylamide in 60% yield (0.025 mol% catalyst loading, 50 °C, 24 h), while (9-Dipp)AuCl (%V_{bur} = 53.0, α = 48.2') was not that effective (6% yield) under same reaction conditions. We chose, namely (9-Dipp)CuBr 8 (%V_{bur} = 57.5), because it is the bulkiest NHC Cu complex, in combination with its well-distributed steric demand (α = 28.4') as discussed above. To further compliment this preliminary catalytic study, we selected the 10-erNHC complex 12 as it also bears the bulky 9-Dipp ligand. The coupling between N-tosylhydrazones and terminal alkyne for the synthesis of Benzofurans was investigated as test reaction (Table 3).[34]

At 2.5 mol% catalyst loading, both complexes 8 (93% yield) and 12 (88% yield), proved capable of bringing about the coupling between a N-tosylhydrazone and phenylacetylene to form benzofuran 3a after 12 h (Table 3, Entries 1 and 2). Lowering (1.25 mol%) the catalyst loading, complex 8 afforded 68% yield (Entry 3) and an acceptable 41% yield when a 0.5 mol% loading was employed (Entry 4). At 0.25–0.05 mol% loadings (Entries 5 and 6), we observed a poor advance in the reaction (5–22% yield) after 24 h. From the outset, Cu catalyst 8 showed good result at 0.25 mol% loading, forging the coupling (22% yield, Entry 5) in spite of longer reaction time (24 h). In general, the contribution of the erNHC ligand to the stabilization of the active Cu species is reflected by the ability of the catalysts to even operate at elevated temperature (100 °C), then complexes 8 and 12 proved their catalytic efficiency (up to 93% yield, 2.5 mol% loading).[34] The nature of the used NHC ligand is also critical. The replacement of the semi rigid biphenyl moiety in (9-Dipp) ligand by a yet flexible diphenyl ether moiety in (10-Dipp) ligand led to a diminished performance at low loadings (0.50 mol%): the coupling catalyzed by 12 gave only 34% product after 2 days.

We next set about assessing the reach of the catalytic activity of novel erNHC-AuBr complex 16 in the cyclosimerization of N-propargylamide 1 (Scheme 4, top).[35] The reaction was promoted by the gold pre-catalyst (2 mol% loading), and AgNTf2 as bromide scavenger. Oxazoline II was obtained (93% yield) as the only product after 8 h, conducting the reaction in

![Figure 10. Visualizing of the steric impact of the top hemisphere of 2 (a) and 8 (b) indicating the buried volume for each quadrant.](Image)

**Table 3. Synthesis of benzo furan 3a by coupling between 2-hydroxy-N-tosylhydrazone and phenylacetylene by using 8 and 12 as catalysts.[36]**

| Entry | [Cu] cat. | [Cu] [mol%][d] | Time [h] | Yield [%][d] |
|-------|----------|---------------|----------|--------------|
| 1     | 2        | 2.5           | 12       | 93[d]        |
| 2     | 12       | 2.5           | 12       | 88[d]        |
| 3     | 8        | 1.25          | 12       | 68[d]        |
| 4     | 8        | 0.50          | 12       | 41           |
| 5     | 8        | 0.25          | 24       | 22           |
| 6     | 8        | 0.05          | 24       | 5            |
| 7     | 12       | 1.25          | 24       | 76[d]        |
| 8     | 12       | 0.50          | 48       | 34[d]        |

[a] Reaction conditions: N-tosylhydrazone (0.10 mmol), phenylacetylene (0.125 mmol), Cs2CO3 (0.3 mmol), CH3CN (2.0 mL), 100 °C, sealed tube. (b) Based on Cu content and with respect to the alkyne. [c] Yields determined by GC-MS using dodecane as internal standard. [d] Isolated yield after column chromatography.
The present work spotlights the first studies on Cu erNHC complexes as catalysts in coupling and cycloisomerization reactions proving their high efficiency and resilience to heating. The positive outcomes disclose their potential use in π-acid catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: buried volume · carbone ligands · copper · N-heterocyclic carbenes · silver

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Commerciably available CuBr was initially employed nonetheless, due to its rapid oxidation in air, a low purity greenish solid prevaled, which resulted in poor yields. To overcome this, we purify CuBr by preparing its rapid oxidation in air, a low purity greenish solid prevailed, which re-