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## Introduction

Pincer-ligated transition metal complexes have found extensive applications in catalysis as well as in materials chemistry.<sup>1</sup> Particularly, the high thermal stability and rigid structure of pincer complexes make them extensively useful in diverse organic transformations, because the tight tridentate coordination keeps the pincer and metal together in a catalytic cycle, wherein the sterics and electronics on a ligand are effectively transferred to the metal centre. Pincer complexes of noble metals, such as Pd, Rh and Ir, are extensively studied and employed as catalysts in important chemical reactions.<sup>2</sup> Recently, pincer complexes based on naturally-abundant, less expensive first-row transition metals have attracted special attention because of the sustainability, economic viability and

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# Synthesis of quinolinyl-based pincer copper(II) complexes: an efficient catalyst system for Kumada coupling of alkyl chlorides and bromides with alkyl Grignard reagents†

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Quinolinamide-based pincer copper(II) complexes,  $\kappa^{N}$ ,  $\kappa^{N}$ ,  $\kappa^{N-1}$ 

unique features of these transition metals.<sup>3</sup> In that regard, complexes of Mn,<sup>4</sup> Fe,<sup>5</sup> Co,<sup>6</sup> Ni,<sup>3a,7</sup> and Cu<sup>8</sup> are developed and efficiently employed in numerous applications. Among them, the pincer copper complexes are used in biological applications such as in luminescence and medicine, and exhibit antioxidant and antibacterial activity.<sup>9</sup> In addition, the pincer copper complexes are explored in several catalytic cross-couplings as well as in direct C–H bond functionalizations.<sup>10</sup>

The Kumada coupling is one of the most important crosscoupling reactions, useful in achieving C-C coupled products by the reaction of a Grignard reagent with an organic halide.<sup>11</sup> Kumada coupling is well precedented by early transition-metal salts, such as Fe,<sup>12</sup> Co,<sup>13</sup> and Ni.<sup>14</sup> Moreover, the pincer complexes of Mn,<sup>15</sup> Fe,<sup>16</sup> and Ni<sup>17</sup> are also employed in the Kumada coupling reaction. However, copper complexes in the Kumada coupling reaction are relatively less explored. For example, Burns and Liu independently demonstrated the Kumada coupling of alkyl tosylates and mesylates employing Cu-precursors with added ligands.<sup>18</sup> Recently, Kirchner utilized a well-defined phosphazine-based PNP-pincer copper complex in the Kumada coupling of aryl triflates and bromides with aryl Grignard reagents.<sup>10b</sup> Unfortunately, the Kumada coupling of challenging alkyl chlorides employing a copper catalyst has been rarely explored, with an extremely limited scope.<sup>18b</sup> We hypothesized that a copper catalyst based on a



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strong sigma-donating tridentate nitrogen-ligand would favour the reactivity of unactivated alkyl chlorides in the Kumada coupling reaction.<sup>19</sup> Thus, as a part of our interest on the development of pincer complexes of 3d metals,<sup>20</sup> herein, we have synthesized a series of quinolinyl-based NNN-pincer copper complexes  $\kappa^N, \kappa^N, \kappa^N-\{C_9H_6N-(\mu-N)-C(O)CH_2NEt_2\}$ CuX [(<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)CuX] (2–5) and demonstrated them in the Kumada coupling of diverse alkyl chlorides and bromides with alkyl magnesium chlorides.

## **Results and discussion**

### Synthesis of (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)-ligated copper(II) complexes

Recently, we have developed a C<sub>9</sub>H<sub>6</sub>N-NHC(O)CH<sub>2</sub>NEt<sub>2</sub> [(<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)-H; 1] ligand and pincer nickel complexes [(<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>) NiX], wherein the pincer nickel complexes were found to be efficient catalysts for the C-H bond alkylation, arylation and benzylation of indoles.<sup>20a,c,d</sup> We further wanted to explore the reactivity of ligand 1 with copper precursors, and demonstrate the catalytic activity of the synthesized copper complexes for the Kumada coupling of unactivated alkyl chlorides. Thus, the metallation of ligand, (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)-H (1), with CuCl<sub>2</sub>, CuBr<sub>2</sub> and Cu(OAc)<sub>2</sub> in the presence of Et<sub>3</sub>N in THF under reflux conditions afforded copper(II) complexes  $\kappa^{N}, \kappa^{N}, \kappa^{N$ (O)CH<sub>2</sub>NEt<sub>2</sub>}CuCl [( $^{Q}$ NNN<sup>Et<sub>2</sub></sup>)CuCl; 2],  $\kappa^{N}$ , $\kappa^{N}$ , $\kappa^{N}$ -{C<sub>9</sub>H<sub>6</sub>N-( $\mu$ -N)-C (O)CH<sub>2</sub>NEt<sub>2</sub>}CuBr [( $^{Q}$ NNN<sup>Et<sub>2</sub></sup>)CuBr; 3] and  $\kappa^{N}$ , $\kappa^{N}$ , $\kappa^{N}$ -{C<sub>9</sub>H<sub>6</sub>N- $(\mu$ -N)-C(O)CH<sub>2</sub>NEt<sub>2</sub>Cu(OAc) {[(<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)Cu(OAc); 4], respectively, in good yields (Scheme 1). The resulting complexes are NMR inactive and hence could not be characterized by <sup>1</sup>H and <sup>13</sup>C NMR analyses. However, all three complexes were characterized by elemental analysis and HRMS. The HRMS of 2 shows peaks at m/z 319.0734 and 355.0500 corresponding to  $[2-Cl]^+$  and  $[2 + H]^+$ , respectively. Similarly, complexes 3 and 4 show peaks at 319.0735, 396.9861, 319.0745 and 379.0307 for  $[3-Br]^+$ ,  $[3-H]^+$ ,  $[4-OAc]^+$  and  $[4 + H]^+$ , respectively. The molecular structures of complexes 2, 3 and 4 were further confirmed by single crystal X-ray diffraction studies.

Furthermore, we planned to synthesize copper(I) complexes  $[(^{Q}NNN^{Et_2})Cu(thf)]$  employing different Cu(I) precursors. However, upon treatment of ligand **1** with CuCl, CuBr and Cu(OAc) in the presence of Et<sub>3</sub>N in THF under reflux conditions, copper(II) complexes **2**, **3** and **4** were obtained in 49%, 50% and 46% yields, respectively. Notably the yields of the complexes **2**, **3** and **4** by the reaction of ligand **1** with Cu(I) salts are around 50% (see the ESI† for experimental details). This may

CuX<sub>2</sub>

Et<sub>3</sub>N, THF

reflux, 3 h

ŃEt₂

75%

74%

X = CI, (2);

X = Br, (3);

X = OAc, (4); 70%



. NEt₂

(1)

be due to the fact that Cu(I) salts in solution undergo disproportionation reaction into Cu(II) and Cu(0) species. The resulting Cu(II) species would react with ligand **1** to produce the corresponding pincer copper(II) complexes in less than 50% yields (Scheme 2). Similarly, the disproportionation reaction of copper is well established by various groups.<sup>21</sup> The molecular composition and the molecular structure of complexes **2–4**, synthesized *via* this approach, are verified that well correlates with the complexes synthesized by employing Cu(II) precursors. The XPS analysis of the crude reaction mixture of complex **4** obtained *via* this method (Scheme 2) indicates the existence of both Cu(III) and Cu(0) species (discussed *vide supra*).

The reaction of complex (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)CuCl (2) with AgOTf in acetonitrile at room temperature resulted in the formation of a cationic complex, [(<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)Cu(CH<sub>3</sub>CN)](OTf) (5), in 80% yield (Scheme 3). Complex 5 was characterized by elemental analysis as well as by MALDI-TOF-MS analysis. The MALDI-TOF analysis of complex 5 showed m/z values of 508.8325 and 318.9736 that correspond to [M]<sup>+</sup> and [M - (CH<sub>3</sub>CN + OTf)]<sup>+</sup>, respectively. The cationic complex 5 was found to be very robust compared to complexes 2–4 as it decomposes above 230 °C.

On the other hand, treatment of ligand **1** with the copper(1) precursor  $[Cu(CH_3CN)_4](ClO_4)$  in acetonitrile under reflux conditions afforded complex  $[(^{Q}NN(H)N^{Et_2})Cu(CH_3CN)](ClO_4)$  (6) in 77% isolated yield (Scheme 4). The <sup>1</sup>H NMR spectrum of complex **6** shows a peak at 10.21 ppm corresponding to coordinated *NH*, which is 1.2 ppm shielded compared to that observed for ligand **1**. Furthermore, NMR analysis indicates the coordination of the quinolinyl-*N* and NEt<sub>2</sub> arm to the copper(1) center. In addition, an acetonitrile moiety is ligated to Cu(1) in complex **6** that appears as a singlet at 2.61 ppm.<sup>8f,22</sup> The MALDI-TOF analysis of complex **6** showed *m/z* values of



Scheme 2 Reaction of ligand ( $^{O}NNN^{Et_2}$ )-H with Cu(i)X to produce ( $^{O}NNN^{Et_2}$ )Cu(ii)X.



Scheme 3 Synthesis of cationic complex [(Et2NNNQ)Cu(MeCN)]OTf (5).



Scheme 4 Synthesis of cationic Cu(1) complex [( $^{Et_2}NN(H)N^{O}$ )Cu(MeCN)] ClO<sub>4</sub> (6).

460.12 and 320.07 that correspond to  $[M]^+$  and  $[M - (CH_3CN + ClO_4)]^+$ , respectively.

## Crystal structure description of (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)CuX complexes

The ORTEP diagrams of complexes 2, 3 and 4 are shown in Fig. 1, 2 and 3, respectively. Selected bond lengths and bond angles are given in Tables S1 and S2 in the ESI.† In all three complexes, ligand 1 provides a tridentate coordination to the copper through quinolinyl-N3, amido-N2 and amine-N1, and the fourth site is occupied by an anionic ligand –Cl (2) or –Br (3) or –OAc (4). The coordination geometry around copper is slightly distorted from the expected square-planar in all three complexes 2, 3 and 4. The Cu–N(2) bond lengths in 2 (1.9086(10) Å) and 3 (1.9097(12) Å) are slightly shorter than the Cu–N bond length (1.936(4) Å) in a similar amido-complex, { $C_9H_6N-(\mu-N)-C(O)$ 



Fig. 1 Thermal ellipsoid plot of  $(^{O}NNN^{Et_2})CuCl$  (2). All the hydrogen atoms are omitted for clarity.



Fig. 2 Thermal ellipsoid plot of  $(^{\Box}NNN^{Et_2})CuBr$  (3). All the hydrogen atoms are omitted for clarity.



Fig. 3 Thermal ellipsoid plot of  $({}^{O}NNN^{Et_2})Cu(OAc) \cdot (H_2O)_{0.5}$  [4·(H<sub>2</sub>O)<sub>0.5</sub>]. All the hydrogens are omitted for clarity except on water molecules.

CH<sub>2</sub>-NH<sub>2</sub>}Cu(OCOCH<sub>3</sub>),<sup>23</sup> whereas the Cu-N(1) bond lengths (2.0690(10) Å in 2 and 2.0691(12) Å in 3) and Cu-N(3) bond lengths (2.0093(10) Å in 2 and 2.0128(12) Å in 3) are comparable to the respective bond lengths in  $\{C_9H_6N-(\mu-N)-C(O)\}$ CH<sub>2</sub>-NH<sub>2</sub>}Cu(OCOCH<sub>3</sub>). The shorter Cu-N(2) bond length compared to Cu-N(1) and Cu-N(3) bond lengths is consistent with the amido sigma Cu-N(2) bond, whereas Cu-N(1) and Cu-N(3) are coordinate bonds. The N(1)-Cu-N(3) bond angles in 2  $(166.80(4)^{\circ})$  and 3  $(166.84(5)^{\circ})$  are comparable to each other, and significantly larger than that reported for  $\{C_9H_6N-(\mu-N) C(O)CH_2NH_2$ Cu(OCOCH<sub>3</sub>) (159.7(2)°).<sup>23</sup> The N(1)-Cu-N(2) bond angles in 2 and 3 are around 84.5°, whereas the N(2)-Cu-N(3) bond angles are slightly smaller (~82.6°). The fivemembered ring containing Cu, N(2), and N(3) is almost planar with the quinolinyl-moiety  $(Cu(1)-N(2)-C(3)-C(11) = -5.17(13)^{\circ}$ for 2 and  $6.02(15)^{\circ}$  for 3), whereas the other five-membered Cu-containing ring is highly distorted (Cu(1)-N(1)-C(1)-C(2))torsion angle 15.80(11)° for 2 and -15.99(13)° for 3). The comparison of important bond parameters of complexes 2 and 3 with that of complex {C<sub>9</sub>H<sub>6</sub>N-(µ-N)-C(O)CH<sub>2</sub>-NH<sub>2</sub>}Cu (OCOCH<sub>3</sub>) suggests that the structural features of newly synthesized complexes are in accordance with the reported ones.23

Complex 4 crystallizes in two different patterns: (i) in one, a molecule of  $H_2O$  bridges between two copper complexes 4 (Fig. 3) and (ii) in the other, complex 4 exists as a catemeric form (Fig. 4). Complex  $4 \cdot (H_2O)_{0.5}$  is most likely obtained due to



**Fig. 4** Complete model of  $[(^{O}NNN^{Et_2})Cu(OAc)]_n$  (4)<sub>n</sub>. All the hydrogen atoms are omitted for clarity.

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the presence of ubiquitous water in the solvent used for recrystallization. Particularly, this complex was isolated from the crystallization process of the reaction of ligand 1 with Cu  $(OAc)_2$ . However, the catemeric form of 4 was often recrystallized from the reaction of 1 with Cu(OAc), and upon complete drying of the mother liquor. In complex  $4 \cdot (H_2O)_{0.5}$ , two molecules of (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)Cu(OAc) are held together by hydrogen bonding between the bonded oxygen atom of acetate and water in a [Cu]-AcO···H-O-H···OAc-[Cu] mode, wherein the AcO-H distance is 2.055 Å and the AcO-H-O bond angle is 177.56° (Fig. 3). In the catemeric structure of complex 4, the ligand carbonyl oxygen of (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)Cu(OAc) forms a bond with the Cu-centre of another (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)Cu(OAc), resulting in the formation of a catemeric structure (Fig. 4). The Cu-N(2) bond lengths in  $4 \cdot (H_2O)_{0.5}$  (1.9109(14) Å) and  $(4)_n$  (1.926(2) Å) are slightly shorter than the similar Cu-N bond length (1.936 (4) Å) in the amido-complex,  $\{C_9H_6N-(\mu-N)-C(O)CH_2-NH_2\}Cu$  $(OCOCH_3)$ <sup>23</sup> whereas the Cu-N(1) bond lengths in  $4 \cdot (H_2O)_{0.5}$ (2.0633(13) Å) and  $(4)_n$  (2.083(2) Å) as well as the Cu–N(3) bond lengths in  $4 \cdot (H_2O)_{0.5}$  (2.0107 Å) and  $(4)_n$  (2.035(2) Å) are comparable. The Cu–O(1) bond length (1.9618(11) Å) in  $4 \cdot (H_2O)_{0.5}$ is slightly longer than the Cu-O(1) bond length (1.9302(19) Å) in  $(4)_n$ , which could be due to the involvement of the oxygen atom O(1) of the former complex in hydrogen bonding with a water molecule. The N(1)-Cu-N(3) bond angles in  $4 \cdot (H_2O)_{0.5}$  $(162.42(6)^\circ)$  and  $(4)_n$   $(162.18(9)^\circ)$  are comparable to each other and significantly larger than that reported for  $\{C_9H_6N-(\mu-N)-C_9M_6N-(\mu-N)-(\mu-N)-(\mu-N)-(\mu-N)-(\mu-N)-(\mu-N)-(\mu-N)$ (O)CH<sub>2</sub>NH<sub>2</sub>}Cu(OCOCH<sub>3</sub>) (159.7(2)°).<sup>23</sup> The N(1)-Cu-N(2) and N(2)-Cu-N(3) bond angles in  $4 \cdot (H_2O)_{0.5}$  and  $(4)_n$  are 83.99(6), 82.51(6) and 82.89(9), 81.50(9)°, respectively. The Cu(1)-O(3)-C (2) bond angle in the catemeric structure of 4 is 134.47°.

### X-ray photoelectron spectroscopy studies of complexes

Compounds  $4 \cdot (H_2O)_{0.5}$  and  $(4)_n$  were characterized by XPS to determine the oxidation state of copper in both the complexes. Although X-ray studies indicate that copper is in the +2 oxidation state in both the complexes  $4 \cdot (H_2O)_{0.5}$  and  $(4)_n$ , XPS analysis has been performed to assign the oxidation state of Cu in bulk compounds. XPS analysis has been carried out using a Thermo Scientific instrument with an Al Ka monochromator source and the obtained results are shown in Fig. S1 in the ESI.<sup>†</sup> The Cu 2p spectrum of both the complexes  $4 \cdot (H_2O)_{0.5}$  and  $(4)_n$  shows two main intense spin orbit splitting peaks for  $2p_{3/2}$  (933.5 eV) and  $2p_{1/2}$  (953.4 eV). Along with the main peaks, two broad satellite peaks (s) at 942.2 and 962.2 eV were also observed. These satellite peaks normally appear for  $Cu(\pi)$  complexes due to charge transfer from the ligand (AcO<sup>-</sup>) to the Cu(II) centre. Hence, both the complexes have the copper centre in the +2 oxidation state. The obtained binding energies are in accordance with the earlier reports.<sup>24</sup>

Furthermore, XPS analysis of the reaction mixture of **4** (crude mixture obtained *via* Scheme 2 before isolation) was carried out to ascertain residual Cu(0) species that would be obtained by the disproportionation of Cu(OAc) into Cu<sup>0</sup> and Cu<sup>2+</sup>. As shown in Fig. S2 in the ESI,† the Cu 2p spectrum shows two main intense asymmetric spin orbit splitting peaks

 $2p_{3/2}$  and  $2p_{1/2}$ . To explain this asymmetric nature of the peaks, each Cu 2p peak is deconvoluted into two peaks – binding energies at 933.5, 953.4 eV correspond to Cu<sup>2+</sup> and 932, 951.8 eV appear due to Cu<sup>0</sup>. Along with the main peaks, a low intense broad satellite peak (s) at 943.6 eV binding energy to the main peaks of Cu  $2p_{3/2}$  was observed. However, due to the presence of Cu<sup>0</sup> species on the surface, the relative intensity of the satellite peak was less than that expected in the case of pure Cu<sup>2+</sup>. The obtained binding energies are in accordance with the earlier reports.<sup>24</sup>

# Catalytic activity of $({}^{Q}NNN^{Et_2})CuX$ complexes for Kumada coupling of alkyl halides

The newly developed neutral pincer copper complexes (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)CuX (2-4) along with cationic complexes, [(<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)  $Cu(CH_3CN)$ ](OTf) (5) and [(<sup>Q</sup>NN(H)N<sup>Et<sub>2</sub></sup>)Cu(CH<sub>3</sub>CN)](ClO<sub>4</sub>) (6), were screened and employed for the Kumada coupling of alkyl halides with alkyl magnesium chloride. Initially, complex 2 was screened for the Kumada coupling of (3-bromopropyl) benzene (0.20 mmol) with cyclohexylmagnesium chloride (8a, 0.40 mmol) using a mild base LiOMe at 0 °C (Table 1), a reaction condition previously reported by Liu for a similar reaction.<sup>18b</sup> The desired coupled product **9aa** was obtained in 15% yield using catalyst 2 (entry 1). By employing catalysts 3 and 4, the NMR yield of product 9aa was 20% and 18%, respectively (entries 2 and 3). Notably, the use of cationic complex 5 as a catalyst afforded 9aa in 57% isolated yield (entry 4). The better activity of catalyst 5 might be due to the more electrophilic nature of copper in complex 5 that would prefer the Grignard nucleophiles. Furthermore, an easy access of a vacant coordination site around the copper center in complex 5 could be an additional advantage. The use of complex 6 as a catalyst afforded only 12% yield of product 9aa (entry 5), which might be due to the less electrophilic character of 6. Next, we shifted

Table 1 Optimization of reaction conditions for ( $^{\text{Q}}\text{NNN}^{\text{Et}_2}\text{)}\text{CuX}$  catalyzed Kumada coupling\*

ر ×	X = Br (7a) = Cl (7a')	Mg-	cat. [ <b>Cu</b> ] (5.0 m LiOMe (1.0 eq THF 0 °C - r.t.	101%) uiv) 9a	a
Entry	Cat. [Cu]	Х	8a (equiv.)	Time (h)	$\operatorname{Yield}^{b}(\%)$
1	2	Br	2	24	15
2	3	Br	2	24	20
3	4	Br	2	24	18
4	5	Br	2	24	$67(57)^{c}$
5	6	Br	2	24	12
6	5	Cl	2	24	$58 (45)^c$
7	5	Cl	2	16	42
8	5	Cl	3	8	<b>70</b> (63) <sup>c</sup>
9	5	Cl	3	6	38

<sup>*a*</sup> Conditions: (3-Halopropyl)benzene (0.2 mmol), cyclohexylmagnesium chloride (0.3–0.6 mmol), LiOMe (0.2 mmol), THF (1.0 mL). <sup>*b*</sup> Yield determined by <sup>1</sup>H NMR. <sup>*c*</sup> Isolated yield is given in parentheses.

our attention to check the feasibility of the coupling of (3-chloropropyl)benzene, wherein 45% yield of product **9aa** was isolated employing catalyst 5 (entry 6). Notably, the formation of the cyclohexyl-dimer as a by-product from CyMgCl was severe when the reaction was continued for a longer time. Thus, on increasing the amount of CyMgCl to 3.0 equiv. and reducing the reaction time to 8 h, the coupled product **9aa** was isolated in 63% yield (entry 8). Furthermore, lowering the reaction time to 6 h didn't improve the reaction and resulted in 38% yield of **9aa** (entry 9). The optimization data show that performing the reaction for a longer time using a lower amount of Grignard reagent is not suitable for achieving a good yield of the desired product; however, a shorter reaction time with more Grignard reagent was helpful.

With the optimized reaction conditions in hand, we explored the scope for coupling of various alkyl and benzyl halides with different alkyl Grignard reagents (Table 2). Thus, the aryl substituted alkyl chlorides and bromides bearing  $\beta$ -hydrogen atoms efficiently reacted with cyclohexyl magnesium chloride (CyMgCl) to give the desired alkylated products **9aa–9ea** in good yields (Table 2, entries 1–5). Both the

Table 2 Scope for the Kumada coupling of alkyl halides catalyzed by 5<sup>a</sup> Grignard Yield Alkyl halide (7) Product (9)  $(\%)^{b}$ Entry reagent (8) MgC R = H, X = Cl(7a')R = H, (9aa) 63 1 2 R = OMe, X = Br(7b)R = OMe, (9ba) 90 .CI MgCI R 3 R = H, (7c)R = H, (9ca)76 R = OMe, (7d) 4 R = OMe, (9da) 82 5 R = Cl, (7e)R = Cl, (9ea) 62<sup>c</sup> MgCI 6 82 (7f)) (9fa) MgC 7 56 `CI . (7g) (9ga) n-Octyl-Cl (7h) MgCl 8 55 *n*-Octyl (9ha) 9 MeMgCl (8b) 93 ÌΜe (7a) (9ab) 10 7a EtMgCl (8c) 92 (9ac) .Me <sup>i</sup>PrMgCl (8d) 90 11 7a Me (9ad) Me 12 <sup>t</sup>BuMgCl (8e) 90 7a ∩Me Me (9ae)

 $^a$  Conditions: Alkyl halide (0.2 mmol), alkyl magnesium chloride (0.6 mmol), LiOMe (0.2 mmol), THF (1.0 mL), 0 °C, 8 h.  $^b$  Yields of isolated compounds.  $^c$  Yield determined by  $^1{\rm H}$  NMR using  $\rm CH_2Br_2$  as an internal standard.

MeO and Cl<sub>(arvl)</sub> groups are well tolerated under the reaction conditions. Notably, a C(sp<sup>3</sup>)-Cl bond is selectively reacted in the presence of the  $C(sp^2)$ -Cl bond (entry 5). This selectivity is very crucial as the aryl-Cl can be used for further functionalizations. The dioxolane ring containing substrates 7f and 7g reacted with CyMgCl to give the alkylated products 9fa and 9ga in 82% and 56% yields, respectively (entries 6 and 7). Similarly, the linear halide, 1-octyl chloride reacted with CyMgCl and afforded product 9ha in 55% yield. In addition to the coupling of CyMgCl, various acyclic alkyl Grignard coupling partners reacted smoothly with (3-bromopropyl)benzene to deliver the alkylated products in excellent yields (entries 9-12). The major by-products in all these reactions are the alkyl-dimers resulting from the alkyl magnesium chlorides (Grignard reagents). Although some reports exist for the copper-catalyzed Kumada coupling of alkyl tosylates and mesylates with alkyl Grignard reagents,18 herein we have demonstrated the Kumada coupling of unactivated and more challenging alkyl chlorides in addition to alkyl bromides employing a well-defined pincer copper catalyst. Considering the activity of the copper-catalyst for the coupling of challenging alkyl chlorides demonstrated here, the present catalytic protocol is unique from the literature precedented examples.<sup>18</sup>

Apart from the coupling of alkyl halides, diverse benzyl halides could couple with CyMgCl to afford the desired benzyl lated alkylation in moderate yields (Scheme 5). Though the yields of the coupling products were moderate, the functional group tolerability for this coupling is significant. Important functional groups such as -Br, -Cl, and  $-NO_2$  at different positions of the aryl ring are well tolerated. The benzyl halides bearing both the electron-donating (-OMe) as well as electron-withdrawing ( $-NO_2$ ) substituents were reacted with comparative activity. The observed low yields for the coupling of benzyl halides under the optimized reaction conditions.



## Conclusions

In summary, we have demonstrated the synthesis and catalytic application of (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)CuX complexes for Kumada coupling of unactivated alkyl chlorides and bromides. Both neutral and cationic copper(II) complexes, (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)CuX (2-5), were developed from copper(II) as well as from copper(I) precursors. A cationic copper(I) complex,  $[(^{Q}NN(H)N^{Et_2})Cu(MeCN)](ClO_4)$  (6), was synthesized using a  $[Cu(MeCN)_4](ClO_4)$  precursor. Complexes 2-5 were characterized by elemental analysis and HRMS, whereas complex 6 was characterized by NMR, MALDI and elemental analysis. Molecular structures of 2, 3 and 4 were elucidated by single crystal X-ray diffraction studies. Complex 4 crystallizes in dimeric form with bridged  $H_2O$  *i.e.*  $[4 \cdot (H_2O)_{0.5}]$ as well as in catemeric form  $(4)_n$ . XPS analysis of complexes  $[4 \cdot (H_2O)_{0.5}]$  and  $(4)_n$ , obtained from both the Cu(II) and Cu(I) precursors, highlights that the copper species are present in the +2 oxidation state. The cationic copper complex 5 is found to be an active catalyst for the Kumada coupling of unactivated alkyl and benzyl chlorides and bromides with alkyl Grignard reagents.

## **Experimental section**

### General considerations

All manipulations were conducted under an argon atmosphere either in a glove box or using standard Schlenk techniques in pre-dried glassware. The catalytic reactions were performed in flame-dried Schlenk tubes. Solvents were dried over Na/benzophenone or CaH<sub>2</sub> and distilled prior to use. Liquid reagents were flushed with argon prior to use. The ligand  $1^{20a}$  and [(CH<sub>3</sub>CN)<sub>4</sub>Cu]ClO<sub>4</sub><sup>25</sup> were synthesized according to the previously described procedures. All other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure. TLC: TLC Silica gel 60  $F_{254}$ . Detection under UV light at 254 nm. Chromatography: separations were carried out on Spectrochem silica gel (74-149 µm, 100-200 mesh). M.p.: Büchi 540 capillary melting point apparatus, values are uncorrected. NMR (<sup>1</sup>H and <sup>13</sup>C) spectra were recorded at 400 or 500 (<sup>1</sup>H), 100 or 125 {<sup>13</sup>C, DEPT}, respectively on Bruker AV 400 and AV 500 spectrometers in CDCl<sub>3</sub> solutions, if not specified; chemical shifts ( $\delta$ ) are given in ppm. The <sup>1</sup>H and <sup>13</sup>C NMR spectra are referenced to residual solvent signals (CDCl<sub>3</sub>:  $\delta_{\rm H}$  = 7.26 ppm,  $\delta_{\rm C}$  = 77.2 ppm).

**Synthesis of** ( $^{\text{Q}}$ **NNN**<sup>Et<sub>2</sub></sup>)**CuCl** (2). To an oven dried Schlenk flask were introduced ligand ( $^{\text{Q}}$ **NNN**<sup>Et<sub>2</sub></sup>)-H (0.1 g, 0.389 mmol) and CuCl<sub>2</sub> (0.052 g, 0.387 mmol), and THF (10 mL) was added into it. To the resultant reaction mixture, Et<sub>3</sub>N (0.071 mL, 0.506 mmol) was added and the reaction mixture was stirred at 70 °C for 3 h in a preheated oil bath. The reaction was cooled to room temperature and all the volatiles were evaporated. The product was then extracted with toluene (10 mL × 2), concentrated under vacuum and Et<sub>2</sub>O (3 mL) was added to obtain crystalline compound 2. Yield: 0.104 g, 75%. M.p. = 127 °C (dec). Anal. calcd for  $C_{15}H_{18}ON_3ClCu$ : C, 50.70; H, 5.11; N, 11.83. Found: C, 50.35; H, 4.79; N, 11.38. HRMS (ESI): m/z calcd for  $C_{15}H_{18}ON_3ClCu + H^+$  [M + H]<sup>+</sup> 355.0507, found 355.0500 and  $C_{15}H_{18}ON_3ClCu-Cl^+$  [M - Cl]<sup>+</sup> 319.0740, found 319.0734.

*Note*: On employing CuCl as a metal precursor instead of CuCl<sub>2</sub>, compound **2** was obtained in 49% yield (0.067 g).

Synthesis of (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)CuBr (3). This compound was synthesized following a procedure similar to the synthesis of complex 2, using (<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)-H (0.1 g, 0.389 mmol), CuBr<sub>2</sub> (0.087 g, 0.389 mmol) and Et<sub>3</sub>N (0.506 mmol, 0.071 mL). The crude product was recrystallized in toluene/Et<sub>2</sub>O to obtain a crystalline compound 3. Yield: 0.115 g, 74%. M.p. = 124 °C (dec). Anal. calcd for  $C_{15}H_{18}ON_3BrCu$ : C, 45.07; H, 4.54; N, 10.51. Found: C, 44.48; H, 4.28; N, 10.19. HRMS (ESI): *m/z* calcd for  $C_{15}H_{18}ON_3BrCu$ -Br<sup>+</sup> [M – Br]<sup>+</sup> 319.0740, found 319.0735 and  $C_{15}H_{18}ON_3BrCu$ -H<sup>+</sup> [M – H]<sup>+</sup> 396.9846, found 396.9861.

*Note*: On employing CuBr as a metal precursor instead of CuBr<sub>2</sub>, compound **3** was obtained in 50% yield (0.078 g).

**Synthesis of**  $(^{Q}NNN^{Et_2})Cu(OAc) \cdot (H_2O)_{0.5}$  [4·(H<sub>2</sub>O)<sub>0.5</sub>]. This compound was synthesized following the procedure similar to the synthesis of complex 2, using  $(^{Q}NNN^{Et_2})$ -H (0.1 g, 0.389 mmol), Cu(OAc)<sub>2</sub> (0.071 g, 0.389 mmol) and Et<sub>3</sub>N (0.506 mmol, 0.071 mL). The crude product was recrystallized in toluene/Et<sub>2</sub>O to obtain a crystalline compound 4·(H<sub>2</sub>O)<sub>0.5</sub>. Yield: 0.103 g, 70%. M.p. = 131 °C (dec). Anal. calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub>N<sub>3</sub>Cu·(H<sub>2</sub>O)<sub>0.5</sub>: C, 52.64; H, 5.72; N, 10.83. Found: C, 52.57; H, 5.61; N, 10.96. HRMS (ESI): *m/z* calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub>N<sub>3</sub>Cu + H<sup>+</sup> [M + H]<sup>+</sup> 379.0952, found 379.0307 and C<sub>17</sub>H<sub>21</sub>O<sub>3</sub>N<sub>3</sub>Cu–OAc<sup>+</sup> [M – OAc]<sup>+</sup> 319.0740, found 319.0745.

*Note*: On employing Cu(OAc) as a metal precursor instead of Cu(OAc)<sub>2</sub>, compound  $(4)_n$  was obtained in 46% yield (0.068 g).

Synthesis of [(<sup>Q</sup>NNN<sup>Et<sub>2</sub></sup>)Cu(MeCN)]OTf (5). To an oven dried Schlenk flask, complex 2 (0.05 g, 0.141 mmol) and AgOTf (0.036 g, 0.141 mmol) were introduced and acetonitrile (10 mL) was added into it. The reaction mixture was stirred at room temperature for 3 h. The resultant mixture was filtered through a cannula and the mother liquor was concentrated under vacuum and Et<sub>2</sub>O (3 mL) was added to obtain a pure blue-green compound 5. Yield: 0.057 g, 79%. M.p. = 230 °C (dec). Anal. calcd for C<sub>18</sub>H<sub>21</sub>O<sub>4</sub>N<sub>4</sub>F<sub>3</sub>SCu: C, 42.39; H, 4.15; N, 10.99; S, 6.29. Found: C, 42.97; H, 4.22; N, 10.29; S, 6.29. MALDI-TOF: *m/z* calcd for C<sub>18</sub>H<sub>21</sub>O<sub>4</sub>N<sub>4</sub>F<sub>3</sub>SCu [M<sup>+</sup>] 509.0532, found 508.8325 and [C<sub>18</sub>H<sub>21</sub>O<sub>4</sub>N<sub>4</sub>F<sub>3</sub>SCu-(CH<sub>3</sub>CN + OTf)]<sup>+</sup> [M – (CH<sub>3</sub>CN + OTf)]<sup>+</sup> 319.0740, found 318.9736.

Synthesis of  $[(^{Q}NN(H)N^{Et_2})Cu(CH_3CN)]ClO_4$  (6). A Schlenk flask was charged with ligand 1 (0.1 g, 0.389 mmol) and  $[(CH_3CN)_4Cu]ClO_4$  (0.127 g, 0.389 mmol), and acetonitrile (10 mL) was added into it. The reaction mixture was refluxed for 3 h and was cooled to ambient temperature. The resultant reaction mixture was filtered and the filtrate was evaporated under vacuum. Washing the solid residue with diethyl ether (8 mL × 3) afforded the crystalline compound  $[(^{Q}NN(H)N^{Et_2})$  $Cu(CH_3CN)]ClO_4$  (6). Yield: 0.138 g, 77%. <sup>1</sup>H NMR (400 MHz,  $CD_3CN)$ :  $\delta$  10.22 (br s, 1H, NH), 8.89 (d, J = 3.8 Hz, 1H, Ar–H), 8.64 (d, J = 7.6 Hz, 1H, Ar–H), 8.33 (d, J = 8.4 Hz, 1H, Ar–H), 7.71 (d, J = 8.4 Hz, 1H, Ar–H), 7.63–7.55 (m, 2H, Ar–H), 4.21 (s, 2H, CH<sub>2</sub>), 3.30 (q, J = 6.9 Hz, 4H, CH<sub>2</sub>), 2.61 (s, 3H, CH<sub>3</sub>CN), 1.31 (t, J = 7.2 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN):  $\delta$  164.1 (C<sub>q</sub>), 150.0 (CH), 138.9 (C<sub>q</sub>), 137.3 (CH), 134.2 (C<sub>q</sub>), 128.9 (C<sub>q</sub>), 127.7 (CH), 124.0 (CH), 123.1 (CH), 117.8 (CH), 55.5 (CH<sub>2</sub>), 51.0 (2C, CH<sub>2</sub>), 9.5 (2C, CH<sub>3</sub>), 1.8 (CH<sub>3</sub>CN). Anal. calcd for C<sub>17</sub>H<sub>22</sub>ClO<sub>5</sub>N<sub>4</sub>Cu: C, 44.26; H, 4.81; N, 12.14. Found: C, 43.97; H, 4.52; N, 11.94. MALDI-TOF: m/z calcd for C<sub>17</sub>H<sub>22</sub>ClO<sub>5</sub>N<sub>4</sub>Cu [M<sup>+</sup>] 460.06, found 460.12 and [C<sub>17</sub>H<sub>22</sub>ClO<sub>5</sub>N<sub>4</sub>Cu–(CH<sub>3</sub>CN + ClO<sub>4</sub>)]<sup>+</sup> [M – (CH<sub>3</sub>CN + ClO<sub>4</sub>)]<sup>+</sup> 320.08, found 320.07.

### Representative procedure for Kumada coupling

Synthesis of (3-cyclohexylpropyl)benzene (9aa). To a flamedried Schlenk tube equipped with a magnetic stir bar was introduced catalyst 5 (0.005 g, 0.01 mmol), LiOMe (0.008 g, 0.2 mmol) and (3-chloropropyl)benzene (0.031 g, 0.2 mmol), and THF (1.0 mL) was added under an argon atmosphere. The reaction mixture was cooled to 0 °C and CyMgCl (8a, 0.3 mL, 2.0 M in Et<sub>2</sub>O, 0.6 mmol) was added under argon. The resultant reaction mixture was then stirred at 0 °C for 8 h. At ambient temperature, saturated aqueous ammonium chloride solution (10 mL) was added and the reaction mixture was extracted with  $CH_2Cl_2$  (20 mL × 3). The combined organic layers were dried over  $Na_2SO_4$  and the solvent was evaporated *in vacuo*. The resulting residue was purified by column chromatography on silica gel (petroleum ether) to yield 9aa (0.0255 g, 63%) as a colorless liquid.

# Conflicts of interest

There are no conflicts to declare.

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