# Synthetic Access to Ring-Expanded N-Heterocyclic Carbene (RE-NHC) Copper Complexes and their Performance in Click Chemistry

Jonathan W. Hall[a], Damien Bouchet[b], Mary F. Mahon[a], Michael K. Whittlesey [a] and Catherine S. J. Cazin[b*]

[a]Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

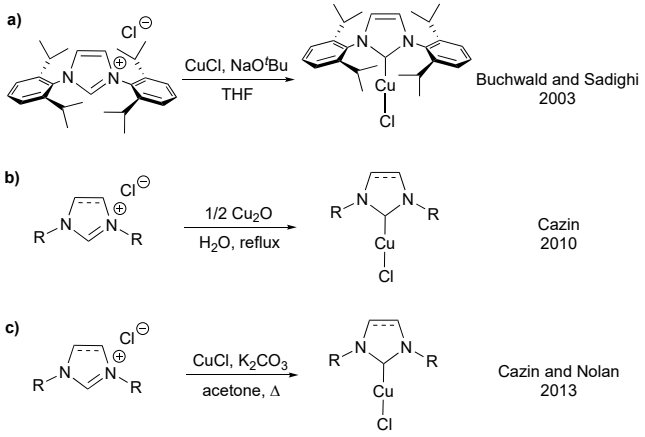
[b]Department of Chemistry and Center for Sustainable Chemistry, Ghent University, Krijgslaan 283 (S3), Ghent 9000, Belgium.

**ABSTRACT:** The facile syntheses of ring-expanded N-heterocyclic carbene (RE-NHC) copper (I) halide complexes are reported. The method makes use of a weak inorganic base in a green solvent and can be carried out in air. Reaction times can be greatly reduced by use of this weak base route under microwave irradiation. The easy access to these complexes permits the evaluation of the catalytic activity and reaction profiling of [Cu(RE-NHC)X] complexes in the Huisgen 1,3 cycloaddition reaction.

## INTRODUCTION

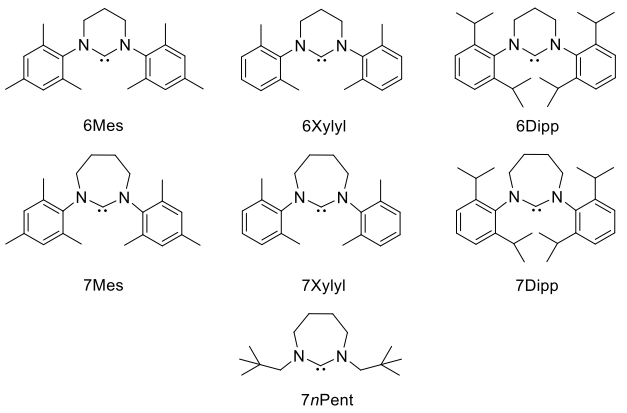
The use of copper-NHC[1] (NHC = N-heterocyclic carbene) complexes has had a significant impact in permitting important developments in organic synthesis.[2] One class that has been a longstanding interest of ours has been the simple [Cu(NHC)(halide)] systems.[3] The synthetic methodology leading to such complexes has evolved significantly since the initial report of [Cu(IPr)Cl] (IPr = *N,N'*-bis[2,6-(diisopropyl)phenyl]imidazol-2-ylidene)[4] by Buchwald and Sadighi in 2003.[5] From generating the free carbene *in sit*u or using an isolated NHC to bind CuCl (Scheme 1, a), the synthetic protocol has increased in simplicity. Initially carried out under anaerobic and water-free conditions, where Schlenk conditions were the norm, the advent of a simpler method making use of the reaction of $Cu_2O$ with an imidazolium salt, has made the [Cu(NHC)Cl] systems readily accessible (Scheme 1, b).[6] This method developed by Cazin is reminiscent of the Lin protocol for the synthesis of [Ag(NHC)Cl] using $Ag_2O$.[7] The more recent *weak base* approach to [Cu(NHC)Cl] where NHC can be readily varied has become the state-of-the-art as it can be carried out in air, using reagent grade sustainable solvents and weak inorganic bases (Scheme 1,c).[8]

Having a general synthetic access is key to the development of chemistry/catalysis revolving around specific compositions. The workhorse in this area has been the [Cu(IPr)Cl] complex, which has enabled fluorination[9] and carboxylation[10] catalysis, in addition to the early examples of catalytic reductions.[5]




**Scheme 1.** Evolution of the synthetic route to [Cu(NHC)Cl] complexes.

The extent of ring-expansion of the basic 5-membered ring NHC in copper mediated catalysis has been much less explored.[11] The reasons for this relative paucity of studies might be linked to the tedious routes to [Cu(RE-NHC)X] complexes. Again, the use of the deprotonation with strong base approach appears most used in this area. It is noteworthy that simple copper complexes bearing members of the RE-NHC class of ligands (Scheme 2) have not yet been reported as accessible using the weak-base method.




**Scheme 2.** Members of the ring-expanded N-heterocyclic carbene (RE-NHC) family employed in his study.

In combining our expertise and mutual interest in Cu-NHC chemistry, we disclose here efforts in this direction and present a practical protocol allowing access to such compounds. The simpler synthetic access permitted here will undoubtedly allow researchers to explore and evaluate the performance of these [Cu(RE-NHC)X] complexes in catalysis.

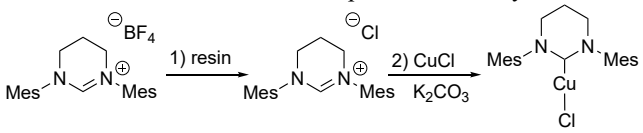
The role of [Cu(NHC)Cl] and congeners has been explored in the copper-mediated azide–alkyne Click (Huisgen) cycloaddition reactions.[12] More recently Díez-González has reported a study involving some RE-NHC complexes which were synthesized using CuBr, CuI and the free carbene, generated by the deprotonation of the RE-NHC salt precursor using a very strong base (KHMDS).[13,14]

Here, in addition to disclosing a facile and practical synthetic route to the [Cu(RE-NHC)X] motif, our studies allow us to probe the role of ring size and of the halide on catalytic activity in the ubiquitously encountered Huisgen cycloaddition reaction.

## RESULTS AND DISCUSSION

The study into the synthesis [Cu(RE-NHC)Cl] chemistry begins with exploring the compatibility of the weak base method with the RE-NHC·HX precursors under conditions previously employed for 5-membered NHCs for copper[8] and other metals.[15-18]

The 6Mes·HX ligand precursor was selected for initial screening and we rapidly found that the 6Mes·HCl salt is best used in these conditions. The 6Mes·HCl is obtained from the 6Mes·$HBF_4$ analogue by anion exchange using an Amberlite resin (Scheme 3 and ESI for details). Under an argon atmosphere and upon heating at 60°C in an oil bath, the reaction proceeds to yield 61% of the desired product **1** after 20 h in acetone. Conducting the reaction under microwave heating (60°C) reduces the reaction time to 2 h and provides a 52% yield.



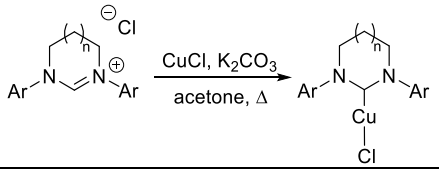

Mes = 2,4,6-$Me_3C_6H_2$

**Reaction conditions:** 1) Amberlite® IRA402 chloride resin, MeOH, r.t., 16h. 2) CuCl (100 mg), $K_2CO_3$ (2 equiv), acetone (2 mL), 60°C.

**Scheme 3.** Initial weak base reaction conditions leading to [Cu(6Mes)Cl] (**1**).

We viewed the microwave approach as the most rapid to yield material for catalytic studies. The microwave approach using the weak base in acetone was then tested on various ring-expanded azolium chlorides and results of reactions performed on 100 mg scale of the azolium chloride are presented in Table 1. Noteworthy are the lower yields obtained and/or longer reaction times required when sterically more congested substituents are present on the azolium nitrogens (e.g. 7Dipp·HCl) and when larger ring sizes are employed (Table 1, entries 4-7).

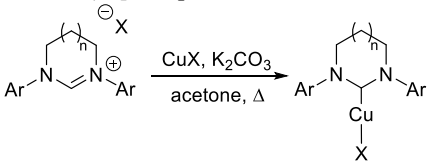
**Table 1.** Scope of azolium chlorides used to yield [Cu(NHC)Cl] complexes **1**-**7**.[a]




| Entry | NHC·HCl | Time (h) | NMR Conv. (%) | Isolated yield (%) |
|---|---|---|---|---|
| 1 | 6Mes | 1.5 | 94 | **1** (82) |
| 2 | 6Xylyl | 1.5 | 99 | **2** (98) |
| 3 | 6Dipp | 1.5 | 88 | **3** (73) |
| 4 | 7Mes | 2.5 | 94 | **4** (77) |
| 5 | 7Xylyl | 2.5 | 95 | **5** (58) |
| 6 | 7Dipp | 2.5 | 54 | **6** (50) |
| 7 | 8Mes | 6 | 95 | **7** (36) |

[a]Reaction conditions: NHC·HCl (100 mg), CuCl (1.2 equiv.), $K_2CO_3$ (3 equiv.), acetone (2 mL), MW 80°C.

**Table 2.** Scope of azolium halides and copper source used to yield [Cu(RE-NHC)X] complexes **8**-**11**.[a]




| Entry | NHC·HX | Cu Source | Product | Time (h) | Isolated yield (%) |
|---|---|---|---|---|---|
| 1 | 6Mes·HCl | CuI | [Cu(6Mes)I] **8** | 6 | 54 |
| 2 | 6Mes·HBr | CuCl | [Cu(6Mes)Br] **9** | 2.5 | 77 |
| 3 | 6Dipp·HBr | CuCl | [Cu(6Dipp)Br] **10** | 2.5 | 98 |
| 4 | 6Mes·HBr | CuI | [Cu(6Mes)I] **8** | 2.5 | 37 |
| 5 | 7Mes·HI | CuCl | [Cu(7Mes)I] **11** | 6 | 18 |
| 6 | 7Dipp·HI | CuCl | - | 6 | - |

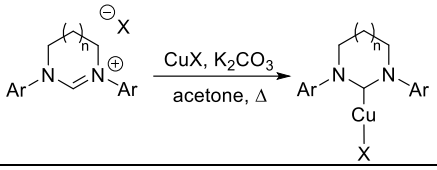
[a]Reaction conditions: NHC·HCl (100 mg), CuCl (1.2 equiv), $K_2CO_3$ (3 equiv), acetone (2 mL), MW 80°C.

The role and effect of varying the identity of the counterion associated with the azolium salt and the copper source were next examined in smaller scale reactions (Table 2). The reactivity obtained is in agreement with previous observations made on 5-membered ring carbene Cu complex formation[8] and points towards a mechanism involving a cuprate intermediate of the type [NHC·H][CuXX′]. A combination of halide *trans* effect and energy associated with KX formation (salt precipitation) account for the products obtained in reactions involving mixed halides.

As can be seen, the method proves effective to various degrees as a function of the copper source and of the azolium ring size and associated counterion. The larger size RE-NHC complexes are again troublesome to form and/or isolate.

In order to obtain enough of the materials synthesized using the weak base method and to benefit from an economy of scale, large scale reactions were launched on a gram scale of the azolium salts. This also serves as proof of the scalability of the synthetic route. Results of these larger scale reactions are summarized in Table 3. Overall, larger scale reactions afford desired materials in modest to very good yields. The poorer yield obtained for [Cu(6Mes)I] (**8**, entry 4) is associated with the poor solubility of the product in the reaction medium, necessitating extraction from benzene, which is not a desirable solvent (carcinogen).

**Table 3.** Larger scale reactions leading to [Cu(RE-NHC)X] complexes.[a]




| Entry | NHC·HX | X | Product | Time (h) | Isolated Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | 6Mes·HCl | Cl | [Cu(6Mes)Cl] **1** | 2 | 78 |
| 2 | 7Mes·HCl | Cl | [Cu(7Mes)Cl] **4** | 10 | 64 |
| 3 | 6Mes·HBr | Cl | [Cu(6Mes)Br] **9** | 4 | 82 |
| 4 | 6Mes·HBr | I | [Cu(6Mes)I] **8** | 20 | 64 |

[a]Reaction conditions: NHC·HX (1 g), CuX (1.2 equiv.), $K_2CO_3$ (3 equiv.), acetone (10 mL), MW 80°C. [b]Yields are isolated and average of two reactions.

We had previously clearly demonstrated that 5-membered imidazol-based NHC are initially partners in rapidly forming an imidazolium cuprate compound *via* simple mixing of solutions of the azolium and copper source in solution[8] or in the solid state by simple grinding. We have recently expanded on these observations and confirmed in a study dealing with mechanochemical synthesis that the weak base route can be simply applied using grinding by ball milling.[19]

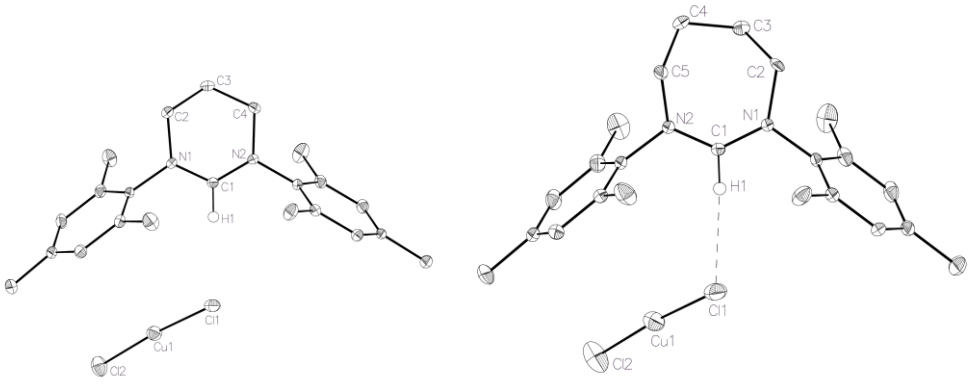
In our initial mechanistic studies, the existence of cuprates shed light on the intermediacy of these ionic compounds along the weak base assisted synthesis. We have also found this to be the case for the RE-NHC systems. By simply mixing the azolium salts and the copper source in the absence of the base, the cuprates are readily formed. A number of these were unambiguously characterized by single crystal X-ray diffraction, with four examples illustrated in Figure 1. These, all show hydrogen bonding of the azolium C-H to the $[CuCl_2]^-$ anion. The donor (C)-acceptor (Cl) distances in [6MesH][$CuCl_2$] (**13**), [7MesH][$CuCl_2$] (**15**), and [7XylylH][$CuCl_2$] (**16**) are in the range 3.4388(19)-3.476(3) Å, noticeably shorter than that in N-alkyl derivative [$7^n$Pent][$CuCl_2$] (**17**; 3.560(3) Å).

From a mechanistic perspective, the synthetic route leading to the neutral complexes is identical to the 5-membered congeners. We propose initial formation of the cuprate azolium that is converted into the neutral product *via* a concerted metalation deprotonation (CMD) mechanism.[18] When the cuprate is reacted with the weak base in acetone or when all components are mixed together in the MW reactor, the outcome pleasingly yields the neutral [Cu(RE-NHC)X] complexes. Full characterisation of these is reported in the experimental section along with spectroscopic and elemental analytical data. The compounds are microcrystalline materials that could easily produce single crystals suitable for diffraction studies. The X-ray crystal structures of complexes **1**, **4**, **5** and **7** are presented in Figure 2 (see ESI for structures of **8** and **9**). The solid-state structures highlight one of the significant features of RE-NHC ligands, namely, the variation of NCN angle with ring size (e.g. **1**, 117.5(2)°;[25] **4**, 118.7(6), 120.5(5)°; **7**, 123.05(16)°).

To test the catalytic performance of these RE-NHC complexes, the Huisgen reaction was selected as it has been studied extensively using 5-membered imidazole-based systems.[2] Having material in hand in larger amounts allowed us to probe numerous factors influencing the catalytic performance of this motif and the influence of its structural diversity. Simple synthetic access to materials is key in order to conduct such a study. We began this section of the investigation by comparison of (SIMes)CuCl (**18**), 6Mes complex **1** and 7Mes complex **4** in the copper mediated alkyne-azide cyclisation (CuAAC) reaction for three different combinations of substrates.

Initially exploring the ring-size influence on catalytic performance of the CuAAC of azidoheptane and phenylacetylene (eq 1, Figure 3a), we note that the order of reactivity decreases with decreasing ring size and is found to be 7>6>5 within the substituted mesityl series. This order was found to reverse when the azide was changed to phenylazide (eq 2 and 3, Figures 3b, c). Of note was that after 300 min reaction time, the coupling of phenylazide and 1-octyne produced the product in nearly the same yield with all three catalysts (eq 3, Figure 3c).

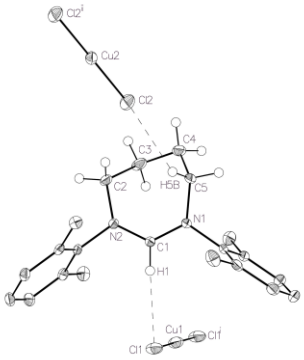
Reaction profiling of a series of [Cu(6Mes)X] (X= F, Cl, Br and I) complexes permits the first study of the entire halogen group bound to copper, following the recent disclosure of a synthetic route to [Cu(6Mes)F] (**19**).[3b] For the CuAAC of azidoheptane and phenylacetylene (eq 1, Figure 4a), all complexes are fairly effective, with the exception of [Cu(6Mes)Cl] (**1**), which is more sluggish, yet still active enough to reach complete conversion to the triazole in some 300 min. [Cu(6Mes)I] (**8**) and the fluoro complex, Cu(6Mes)F (**19**), work best and reach completion in 75 min. The superior behaviour of the iodo complex had previously been noted for the [Cu(IPr)I] complex.[13,19] Both **19** and **8** demonstrate the best activity in the other systems (eq 2 and 3, Figures 4b, c), while Cu(6Mes)Br (**9**) and **1** continued to perform more sluggishly to afford the order F ≈ I > Br > Cl. Of note is the significantly enhanced activity of **19** at an elevated temperature (45 °C) for the CuAAC of phenyl azide and 1-octyne (Figure 4c).



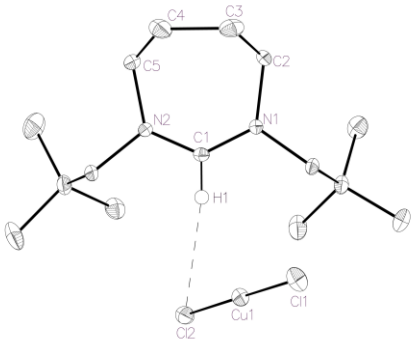

**13**




**15**




**16**




**17**

**Figure 1.** Molecular structures of RE-azolium cuprates **13**, **15**, **16** and **17**. Ellipsoids are represented at 30% probability. Hydrogens, with the exception of H1 (in all cases) and those on the tetrahydrodiazepin-2-ylidene ring (in **16**), together with disorder in **15**, have been omitted for clarity. Symmetry operations in **16**: [i] 3/2 − *x*, 3/2 − *y*, ½ − *z* ; [ii] ½ − *x*, *y*, 1 − *z*.

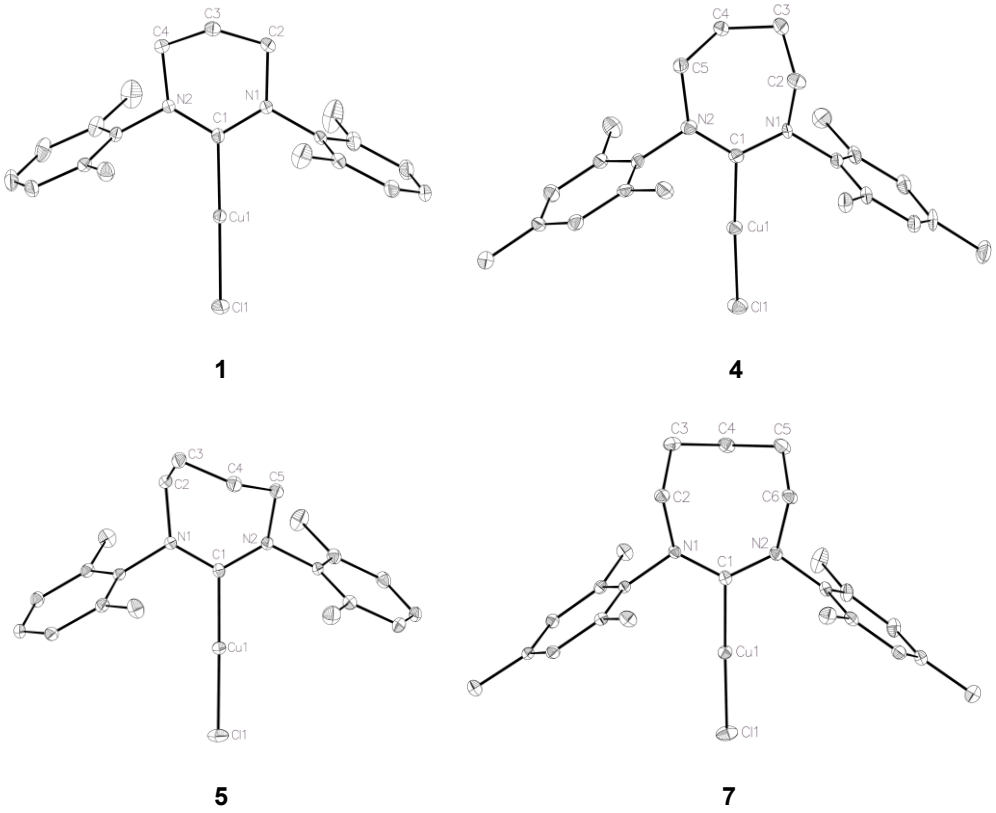



**Figure 2.** Molecular structures of [Cu(RE-NHC)Cl] complexes **1, 4**, **5** and **7**. Ellipsoids are represented at 30% probability and, in all cases, hydrogens have been omitted for clarity. For **4**, only one of the two molecules in the asymmetric unit of the crystal structure is shown.

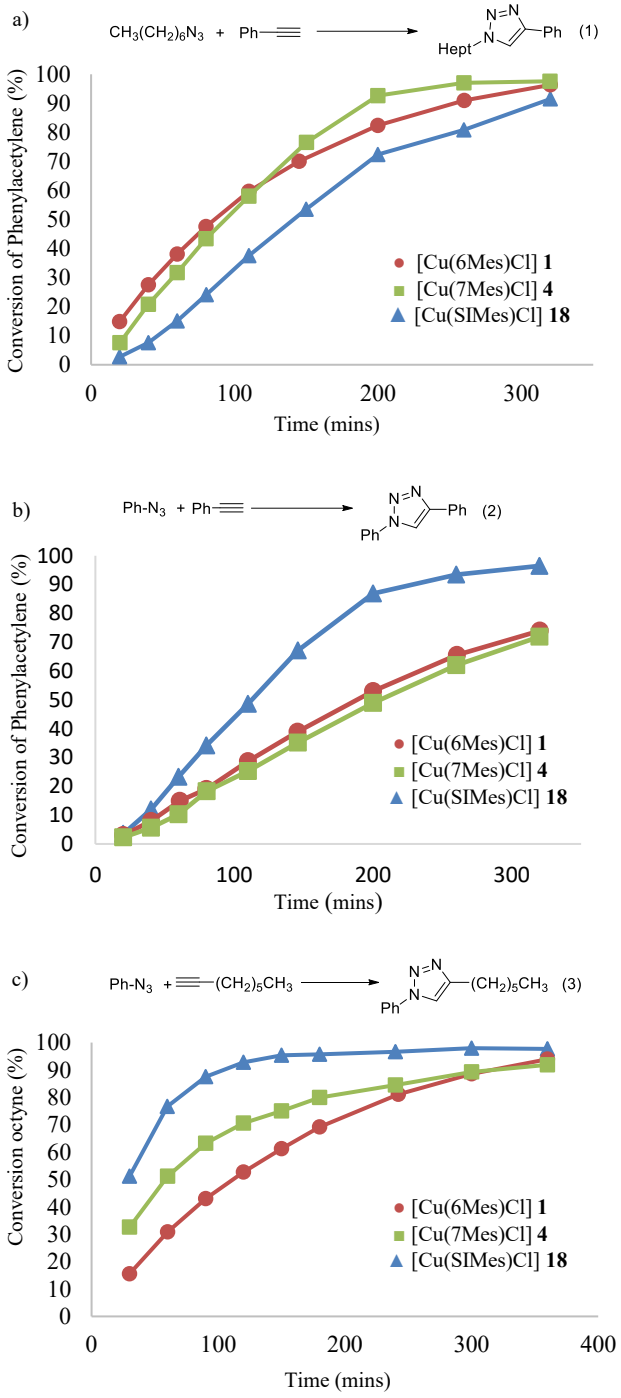



**Figure 3.** Kinetic profiles of [3+2] cycloaddition of a) azidoheptane and phenylacetylene (room temperature), b) phenylazide and phenylacetylene (room temperature), and c) azidobenzene and 1-octyne (45°C) by **1**, **4** and **18**. Lines are visual aids and not curve fits. Each point represents an average of at least two independent reactions quenched at that time.

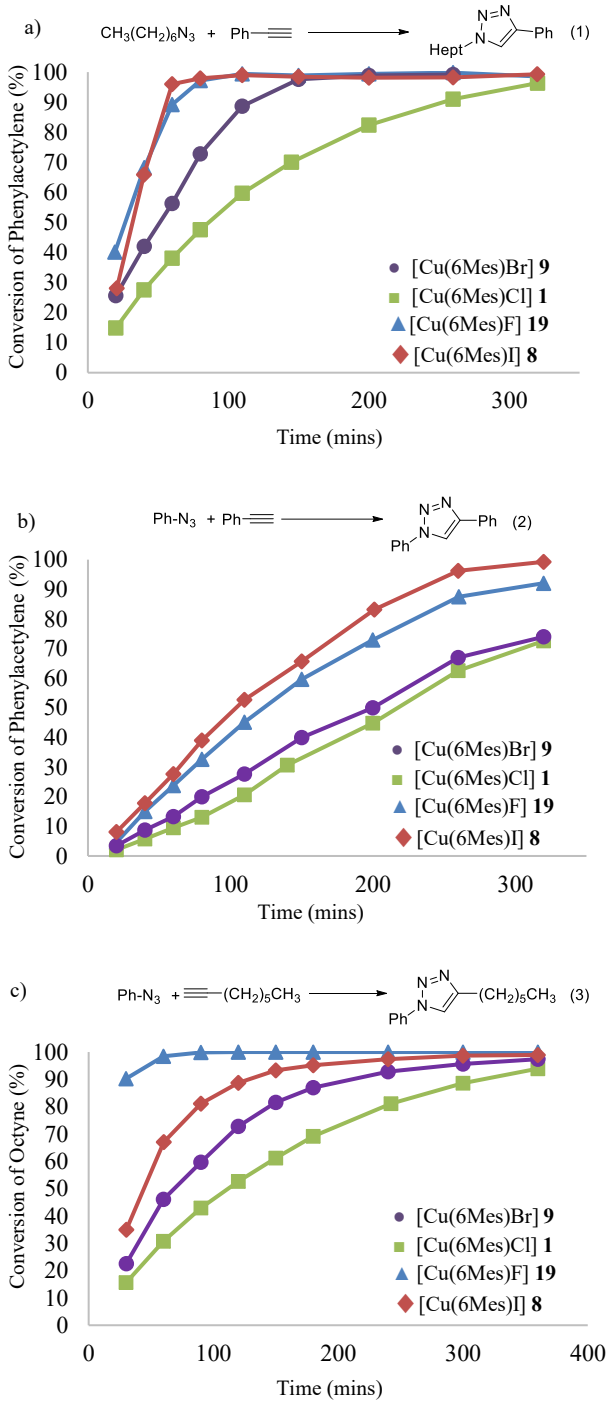



**Figure 4.** Kinetic profiles of [3+2] cycloaddition of a) azidoheptane and phenylacetylene (room temperature), b) phenylazide and phenylacetylene (room temperature), and c) azidobenzene and 1-octyne (45°C) by **1**, **8**, **9** and **19**. Lines are visual aids and not curve fits. Each point represents an average of at least two independent reactions quenched at that time.

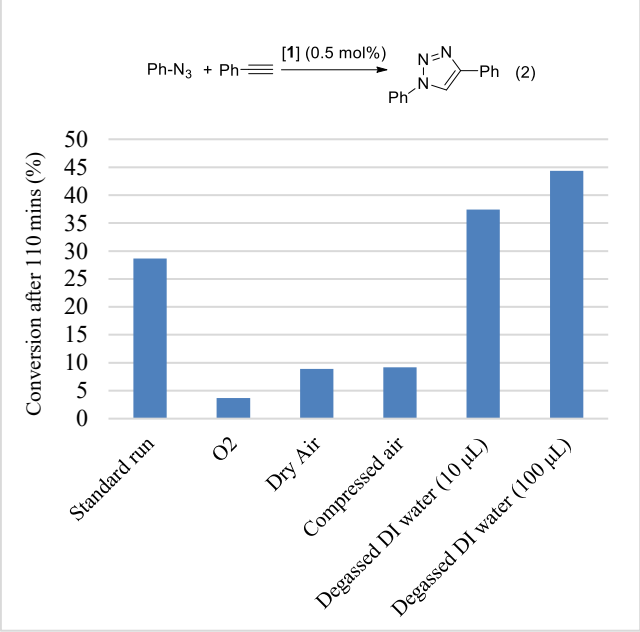



**Figure 5.** Conversions (after 110 min) in the room temperature [3+2] cycloaddition of phenylazide (100 mol%) and phenylacetylenene (1 mmol) catalysed by **1** (0.5 mol%). Addition of substrates occurred after 10 mins of the catalytic run. Average of 2 runs.

Figures 3 and 4 illustrate quite clearly that catalytic performance of the different [(RE-NHC)CuX] catalysts is a function of substrate. Our studies also revealed that even relatively subtle changes to reaction conditions affected the activity of an individual catalyst upon a single reaction. We note that replacing the standard blanket of argon used for the CuAAC of phenyl azide and phenylacetylene by an atmosphere of oxygen, dry air or compressed air had a deleterious impact on the efficiency of the reaction when catalysed by **1** (Figure 5). However, upon introducing even a few microlitres of water into the reaction mixture (Ar atmosphere) lead to enhancement of the reaction. While it is known that on-water effects can influence reactivity, the beneficial impact of such small amounts of water as shown in Figure 5 implies that even small differences in the dryness of azide and alkyne substrates could disturb activity, making meaningful comparisons across different [(NHC)CuX] complexes difficult.

## SUMMARY AND CONCLUSIONS

The weak base synthetic route leading to [Cu(NHC)X] complexes has been shown to be fully compatible with the [Cu(RE-NHC)X] architecture. Here the use of sustainable reagents and green solvents are noteworthy. The simple synthetic route will surely encourage efforts in the exploration of chemistry mediated by these now readily accessible complexes. The existence of imidazolium cuprates intermediates is again confirmed and mimics finding found for 5-membered congeners. In terms of catalysis, we have explored the CuAAC reaction but this time investigating three different reactions and find there is no universal catalysts for the Huisgen reaction. Some generalisations can be drawn but realistically, ease of access not only to the final complex but to the azolium precursor must be considered before finalizing catalyst selection.

## EXPERIMENTAL SECTION

**General considerations**: All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques unless otherwise stated. Reagent grade $K_2CO_3$ was used after being left at 140°C overnight and ground in the glovebox to a fine powder. Solvents were purified using an MBraun SPS solvent system (hexane, $Et_2O$, pentane), under a nitrogen atmosphere from sodium benzophenone ketyl (benzene), with Drierite™ (acetone) or standing over activated 3 Å molecular sieves (MeCN). For catalytic studies, reagent grade acetone (Sigma-Aldrich) was used as received. NMR solvents were dried and vacuum transferred ($C_6D_6$ from K, $CD_2Cl_2$/$CDCl_3$ from $CaH_2$). NMR spectra were recorded at 298 K on Bruker Avance 300, 400 and 500 or Agilent 500 MHz NMR spectrometers and referenced to solvent signals as follows: benzene ($^1$H, δ 7.16; $^{13}$C{$^1$H}, δ 128.0), $CD_2Cl_2$ (δ 5.32; δ 54.0), $CDCl_3$ (δ 7.24; δ 77.2). All $^{13}$C{$^1$H} resonances were singlets. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK.

N,N'-dimesitylformamidine, 6Mes·HBr, 6Dipp·HBr, 6Xylyl·HBr, 7Mes·HI, 7Dipp·HI, 7Xylyl·HI and their corresponding $BF_4$ salts were all synthesised following published literature.[21] 7$^n$Pent·HI also following published literature.[22] Salt exchanges to form RE-NHC·HCl were carried out following a published procedure.[23]

General note: The RE-NHC·HCl salts in most cases are extremely hygroscopic. With excessive heat (ca 140 °C), Amberlite IRA402 chloride resin gave a by-product during attempted conversions of tetrafluoroborate salts to their chloride analogues. Thus, the resin was dried instead on a rotary evaporator until the beads fell fluidly. Although this approach did not completely dry the beads, it allowed for RE-NHC·HCl salts to be obtained with less difficulty.

**6Mes·HCl**.$^1$H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 1H, NC*H*N), 6.90 (s, 4H, $C_6Me_3H_2$), 4.13 (t, $^3J_{HH}$ = 5.8 Hz, 4H, NC$H_2$), 2.61 (quint, $^3J_{HH}$ = 5.8 Hz, 2H, $NCH_2CH_2$), 2.30 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.23 (s, 6H, p-*Me*-$C_6Me_3H_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): δ 153.8 (N*C*HN), 140.6, 136.6, 134.5, 130.2, 47.2, 21.1, 19.8, 18.1.

**6Xylyl·HCl**. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.65 (s, 1H, NC*H*N), 7.29-7.24 (m, 2H, p-*H*-$C_6Me_2H_3$; overlap with residual $CHCl_3$ peak), 7.17-7.15 (m, 4H, m-*H*-$C_6Me_2H_3$), 4.31 (t, $^3J_{HH}$ = 5.7 Hz, 4H, NC$H_2$), 2.67 (quint, $^3J_{HH}$ = 5.7 Hz, 2H, $NCH_2CH_2$), 2.43 (s, 12H, $C_6Me_2H_3$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): δ 153.5 (N*C*HN), 139.0, 135.0, 130.5, 129.7, 47.1, 19.7, 18.2.

**6Dipp·HCl**. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.54 (s, 1H, NC*H*N), 7.43 (m, 2H, p-*H*-$C_6{}^i Pr_2H_3$), 7.25 (d, $^3J_{HH}$ = 7.8 Hz, 4H, p-*H*-$C_6{}^i Pr_2H_3$; overlaps with residual $CHCl_3$ peak), 4.27 (t, $^3J_{HH}$ = 5.7 Hz, 4H, NC$H_2$), 3.05 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, C*H*Me$_2$), 2.83 (quint, $^3J_{HH}$ = 5.7 Hz, 2H, $NCH_2CH_2$), 1.38 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$).$^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): δ 153.0 (N*C*HN), 145.8, 136.0, 131.3, 125.3, 49.3, 29.0, 25.0, 24.9, 19.5.

**7Mes·HCl**. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.22 (s, 1H, NC*H*N), 6.94 (s, 4H, $C_6Me_3H_2$), 4.67 (m, 4H, NC$H_2$), 2.57 (quint, $^3J_{HH}$ = 5.6 Hz, 4H, $NCH_2CH_2$), 2.41 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.27 (s, 6H, o-*Me*-$C_6Me_3H_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): δ 158.0 (N*C*HN), 140.3, 139.6, 133.9, 130.3, 54.8, 25.4, 21.1, 18.5.

**7Xylyl·HCl**. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.27 (s, 1H, NC*H*N), 7.22 (dd, $^3J_{HH}$ = 8.7, 6.3 Hz, 2H, p-*H*-$C_6Me_2H_3$), 7.17-7.11 (m, 4H, m-*H*-$C_6Me_2H_3$), 4.71 (m, 4H, NC$H_2$), 2.59 (m, 4H, $NCH_2CH_2$), 2.47 (s, 12H, $C_6Me_2H_3$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): δ 157.8 (N*C*HN), 141.8, 134.3, 130.3, 129.8, 54.8, 25.5, 18.6.

**7Dipp·HCl**. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 8.4, 7.2 Hz, 2H, p-*H*-$C_6{}^i Pr_2H_3$), 7.25-7.22 (m, 5H, *m*-H-$C_6{}^i Pr_2H_3$ + NC*H*N), 4.74 (m, 4H, NC$H_2$), 3.23 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*Me$_2$), 2.64 (m, 4H, $NCH_2CH_2$), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): δ 157.1 (N*C*HN), 145.0, 139.1, 131.0, 125.4, 56.2, 29.1, 25.2, 25.1, 24.8.

**7$^n$Pent·HCl**. $^1$H NMR (500 MHz, $CDCl_3$): δ 9.37 (s, 1H, NC*H*N), 3.75 (m, 4H, $NCH_2CH_2$), 3.65 (s, 4H, $NCH_2CMe_3$), 2.19 (m, 4H, $NCH_2CH_2$), 1.06 (s, 18H, $NCH_2CMe_3$). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$): 162.7 (N*C*HN), 69.6, 52.7, 33.4, 27.8, 25.4.

**8Mes·HCl**. $^1$H NMR (300 MHz, $CDCl_3$): δ 7.38 (s, 1H, NC*H*N), 6.93 (s, 4H, $C_6Me_3H_2$), 4.86 (br s, 4H, $NCH_2$), 2.41 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.35-2.21 (s, 10H, p-*Me*-$C_6Me_3H_2$ + $NCH_2CH_2$), 2.17-2.06 (m, 2H, $NCH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 158.1 (N*C*HN), 142.0, 140.1, 133.7, 130.4, 53.8, 28.4, 21.0, 18.8.

**Synthesis of 8Mes·HBr**. 1,5-Dibromopentane (486 μL, 3.57 mmol), N,N'-dimesitylformimidamide (1.00g, 3.57 mmol), $K_2CO_3$ (493 mg, 3.57 mmol) and MeCN (10 mL) were added to a 10-20 mL microwave vial, which was sealed and heated in a microwave reactor at 110 °C for 12 h. The suspension was then filtered, washed with MeCN (2 x 5 mL) and dried under vacuum to afford an oil. $Et_2O$ was added with vigorous stirring to the oil to yield a white precipitate. This was recrystallised from $CH_2Cl_2$/pentane to yield an off-white powder (843 mg, 55% yield). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.38 (s, 1H, NC*H*N), 6.93 (s, 4H, $C_6Me_3H_2$), 4.85 (br s, 4H, $NCH_2CH_2$), 2.41 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.30-2.26 (m, 10H, p-*Me*-$C_6Me_3H_2$ + $NCH_2CH_2$), 2.15-2.10 (m, 2H, $NCH_2CH_2CH_2$). ESI-TOF MS: $[M]^+$ *m*/*z* = 349.2643 (theoretical *m*/*z* = 349.2644).[24]

**General synthetic procedure for [Cu(RE-NHC)X].** In a glovebox, NHC·HX (0.3 mmol), CuCl (0.36 mmol, 1.2 equiv) and acetone (2 mL) were loaded into a 2-5 mL microwave vial. The mixture was stirred for 5 min before the addition of $K_2CO_3$ (3 equiv) and then sealed/capped. For larger scale reactions, the same procedure was adopted using NHC·HX (1.00 g), CuCl (1.1 equiv) and acetone (10 mL) in a 10-20 mL microwave vial. The vials were then heated in a microwave reactor for the allocated time and then reloaded into the glovebox, whereupon the suspension was filtered through Celite®. The filtrate was reduced to dryness, the residue extracted into $CH_2Cl_2$ and the solution filtered through a silica plug to afford, upon concentrating in vacuo, a white precipitate. Crystalline samples of all [Cu(RE-NHC)X] complexes were obtained from $CH_2Cl_2$/pentane unless otherwise stated. [(6Mes)CuI] (**9**) and [(7Mes)CuI] (**11**) were extracted with $C_6H_6$ before filtering through silica with $CH_2Cl_2$. Once purified, these compounds only redissolved into solution at elevated temperatures.

**[Cu(6Mes)Cl] (1).** As for the general synthetic procedure with 6Mes·HCl (100 mg, 0.28 mmol), CuCl (33 mg, 0.34 mmol) and $K_2CO_3$ (116 mg, 0.84 mmol) to afford **1** as a white powder in 82% yield (96 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 7.00 (s, 4H, $C_6Me_3H_2$), 3.35 (t, *J* = 5.9 Hz, 6H, $NCH_2$), 2.32-2.29 (m, 20H, $C_6Me_3H_2$ + $NCH_2CH_2$). $^1$H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 4H, $C_6Me_3H_2$), 3.36 (m, 4H, $NCH_2$), 2.31 (m, 2H, $NCH_2CH_2$), 2.29-2.26 (m, 18H, $C_6Me_3H_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.0 (N*C*N), 142.1, 138.2, 134.6, 130.0, 44.3, 21.2, 18.1. Anal. Calcd. (%) for $C_{22}H_{28}ClCuN_2$: C 62.99, H 6.73, N 6.68; Found C 62.32, H 6.69, N 6.56. Data match those found in the literature.[25]

**[Cu(6Xylyl)Cl] (2).** As for **1** with 6Xylyl·HCl (100 mg, 0.31 mmol), CuCl (36 mg, 0.37 mmol) and $K_2CO_3$ (126 mg, 0.92 mmol) to give **2** as a white powder in 98% yield (117 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 7.24 (dd, $^3J_{HH}$ = 8.6, 6.3 Hz, 2H, p-*H*-$C_6Me_2H_3$), 7.19 (d, $^3J_{HH}$ = 7.4 Hz, 4H, m-*H*-$C_6Me_2H_3$), 3.41 (t, $^3J_{HH}$ = 5.9 Hz, 4H, $NCH_2$), 2.39-2.34 (m, 14H, $C_6Me_2H_3$ + $NCH_2CH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): δ 200.7 (N*C*N), 144.9, 135.6, 129.3, 128.7, 44.5, 21.1, 18.3. Anal. Calcd. (%) for $C_{23}H_{30}ClCuN_2$: C 61.37, H 6.18, N 7.16; Found C 61.48, H 6.14, N 7.27.

**[Cu(6Dipp)Cl] (3).** As for **1** with 6Dipp·HCl (100 mg, 0.25 mmol), CuCl (29 mg, 0.30 mmol) and $K_2CO_3$ (102 mg, 0.74 mmol) to give **3** as a white powder in 73% yield (90 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.36 (t, $^3J_{HH}$ = 7.7 Hz, 2H, p-*H*-$C_6{}^iPr_2H_3$), 7.21 (d, $^3J_{HH}$ = 7.7 Hz, 4H, m-*H*-$C_6{}^iPr_2H_3$), 3.42 (m, 4H, $NCH_2$), 3.06 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me$_2$), 2.37 (m, 2H, $NCH_2CH_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.31 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.0 (N*C*N), 145.6, 141.6, 129.6, 124.9, 46.4, 28.8, 25.0, 24.8, 20.7. Data match those found in the literature.[26]

**[Cu(7Mes)Cl] (4).** As for **1** with 7Mes·HCl (100 mg, 0.27 mmol), CuCl (32 mg, 0.32 mmol) and $K_2CO_3$ (112 mg, 0.81 mmol) to give **4** as a white powder in 77% yield (90 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 6.98 (s, 4H, $C_6Me_3H_2$), 3.86 (m, 4H, $NCH_2$), 2.37 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.32-2.26 (m, 10H, p-*Me*-$C_6Me_3H_2$ + $NCH_2CH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): δ 210.2 (N*C*N), 144.9, 138.2, 134.8, 130.0, 52.9, 26.0, 21.1, 18.7. Anal. Calcd. for $C_{20}H_{24}ClCuN_2$: C 63.73, H 6.98, N 6.46, Found: C 63.65, H 7.05, N 6.55.

**[Cu(7Xylyl)Cl] (5).** As for **1** with 7Xylyl·HCl (100 mg, 0.29 mmol), CuCl (35 mg, 0.30 mmol) and $K_2CO_3$ (121 mg, 0.88 mmol) to give **5** as a white powder in 58% yield (69 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 7.25-7.12 (m, 6H, $C_6Me_2H_3$), 3.91 (m, 4H, $NCH_2$), 2.42 (s, 12H, $C_6Me_2H_3$), 2.32 (m, 4H, $NCH_2CH_2$) $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): δ 210.7 (N*C*N), 147.3, 135.2, 129.5, 128.5, 52.8, 26.1, 18.9. Anal. Calcd. (%) for $C_{23}H_{30}N_2ClCu$: C 62.21, H 6.46, N 6.19; Found: C 62.02, H 6.36, N 6.87.

**[Cu(7Dipp)Cl] (6).** As for **1** with 7Dipp·HCl (100 mg, 0.22 mmol), CuCl (26 mg, 0.26 mmol) and $K_2CO_3$ (91 mg, 0.66 mmol) to give **6** as a white powder in 50% yield (57 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 7.37 (t, *J* = 7.7 Hz, 2H, p-*H*-$C_6{}^iPr_2H_3$), 7.24 (d, $^3J_{HH}$ = 7.7 Hz, 4H, m-*H*-$C_6{}^iPr_2H_3$), 3.97 (m, 4H, $NCH_2$), 3.27 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me$_2$), 2.33 (quint, $^3J_{HH}$ = 2.7 Hz, 4H, $NCH_2CH_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): δ 210.3 (N*C*N), 145.6, 144.6, 129.2, 125.1, 54.4, 29.2, 25.6, 24.9, 24.7. $^1$H NMR (500 MHz, $C_6D_6$): δ 7.17-7.14 (m, p-*H*-$C_6{}^iPr_2H_3$, 2H; partially obscured by $C_6D_5H$), 7.05 (d, $^3J_{HH}$ = 7.8 Hz, 4H, m-*H*-$C_6{}^iPr_2H_3$), 3.26 (m, 4H, $NCH_2$), 3.18 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me$_2$), 1.61 (m, 4H, $NCH_2CH_2$), 1.48 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$). Data match those found in the literature.[26]

**[Cu(8Mes)Cl] (7).** As for **1** with 8Mes·HCl (100 mg, 0.26 mmol), CuCl (31 mg, 0.31 mmol) and $K_2CO_3$ (108 mg, 0.78 mmol) to give **7** as a white powder in 36% yield (42 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 6.96 (s, 4H, $C_6Me_3H_2$), 4.04 (t, $^3J_{HH}$ = 6.4 Hz, 4H, $NCH_2$), 2.37 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.29 (s, 6H, p-*Me*-$C_6Me_3H_2$), 2.12-1.96 (m, 8H, $NCH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): δ 208.4 (N*C*N; via HMBC), 147.2, 137.9, 134.4, 130.2, 52.2, 29.4, 22.0, 21.1, 19.2. Anal. Calcd. (%) for $C_{24}H_{32}N_2ClCu$: C, 64.41; H, 7.42; N, 6.25; Found: C, 63.76; H, 7.21; N, 6.24.

**[Cu(6Mes)I] (8).** As for **1** with 6Mes·HCl (100 mg, 0.28 mmol), CuI (64 mg, 0.34 mmol) and $K_2CO_3$ (116 mg, 0.84 mmol) to give **8** as a white powder in 54% yield (77 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 4H, $C_6Me_3H_2$), 3.36 (t, $^3J_{HH}$ = 5.9 Hz, 4H, $NCH_2$), 2.32 (quint, $^3J_{HH}$ = 6.1 Hz, 2H, $NCH_2CH_2$), 2.28 (s, 18H, $C_6Me_3H_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 202.9 (N*C*N), 141.7, 138.3, 134.7, 129.9, 44.4, 21.2, 21.0, 18.2. $^1$H NMR (500 MHz, $C_6D_6$): δ 6.75 (s, 4H, $C_6Me_3H_2$), 2.48 (m, 4H, $NCH_2$), 2.12 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.08 (s, 6H, p-*Me*-$C_6Me_3H_2$), 1.38-1.27 (m, 2H, $NCH_2CH_2$). $^{13}C$ NMR (126 MHz, $C_6D_6$): δ 203.6 (N*C*N; via HMBC), 142.1, 138.2, 134.7, 130.1, 43.8, 21.1, 20.6, 18.1. Anal. Calcd. (%) for $C_{22}H_{28}N_2ICu$: C 51.72, H 5.52, N 5.48; Found C 51.70, H 5.52, N 5.54. Data match those found in the literature.[13]

**[Cu(6Mes)Br] (9).** As for **1** with 6Mes·HBr (100 mg, 0.25 mmol), CuCl (30 mg, 0.30 mmol) and $K_2CO_3$ (103 mg, 0.75 mmol) to give **9** as a white powder in 77% yield (89 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 6.99 (s, 4H, $C_6Me_3H_2$), 3.35 (m, 4H, $NCH_2$), 2.34-2.27 (m, 20H, $C_6Me_3H_2$ + $NCH_2CH_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): δ 201.6 (N*C*N; via HMBC), 142.5, 138.6, 135.2, 130.0, 44.7, 21.2, 21.2, 18.2. $^1$H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 4H, $C_6Me_3H_2$), 3.36 (t, $^3J_{HH}$ = 5.9 Hz, 4H, $NCH_2$), 2.35-2.29 (m, 2H, $NCH_2CH_2$), 2.28 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.27 (s, 6H, p-*Me*-$C_6Me_3H_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 201.5 (N*C*N), 142.0, 138.2, 134.6, 130.0, 44.3, 21.2, 21.0, 18.1. Anal. Calcd. (%) for $C_{22}H_{28}N_2BrCu$: C 56.96, H 6.08, N 6.04; Found C 57.09, H 6.10, N 5.96. Data match those found in the literature.[13]

**[Cu(6Dipp)Br] (10).** As for **1** with 6Dipp·HBr (100 mg, 0.21 mmol), CuCl (25 mg, 0.25 mmol) and $K_2CO_3$ (86 mg, 0.62 mmol) to give **10** as a white powder in 89% yield (100 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 7.41 (t, $^3J_{HH}$ = 7.7 Hz, 2H, p-*H*-$C_6{}^iPr_2H_3$), 7.25 (d, $^3J_{HH}$ = 7.8 Hz, 4H, m-*H*-$C_6{}^iPr_2H_3$), 3.42 (m, 4H, $NCH_2$), 3.08 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me$_2$), 2.36 (m, 2H, $NCH_2CH_2$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.31 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): δ 201.3 (N*C*N), 146.2, 142.0, 129.6, 125.0, 46.7, 29.0, 25.0, 24.7, 20.8. Anal. Calcd. (%) for $C_{28}H_{40}N_2BrCu·CH_2Cl_2$: C, 55.03 H, 6.69; N, 4.43; Found: C, 55.54; H, 6.74; N, 4.41.

**[Cu(7Mes)I] (11).** As for **1** with 7Mes·HCl (100 mg, 0.23 mmol), CuI (53 mg, 0.28 mmol) and $K_2CO_3$ (96 mg, 0.69 mmol) to give **11** as a white powder in 18% yield (22 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 6.92 (s, 4H, $C_6Me_3H_2$), 3.87 (m, 4H, $NCH_2$), 2.35 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.31 (m, 4H, $NCH_2CH_2$), 2.27 (s, 6H, p-*Me*-$C_6Me_3H_2$). $^1$H NMR (300 MHz, $C_6D_6$): δ 6.78 (s, 4H, $C_6Me_3H_2$), 3.05 (m, 4H, $NCH_2$), 2.22 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.11 (s, 6H, p-*Me*-$C_6Me_3H_2$), 1.49 (quint, $J$ = 2.9 Hz, 4H, $NCH_2CH_2$). Data match those found in the literature.[13]

**[Cu(7$^n$Pent)Cl] (12).** As for **1** with [7$^n$Pent]HCl (100 mg, 0.364 mmol), CuCl (43.2 mg, 0.437 mmol), $K_2CO_3$ (151 mg, 1.09 mmol) to give **12** as a white powder in 19% yield (22 mg). $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 3.75 (s, 4H, $NCH_2CMe_3$), 3.58 (m, 4H, $NCH_2CH_2$), 1.92 (m, 4H, $NCH_2CH_2$), 1.03 (s, 18H, $NCH_2CMe_3$). $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): δ 212.5 (N*C*N), 75.3, 54.2, 33.0, 28.0, 25.1. Anal. Calcd. (%) for $C_{15}H_{30}N_2ClCu$: C 53.40, H 8.96, N 8.30; Found: C 53.14, H 8.73, H 7.95

**[6MesH][$CuCl_2$] (13).** 6Mes·HCl (100 mg, 0.28 mmol) and CuCl (31 mg, 0.31 mmol) were added to a vial in the glovebox and 1 mL acetone added. The mixture was stirred for 1 h and then filtered through Celite®. The filtrate was reduced to dryness to afford **13** as a white powder in 75% yield (96 mg). Crystalline material was isolated from $CH_2Cl_2$/pentane. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.70 (s, 1H, NC*H*N), 6.98 (s, 4H, $C_6Me_3H_2$), 4.00 (t, $^3J_{HH}$ = 5.7 Hz, 4H, $NCH_2$), 2.64 (quint, $^3J_{HH}$ = 5.8 Hz, 2H, $NCH_2CH_2$), 2.34 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.30 (s, 6H, p-*Me*-$C_6Me_3H_2$).$^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$): δ 154.4 (N*C*HN), 141.0, 136.3, 134.3, 130.5, 46.8, 21.2, 19.7, 18.1. Anal. Calcd. (%) for $C_{22}H_{29}Cl_2CuN_2$: C 57.96, H 6.41, N 6.14; Found: C 57.52, H 6.47, N 6.14.

**[6XylylH][$CuCl_2$] (14).** As for **13** with 6Xylyl·HCl (100 mg, 0.34 mmol) and CuCl (30 mg, 0.31 mmol) to give **14** as a white powder in 31% yield (23 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.80 (s, 1H, NC*H*N), 7.32-7.26 (m, 2H, p-*H*-$C_6Me_2H_3$), 7.19 (d, $^3J_{HH}$ = 7.7 Hz, 4H, m-*H*-$C_6Me_3H_2$), 4.05 (t, $^3J_{HH}$ = 5.7 Hz, 4H, $NCH_2$), 2.67 (quint, $^3J_{HH}$ = 5.8 Hz, 2H, $NCH_2CH_2$), 2.40 (s, 12H, $C_6Me_2H_3$). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$): δ 154.2 (N*C*HN), 138.6, 134.7, 130.8, 129.9, 46.7, 19.7, 18.2. Anal. Calcd. (%) for $C_{23}H_{31}Cl_2CuN_2$: C 56.14, H 5.89, N 6.55; Found: C 55.64, H 5.89, N 6.44

**[7MesH][$CuCl_2$] (15).** As for **13** with 7Mes·HCl (100 mg, 0.27 mmol) and CuCl (30 mg, 0.31 mmol), to give **15** as a while powder in 74% yield (93 mg). Crystalline material was isolated from $CH_2Cl_2$/pentane. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.38 (s, 1H, NC*H*N), 6.97 (s, 4H, m-*H*-$C_6Me_3H_2$), 4.33 (br s, 4H, $NCH_2$), 2.58 (br s, 4H, $NCH_2CH_2$), 2.39 (s, 12H, o-*Me*-$C_6Me_3H_2$), 2.28 (s, 6H, p-*Me*-$C_6Me_3H_2$). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$): δ 158.7 (N*C*HN), 140.7, 139.3, 133.6, 130.6, 55.1, 25.6, 21.1, 18.4.

**[7XylylH][$CuCl_2$] (16).** As for **13** with 7Xylyl·HCl (100 mg, 0.29 mmol) and CuCl (32 mg, 0.32 mmol) to give **16** as a white powder in 12% yield (15 mg). Crystalline material was isolated from $CH_2Cl_2$/pentane. $^1$H NMR (500 MHz, $CDCl_3$): δ 7.43 (s, 1H, NC*H*N), 7.30-7.25 (m, 2H, p-*H*-$C_6Me_2H_3$), 7.18 (d, $^3J_{HH}$ = 7.7 Hz, 4H, m-*H*-$C_6Me_2H_3$), 4.39 (m, 4H, $NCH_2$), 2.61 (m, 4H, $NCH_2CH_2$), 2.46 (s, 12H, o-*Me*-$C_6Me_2H_3$).$^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$): δ 158.5 (N*C*HN), 141.6, 134.0, 130.1, 55.1, 25.6, 18.5. Anal. Calcd. (%) for $C_{23}H_{31}N_2Cl_2Cu$: C 57.08, H 6.16, N, Found: C 55.33, H 5.83, N 6.07.

**[7$^n$PentH][$CuCl_2$] (17).** As for **13** with 7$^n$Pent·HCl (100 mg, 0.37 mmol) and CuCl (40 mg, 0.40mmol) to give **17** as a white powder in 91% yield (123 mg). $^1$H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 1H, NC*H*N), 3.86 (m, 4H, $NCH_2CH_2$), 3.47 (s, 4H, $NCH_2CMe_3$), 2.24 (m, 4H, $NCH_2CH_2$), 1.03 (s, 18H, $NCH_2CMe_3$) $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$): δ 160.6 (N*C*HN), 70.6, 53.1, 33.5, 27.8, 25.2. Anal. Calcd. (%) for $C_{15}H_{31}N_2Cl_2Cu$: C 48.19, H 8.36, N 7.49 Found: C 46.60, H 7.91, N 7.06.

**General procedure for catalytic experiments.** In a dry argon glovebox was weighed [Cu(NHC)X] (5 x $10^{-3}$ mmol) into a 4 mL screw cap vial. To this was added the alkyne (1 mmol) followed by the azide (1 mmol) to start the reaction. The vial was closed, removed from the glovebox and remained sealed while stirring at the designated temperature for the appropriate time after which it was quenched with $CH_2Cl_2$ (3 mL) in air. The suspension was sonicated before a sample of 0.3 mL was taken and diluted with $CH_2Cl_2$ (0.9 mL) for GC analysis.

**1-Azidoheptane**. 1-Bromoheptane (6.2 mL, 39.2 mmol) was added to a solution of $NaN_3$ (2.8 g in 86 mL of DMSO, 43.0 mmol). The reaction mixture was stirred at room temperature for 5 h to obtain full conversion by NMR spectroscopy. The solution was cooled to 0°C and water (150 mL) was introduced to quench the reaction. The mixture was extracted with $Et_2O$ (3 x 100 mL) and the combined organic phases were washed with water (4 x 150 mL) and brine (2 x 150 mL), dried with $MgSO_4$, filtered and concentrated under vacuo to afford the product as a colorless oil (4.93 g, 89%). $^1$H NMR (300 MHz, $CDCl_3$): δ 3.26 (t, $J$ = 7.0 Hz, 2H), 1.70-1.49 (m, 2H), 1.46-1.16 (m, 8H), 1.01-0.78 (m, 3H). Data match those found in the literature.[23,27]

**Azidobenzene**. A suspension of distilled aniline (6.0 mL, 66.4 mmol) in water (50 mL) was cooled to 0°C. Concentrated 96% sulfuric acid (14.0 mL, 263 mmol) was carefully added to the mixture followed by the dropwise introduction of a sodium nitrite aqueous solution (5.3 g in 31 mL of water, 76.1 mmol). The reaction mixture was allowed to warm to room temperature and *n*-hexane (100 mL) was added. After a slow and portion wise introduction of $NaN_3$ (4.6 g, 70.8 mmol), the biphasic mixture was vigorously stirred at room temperature for 3 h (NMR monitoring). The organic layer was then collected, dried with $Na_2SO_4$, filtered and concentrated under vacuo to afford the product as a dark red oil (6.02 g, 76%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 2H), 7.19-7.10 (m, 1H), 7.07-7.01 (m, 2H). EI-MS: *m/z* 119 $[M]^{+\cdot}$. Data match those found in the literature.[28]

**1,4-Diphenyl-1H-1,2,3-triazole**. The typical catalytic procedure was applied to phenylacetylene (110 µL) and azidobenzene (110 µL). The crude reaction mixture was dissolved in $CH_2Cl_2$, filtered through a silica plug and recrystallised from $CH_2Cl_2$/pentane to yield an off-white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.97-7.87 (m, 2H), 7.85-7.76 (m, 2H), 7.61-7.51 (m, 2H), 7.52-7.42 (m, 3H), 7.42-7.33 (m, 1H). $^{13}$C{$^1$H} NMR: (101 MHz, $CDCl_3$) δ 148.6, 137.2, 130.4, 129.9, 129.1, 128.9, 128.6, 126.0, 120.7, 117.7. Data match those found in the literature.[29]

**4-Hexyl-1-phenyl-1H-1,2,3-triazole**. The typical catalytic procedure was applied to oct-1-yne (150 µL) and azidobenzene (110 µL) at 45°C. The crude reaction mixture was dissolved in $CH_2Cl_2$, filtered through a silica plug and recrystallised from $CH_2Cl_2$/pentane at -30 ºC to yield an off-white solid, which liquified at room temperature). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.77-7.68 (m, 3H), 7.55-7.46 (m, 2H), 7.45-7.37 (m, 1H), 2.79 (t, $J$ = 7.6 Hz, 2H), 1.73 (quint, $J$ = 7.6 Hz, 2H), 1.49-1.22 (m, 6H), 0.89 (t, $J$ = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$): δ 149.3, 137.4, 129.8, 128.6, 120.6, 118.9, 31.7, 29.5, 29.1, 25.8, 22.7, 14.2. Data match those found in the literature.[30]

**1-Heptyl-4-phenyl-1H-1,2,3-triazole**. The typical catalytic procedure was applied to phenylacetylene (110 µL) and 1-azidoheptane (160 µL) at room temperature. The crude reaction mixture was dissolved in $CH_2Cl_2$, filtered through a silica plug and concentrated to yield an off-white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.87-7.79 (m, 2H), 7.74 (s, 1H), 7.47-7.38 (m, 2H), 7.37-7.29 (m, 1H), 4.39 (t, $J$ = 7.2 Hz, 2H), 1.94 (m, 2H), 1.42-1.20 (m, 8H), 0.88 (t, $J$ = 7.0 Hz, 3H). $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$): δ 147.8, 130.8, 128.9, 128.2, 125.8, 119.5, 50.6, 31.7, 30.5, 28.8, 26.6, 22.6, 14.1. Data match those found in the literature.[28]

**X-ray crystallography.** Data for all crystallographic studies were obtained using an Agilent Xcalibur diffractometer and a Mo-Kα source. All experiments were conducted at 150 K, solved using SHELXT[31] and refined using SHELXL[32] via the Olex2[33] interface. Aside from the following points of note, refinements were generally unremarkable. The asymmetric unit in **4** was seen to contain one cation and two crystallographically independent $[CuCl_2]^-$ halves. There is evidence for C–H…Cl interactions in the gross structure. H1 (attached to C1) was located and refined without restraints in the structure of **5**. There is also evidence for C–H…Cl interactions in the asymmetric unit in this structure. The asymmetric unit in **9** was noted to comprise two independent molecules. While this latter structure determination is unambiguous, twinning of the sample (although resolved) compromised the raw data to a degree. This legacy is evidenced in the *R*(int) value

and the estimated standard deviations pertaining to the unit cell parameters.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2016583-2016592 for **1, 3**-**6**, **9**, **10**, **13**, **14** (ESI only) and **16** (ESI only), respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk.

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details. Multinuclear NMR spectra of all complexes.

## AUTHOR INFORMATION


### Corresponding Author

* E-mail: catherine.cazin@ugent.be


### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENT


We acknowledge financial support from the EPSRC Centre for Doctoral Training in Catalysis (EP/L016443/1) for JWH and the Erasmus Programme for DB. For work performed in Ghent the UGent BOF and FWO are gratefully acknowledged for support.


### REFERENCES


(1) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic carbene in late transition metal catalysis. *Chem. Rev.* **2009**, *109*, 3612-3676.

(2) (a) Lazreg, F.; Cazin, C. S. J. NHC-Copper complexes and their applications. In N-Heterocyclic Carbenes - Effective Tools for Organo- metallic Synthesis; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2014; pp 199-242; (b) Egbert, J. D.; Cazin, C. S. J.; Nolan, S. P. Copper N-heterocyclic carbene complexes in catalysis. *Catal. Sci. Technol.* **2013**, *3*, 912-926; (c) Lazreg, F.; Nahra, F.; Cazin, C. S. J. Copper-NHC complexes in catalysis. *Coord. Chem. Rev.* **2015**, *293-294*, 48-79; (d) Boreux, A.; Marion, N.; Gagosz, F. NHC-Copper, silver and gold complexes in catalysis. In *N-Heterocyclic Carbenes From Laboratory Curiosities to Efficient Synthetic Tools* (2nd Edition); Díez-González, S., Ed.; RSC Catalysis Series; RSC: Cambridge, U.K., 2017; pp 421-455; (e) Danopoulos, A. A.; Simler, T.; Braunstein, P. N-heterocyclic carbene complexes of copper, nickel and cobalt. *Chem. Rev.* **2019**, *119*, 3730-3961.

(3) (a) Nahra, F.; Gómez-Herrera, A.; Cazin, C. S. J. Copper(I)–NHC complexes as NHC transfer agents. *Dalton Trans.,* **2017**, *46*, 628-631; (b) for a recent contribution from the MKW group, see: Hall, J. W.; Seeberger, F.; Mahon, M. F.; Whittlesey, M. K., (carbene)CuF Complexes Featuring Bulky Arduengo-Type, Ring- Expanded, and Cyclic (Alkyl)(amino)carbenes: Applications in Catalytic Aldehyde Allylation. *Organometallics* **2020**, *39*, 227−233.

(4) For the first reported synthesis of IPr·HCl, see: Huang, J.; Nolan, S. P. Efficient Cross-Coupling of Aryl Chlorides with Aryl Grignard Reagents (Kumada Reaction) Mediated by a Palladium/Imidazolium Chloride System. *J. Am. Chem. Soc.* **1999**, *121*, 9889-9890.

(5) Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. Conjugate reduction of α,β-unsaturated carbonyl compounds catalyzed by a copper carbene complex. *Org. Lett.* **2003**, *5*, 2417-2420.

(6) Citadelle, C. A.; Le Nouy, E.; Bisaro, F., Slawin, A. M. Z., Cazin, C. S. J. Simple and versatile synthesis of copper and silver N-heterocyclic carbene complexes in water or organic solvents. *Dalton Trans.* **2010**, *39*, 4489–91.

(7) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. Coinage metal-N-heterocyclic carbene complexes. *Chem. Rev.* **2009**, *109*, 3561−3598.

(8) Santoro, O.; Collado, A.; Slawin, A. M. Z.; Nolan, S. P.; Cazin, C. S. J. A General Synthetic Route to [Cu(X)(NHC)] (NHC = N-heterocyclic carbene, X= Cl, Br, I) Complexes. *Chem. Commun.* **2013**, *49*, 10483-10485; (b) Nelson, D. J. Accessible Syntheses of Late Transition Metal (Pre)Catalysts Bearing N-Heterocyclic Carbene Ligands. *Eur. J. Inorg. Chem.* **2015,** 2012-2027.

(9) Sharninghausen, L. S.; Brooks, A. F.; Winton, W. P.; Makaravage, K. J.; Scott, P. J. H.; Sanford, M. S. NHC-Copper Mediated Ligand-Directed Radiofluorination of Aryl Halides. *J. Am. Chem. Soc.* **2020**, *142*, 7362-7367.

(10) (a) Zhang, L.; Hou, Z. *N*-Heterocyclic carbene (NHC)-copper-catalysed transformations of carbon dioxide. *Chem. Sci.* **2013,** *4*, 3395-3403; (b) Boogaerts, I. F. F.; Fortman, G. C.; Furst, M. R. L.; Cazin C. S. J; Nolan, S. P. Carboxylation of N-H/C-H Bonds Using N-Heterocyclic Carbene Copper(I) Complexes. *Angew. Chem. Int. Ed.* **2010**, *44*, 8674-8677.

(11) For recent contributions, see ref 3b and Hall, J. W.; Unson, D. M. L.; Brunel, P.; Collins, L. R.; Cybulski, M. K.; Mahon, M. F.; Whittlesey, M. K. Copper-NHC-Mediated Semi-hydrogenation and Hydroboration of Alkynes: Enhanced Catalytic Activity Using Ring-Expanded Carbenes. *Organometallics* **2018**, *37*, 3102−3110.

(12) See for example: (a) Díez-González, S.; Nolan, S. P. (NHC)Copper(I)-Catalyzed [3+2]-Cycloaddition of Azides and Mono- or Disubstituted Alkynes (NHC = *N*-Heterocyclic Carbene). *Chem. Eur. J.* **2006**, *12*, 7558-7564; (b) Díez-González, S.; Nolan, S. P. $[(NHC)_2Cu]X$ Complexes as Efficient Catalysts for Azide-Alkyne Click Chemistry at Low Catalyst Loadings. *Angew. Chem. Int. Ed.* **2008**, *48*, 8881-8884.

(13) Sebest, F.; Dunsford, J. J.; Adams, M.; Pivot, J.; Newman, P. D.; Díez-González, S. Ring-Expanded N-Heterocyclic Carbenes for Copper-Mediated Azide–Alkyne Click Cycloaddition Reactions. *ChemCatChem* **2018**, *10*, 2041-2045.

(14) During the assembly of this manuscript, the Hashmi group described the Ag transfer route to prepare RE-NHC copper complexes. Cervantes-Reyes, A.; Rominger, F.; Hashmi, A. S. K. Sterically Demanding $Ag^{I}$ and $Cu^{I}$ N-Heterocyclic Carbene Complexes: Synthesis, Structures, Steric Parameters, and Catalytic Activity. *Chem. Eur.J.* **2020**, *26*,5530-5540.

(15) For Au: Collado, A.; Gómez-Suárez, A.; Martin, A. R.; Slawin, A. M. Z.; Nolan, S. P. Straightforward Synthesis of [Au(NHC)Cl] (NHC = *N*-Heterocyclic Carbene) Complexes *Chem. Comm.* **2013**, *49*, 5541-5543.

(16) For Pd: (a) Zinser, C. M.; Nahra, F.; Brill, M.; Meadows, R. E.; Cordes, D. B.; Slawin, A. M. Z.; Cazin, C. S. J.; Nolan, S. P. A Simple Synthetic Entryway into Palladium Cross-Coupling Catalysis. *Chem. Comm.* **2017**, *53*, 7990-7993; (b) Guillet, S. G.; Voloshkin, V. A.; Saab, M.; Beliš, M.; Van Hecke, K.; Nahra, F.; Nolan, S. P. Designing a novel synthetic route to $[Pd(Cl)_2(L)(py)]$ (L = NHC and $PR_3$) precatalysts. *Chem. Commun.* **2020**, *56*, 5953-5956.

(17) For Ir and Rh: Savka, R.; Plenio, H. Facile synthesis of [(NHC)MX(cod)] and $[(NHC)MCl(CO)_2]$ (M = Rh, Ir; X = Cl, I) complexes. *Dalton Trans.,* **2015**, *44*, 891-893.

(18) For main group examples: Tzouras, N. V.; Nahra, F.; Falivene, L.; Cavallo, L.; Saab, M.; Van Hecke, K.; Collado, A.; Collett, C. J.; Smith, A. D.; Cazin, C. S. J.; Nolan, S. P. A Mechanistically and Operationally Simple Route to Metal Carbene Complexes and Compounds. *Chem. Eur J.* **2020**, *26*, 4515-4519.

(19) Pisano, G.; Cazin, C. S. J. Mechanochemical synthesis of Cu(I)-N-heterocycllic carbene complexes. *Green Chem.* **2020**, *22*, 5253-5256.

(20) Díez-González, S.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Stevens, E. D.; Slawin, A. M. Z.; Nolan, S. P. Well-Defined [(NHC)CuX] Complexes: Synthesis, Characterization and Catalytic Activities in Reduction Reactions and Click Chemistry. *Dalton Trans.* **2010**, *39*, 7595-7606.

(21) Iglesias, M.; Male, L.; Hursthouse, M. B.; Dervisi, A.; Fallis, I. A.; Knight, J. C.; Stasch, A.; Ooi, L.-L.; Coles, S.; Beetstra, D. J.; Cavell, K. J. Novel Expanded Ring N-Heterocyclic Carbenes: Free Carbenes, Silver Complexes, And Structures. *Organometallics*, **2008**, *27*, 3279–3289.

(22) Dunsford, J. J.; Tromp, D. S.; Cavell, K. J.; Elsevier, C. J.; Kariuki, B. M. N-alkyl functionalised expanded ring N-heterocyclic carbene complexes of rhodium(I) and iridium(I): structural investigations and preliminary catalytic evaluation. *Dalton Trans.*, **2013**, *42*, 7318–7329.

(23) Bidal, Y. D.; Lesieur, M.; Melaimi, M.; Cordes, D. B.; Slawin, A. M. Z.; Bertrand, G.; Cazin, C. S. J. A simple access to transition metal cyclopropenylidene complexes. *Chem. Commun.*, **2015**, *51*, 4778–4781.

(24) Lu, W. Y.; Cavell, K. J.; Wixey, J. S.; Kariuki, B. First Examples of Structurally Imposing Eight-Membered-Ring (Diazocanylidene) N-Heterocyclic Carbenes: Salts, Free Carbenes, and Metal Complexes. *Organometallics*, **2011**, *30*, 5649–5655.

(25) For similar structures to **8** and **9**, see: Pawar, G. M.; Bantu, B.; Weckesser, J.; Blechert, S.; Wurst, K.; Buchmeiser, M. R. Ring-opening metathesis polymerization-derived, polymer-bound Cu-catalysts for click-chemistry and hydrosilylation reactions under micellar conditions. *Dalton Trans.*, **2009**, 9043–9051.

(26) Jordan, A. J.; Wyss, C. M.; Bacsa, J.; Sadighi, J. P. Synthesis and Reactivity of New Copper(I) Hydride Dimers. *Organometallics*, **2016**, *35*, 613–616.

(27) Alvarez, S. G.; Alvarez, M. T. A Practical Procedure for the Synthesis of Alkyl Azides at Ambient Temperature in Dimethyl Sulfoxide in High Purity and Yield. *Synthesis*, **1997**, 413–414.

(28) Díez-González, S.; Correa, A.; Cavallo, L.; Nolan, S. P. (NHC)Copper(I )-Catalyzed [3+2] Cycloaddition of Azides and Mono- or Disubstituted Alkynes. *Chem. Eur. J.*, **2006**, *12*, 7558–7564.

(29) Kafle, A.; Handy, S. T. A one-pot, copper-catalyzed azidation/click reaction of aryl and heteroaryl bromides in an environmentally friendly deep eutectic solvent. *Tetrahedron*, **2017**, *73*, 7024–7029.

(30) Chesnokov, G. A.; Topchiy, M. A.; Dzhevakov, P. B.; Gribanov, P. S.; Tukov, A. A.; Khrustalev, V. N.; Asachenko, A. F.; Nechaev, M. S. Eight-membered-ring diaminocarbenes bearing naphthalene moiety in the backbone: DFT studies, synthesis of amidinium salts, generation of free carbene, metal complexes, and solvent-free copper catalyzed azide–alkyne cycloaddition (CuAAC) reaction. *Dalton Trans.*, **2017**, *46*, 4331-4345.

(31) Sheldrick, G. M. SHELXT - Integrated space-group and crystal structure determination. *Acta Cryst.* **2015**, *A71*, 3-8.

(32) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3-8.

(33) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2011**, *42*, 339-341.