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N-heterocyclic silylene stabilized monocordinated copper(I)-arene cationic complexes and their application in click chemistry[†]

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Herein for the first time we report monocoordinated cationic Cu(i) complexes with unsymmetrical arenes (toluene and *m*-xylene) [LCu(η^3 -C₇H₈)]⁺[SbF₆]⁻ and [{LCu(η^2 -Me₂C₆H₄)}]⁺[SbF₆]⁻ [L = {PhC(NtBu)₂SiN(SiMe₃)₂}], [IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)], their reactivity and catalytic applications in CuAAC reactions (12 examples). The bonding analysis was performed in both silylene and carbene complexes using the EDA-NOCV method at the BP86/TZ2P level of theory.

Coinage metal π -complexes are important due to the catalytic functionalisation of π -substrates. Although there are a range of examples on coinage metal(1)-arene complexes,¹⁻³ the examples of structurally authenticated monocoordinated Cu(I)-arene cationic complexes are rare (A, B1 and B2)^{4,5} (Chart 1). Cu-arene complexes are considered to be present as intermediates in several reactions and they have shown their applications in a wide variety of catalytic reactions.⁶⁻¹² Owing to their highly reactive nature it is very challenging to isolate them in the monocoordinated form. In a pioneering work, Hayton and co-workers reported the first Cu(I)-arene complexes (A) where Cu(I) is bound to the hexamethylbenzene ring in a η^6 -fashion.⁴ Very recently, our group has reported the first copper cation [{PhC(NtBu)₂SiN(SiMe₃)₂}Cu(η^6 -C₆H₆)]⁺[SbF₆]⁻ (B1) bound to the benzene ring in an unsupported η^6 mode⁵ using amidinato silylene, [PhC(NtBu)₂SiN(SiMe₃)₂]¹³ as a ligand. The synthetic methodology also led to a copper cation (B2) bound to the hexamethylbenzene ring in η^6 mode.⁵ In light of these recent synthetic advances concerning Cu(I) arene complexes, a thorough study on other common arenes, especially unsymmetrical arenes such as toluene and xylene, is anticipated as no structural evidence exists for N-heterocyclic carbene (NHC)/silylene (NHSi) Cu(I) cations with such

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Scheme 1 Syntheses of complexes 2 and 3.





unsymmetrical arenes. To fill this void, we used [{PhC(NtBu)₂}-Si{N(SiMe₃)₂}]₂Cu₂Br₂ (1)¹⁴ as a precursor and synthesized [{PhC(NtBu)₂SiN(SiMe₃)₂}Cu(η^3 -C₇H₈)][†][SbF₆]⁻ (2) and [{PhC(NtBu)₂-SiN(SiMe₃)₂}Cu(η^2 -Me₂C₆H₄)][†][SbF₆]⁻ (3) complexes. It is noteworthy to mention that this is the first report where a monocoordinated Cu(1) cation is bound to free toluene and *m*-xylene. For an explicit comparison, we carried out the same reaction with NHC (IPr) in place of silylene by using IPr-CuBr¹⁵ with toluene and *m*-xylene which resulted in [IPr-Cu(η^3 -C₇H₈)]⁺[SbF₆]⁻ (5) and [IPr-Cu(η^2 -Me₂C₆H₄)]⁺[SbF₆]⁻ (6), respectively. Further we explored their reactivity with strong donor ligands *i.e.*, MeCN [PhC(NtBu)₂SiN(SiMe₃)₂] and IPr. We also explored 2 and 5 as catalysts in copper-catalyzed azide–alkyne cycloaddition (CuAAC) reactions. Our results are reported herein.

Treatment of **1** with AgSbF₆ in an arene (toluene/*m*-xylene)-CH₂Cl₂ mixture at room temperature for 10 hours afforded **2** and **3**, respectively (Scheme 1). The coordination of the arene ring to the Cu center is accompanied by the ¹H NMR spectrum of **2** displaying a peak for three methyl protons of toluene at 2.51 ppm which is slightly upfield shifted when compared to that in the free toluene (2.36 ppm). The six protons of the methyl group of *m*-xylene



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Fig. 1 The molecular structures of **2** (left) and **3** (right) (ellipsoids are shown at the probability level of 30%). Hydrogen atoms and the SbF₆ anion are omitted for clarity. Selected bond lengths (Å): (**2**) Si1–Cu1 2.234(2), Si1–N3 1.704(6), Cu1–C14 2.230(1), Cu1–C22 2.330(1), Cu1–C23 2.426(1), Cu1–C15 2.64(1), Cu1–C24 2.697(2), and Cu1–C27 2.828(2). (**3**) Si1–Cu1 2.244(8), Si1–N3 1.721(2), Cu1–C18 2.161(5), Cu1–C17 2.195(5), Cu1–C2 2.573(4), Cu1–C6 2.678(3), Cu1–C9 2.827(4), and Cu1–C29 2.957(3).

were observed at 2.28 ppm as a singlet (for free *m*-xylene at 2.40 ppm) in the ¹H NMR spectrum of **3**. The ²⁹Si NMR spectra of **2** and **3** display resonances at 2.28 ppm and 2.80 ppm, respectively, which correspond to the central Si(π) atom and are slightly upfield shifted in comparison to that of **1** (5.72 ppm).¹⁴

2 and 3 crystallize in orthorhombic $P2_12_12_1$ and monoclinic *Pn* space groups, respectively.¹⁶ The molecular structures of 2 and 3 (Fig. 1) unveil the η^3 and η^2 binding mode of the toluene and *m*-xylene rings, respectively (as per the bond distances of Cu–C_{arene} bonds). The assignment of hapticity for the complexes having low hapticities ($\eta^1 - \eta^3$) has always been a tough job. Therefore, we adopted the method developed by Alvarez and co-workers to calculate the hapticity (Table 1).¹⁷ The central Si(π) atom is four coordinate in both the cases and adopts a distorted tetrahedral geometry with the Si \rightarrow Cu bond distances of 2.234(2) Å (2) and 2.244(8) Å (3), which are slightly longer than those in **1** [2.222(2) Å].¹⁴

Furthermore, we treated the IPr \rightarrow CuBr (4) adduct¹⁵ with AgSbF₆ in the presence of toluene and *m*-xylene, respectively, which resulted in the corresponding [IPr·Cu(η^3 -C₇H₈)]⁺[SbF₆]⁻ (5) and [IPr·Cu(η^2 -Me₂C₆H₄)]⁺[SbF₆]⁻ (6) complexes (Scheme 2). The ¹H NMR spectra of 5 and 6 further supported the coordination of the respective arenes to the copper centre. 5 and 6 crystallize in the monoclinic *Cc* and orthorhombic *Pbca* space groups, respectively (Fig. 2).¹⁶ The Cu–C_{IPr} distance of 5 is 1.882(1) Å and matched well with the



Scheme 2 Syntheses of complexes 5 and 6



Fig. 2 The molecular structures of **5** (left) and **6** (right) (ellipsoids are shown at the probability level of 30%). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): (**5**) C2–Cu1 1.882(1), Cu1–C17 2.064(2), Cu1–C20 2.314(2), Cu1–C26 2.316(1), Cu1–C13 2.746(1), Cu1–C21 2.827(9), and Cu1–C15 3.001(1).

previously reported C_{IPr} -Cu bond length of $[IPr \cdot Cu(\eta^3 \cdot C_6H_6)]^+$ $[SbF_6]^-$ (1.890(3) Å) and $[IPr \cdot Cu(\eta^3 \cdot Me_6C_6)]^+[SbF_6]^-$ (1.886(5) Å), respectively.⁵ The Cu-C_{arene} bond distances and the hapticity calculations of 5 and 6 indicate the η^3 and η^2 binding mode of toluene and *m*-xylene to the Cu centre, respectively (Table 1). We attempted to isolate such coordination complexes with bigger arene systems (naphthalene, biphenyl, styrene, *etc.*) but unfortunately it did not work, and instead led to the formation of 7 most of the time.

It is well known that σ -donor ligands bind more strongly than π -donor ligands. Therefore, displacement reactions of arene rings with σ -donor ligands such as MeCN, NHC and NHSi with 2 and 5 were performed. Upon reaction of 2 with MeCN, the formation of a dimeric copper complex 7 along with Cu(CH₃CN)₄SbF₆ salt was noted (Scheme 3). 7 was spectroscopically characterized but the single crystal X-ray data are not sufficiently good to discuss the structural parameters. An analogous reaction of 5 afforded a

Table 1 The EDA-NOCV results (BP86/TZ2P) in **2** and **5**. (a) For the interaction of the L^1L^2Si fragment with Cu(Tol)⁺ and (b) the $L^1L^2SiCu^+$ fragment with Tol in complex **2**. (c) The NHC (IPr) fragment with Cu(Tol)⁺ and (d) the NHCCu⁺ fragment with Tol in complex **5**. $L^1 = N(SiMe_3)_2$, $L^2 = (Ph)C(Nt-Bu)_2$, Tol = $C_6H_5(CH_3)$. Energies are in kcal mol⁻¹

Parameter	(a)	(b)	(c)	(d)
$\Delta E_{\rm int}$	-94.8	-27.2	-94.6	-37.2
ΔE_{Pauli}	102.2	76.1	109.5	69.9
ΔE_{elstat}^{a}	-127.3(64.6%)	-58.4(56.4%)	-141.1(69.1%)	-57.4(53.6%)
$\Delta E_{\rm orb}^{a}$	-69.8 (35.4%)	-45.0(43.6%)	-63.0 (30.9%)	-49.7(46.4%)
$\Delta E_{\text{Tol} \rightarrow \text{Cu}}^{b}$	_	-22.5(50.0%)	_ ` `	-24.7(49.7%)
$\Delta E_{\rm Cu} \rightarrow {\rm Tol}^{b}$	_	-8.7 (19.3%)	_	-11.5(23.1%)
$\Delta E_{\text{Silvlene/NHC} \rightarrow \text{Cu}}^{b}$	-44.8(64.2%)	_ ``	-29.0(46.0%)	_ ` `
$\Delta E_{\rm Cu} \rightarrow {\rm Silvlene/NHC}^{b}$	-4.8(6.9%)	_	-9.7 (15.4%)	_
$\Delta E_{\text{rest}}^{b,c}$	-20.2	-13.8	-24.3	-13.5
$\Delta E_{\rm prep}^{d}$	7.9	3.5	3.2	4.5
$-\dot{D_e^{d}}$	-86.9	-23.7	-91.4	-32.7

^{*a*} Values in parentheses give the percentage contribution to the total attractive interactions, $\Delta E_{\text{orb}} + \Delta E_{\text{elstat}}$, ^{*b*} Values in parentheses give the percentage contribution to the orbital interactions, ΔE_{orb} , ^{*c*} $\Delta E_{\text{rest}} = \Delta E_{\text{orb}} - (\Delta E_{M \to L} + \Delta E_{L \to M})$. ^{*d*} ΔE_{prep} and D_{e} represent the preparatory and dissociation energy, respectively.

Scheme 3 Reaction of 2 with acetonitrile and IPr



Scheme 4 Reaction of 5 with MeCN and 2. The molecular structures of 8 and 9 (ellipsoids are shown at the probability level of 30%). Hydrogen atoms and the SbF₆ anion are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): (8) C1–Cu1 1.939(4), Cu1–Si1 2.271(1); and C1–Cu1–Si1 178.6(1); (9) C1–Cu1 1.926(5), C1–N2 1.361(4), Cu1–N4 1.976(4); N4–Cu1–N4 111.11(19), N4–Cu1–C1 124.38(10), C4–C3–N4 179.7(5), and C3–N4–Cu1 168.6(3).

tricoordinate copper cation **9** where two acetonitrile molecules were coordinated to the Cu center. The Cu–C_{IPr} bond distance is elongated to 1.926(5) Å (Scheme 4). The arene displacement reaction of **2** with IPr or **5** with NHSi afforded an identical complex, **8**, where a dicoordinate copper cation is bound to one silylene and one carbene ligand. This is a rare example of a mixed tetrelylene coinage metal cation. Note that, both the Cu–C_{IPr} [1.939(4) Å] and Cu–Si [2.271(1) Å] bond lengths have been increased compared to their parent bond lengths.

We have carried out quantum mechanical calculations at the M06/def2-TZVPP//BP86/def2-SVP level of theory¹⁷ to explore the bonding interaction between the silylene/IPr and Cu-centre as well as the arene ring in complexes **2**, **3**, **5** and **6**.¹⁸ The NBO charge analysis (Table S4, ESI[†]) of the complexes **2** and **3** shows that the N(SiMe₃)₂ (-0.53 *e*) and (Ph)C(N*t*-Bu)₂ (-0.35 to -0.36 *e*) ligands possess negative group charges. The positive charge is mainly located on the Si(π)-centre (1.43 *e*), Cu (0.27–0.29 *e*) and the arene ligand (0.16–0.189 *e*). Thus, a high positive charge on Si and a low positive charge on the Cu-centre indicate a strong Si(π) → Cu donor acceptor character, which is commonly observed in silylene complexes.¹⁹

The NBO analyses of complexes 2 and 3 suggest that five dorbitals of Cu⁺ (¹S, 3d¹⁰4s⁰) are occupied, and one of the vacant sp-hybrid orbital (79.6% s and 18.4% p) accepts the lone pair from silylene to form the Si(n) \rightarrow Cu bond. The NBO charge analysis (Table S4, ESI†) indicates significant differences in charge distribution on the carbene complexes 5 and 6 compared to that on 2 and 3. The Cu-centre in 5 (0.51–0.51 *e*) has a more positive charge than that in 2. The group charge on the NHC ligand is positive (0.33 *e* and 0.32 *e*) which indicates the IPr \rightarrow Cu donor-acceptor bond in the complexes 5 and 6.²⁰ The NBO analysis further confirms that the five d-orbitals of Cu⁺ (¹S, 3d¹⁰4s⁰) are occupied in the complexes 5 and 6 and one





Fig. 3 Plots of deformation densities (BP86/TZ2P) for (a) donation from the Si(II) \rightarrow sp-hybrid orbital on Cu; (b) backdonation from the d-orbital of Cu \rightarrow Si-N π^{**-} MO of silylene in **2**; (c) donation from the NHC \rightarrow sp-hybrid orbital on Cu and (d) back donation from the d-orbital of Cu $\rightarrow \pi^{**-}$ MO of NHC in **5**. The direction of charge flow is from red to blue. The isosurface value for the plot is 0.0003. The associated energy (ΔE) is given in kcal mol⁻¹.

of the vacant sp-hybrid orbital (80.4% s and 14.9% p) accepts the lone pair from the NHC to form the IPr \rightarrow Cu bond. The nature of bonding between silylene/NHC and the Cu-centre as well as the arene ring and the Cu-centre was further analysed by the EDA-NOCV method and the results of the toluene complexes 2 and 5 are discussed here (see the ESI† for 3 and 6).

The analysis of Si(n) \rightarrow Cu in 2 by the EDA-NOCV method (Table 1) indicates that the electrostatic interaction ($\Delta E_{elstat} = 64.6\%$) is higher than the covalent interaction (σ -type lone pair on silvlene to the vacant sp-hybrid orbital on Cu accounts to 64.2% of the total covalent interaction) (Fig. 3a, -44.8 kcal mol⁻¹). The back donation from the filled d-orbitals on Cu to the Si–N σ^* -molecular orbital (MO) of silvlene contributes to 6.9% of the total orbital interaction (Fig. 3b, -4.8 kcal mol⁻¹). Similar to 2, the IPr \rightarrow Cu bond in 5 (Table 1) also has a significant contribution from electrostatic interaction ($\Delta E_{elstat} = 69.1\%$) (see Table S5 in the ESI† for 3 and 6).

To explore the catalytic activity of our newly synthesized complexes, 2 and 5, we have studied the CuAAC reaction, which has been widely used for the synthesis of 1,2,3-triazoles.²¹ Unlike NHC-Cu(I) complexes, which have ample literature precedence in CuAAC catalysis,22 there is only one report of the CuAAC reaction with NHSi-Cu(1) multinuclear complexes by Stalke et al;²³ however, the methodology is limited to only benzyl azide (5 examples). Moreover, there is no report of a monocoordinated Si(II)–Cu complex for CuAAC reactions. Therefore, we have used 2 as a catalyst for different azides and alkynes under ambient conditions (Scheme 5), which afforded the desired triazoles in good to excellent yields. A higher yield is observed for aromatic alkynes (I, II, V, VI, IX, and X) than for the aliphatic ones (Scheme 5). Aromatic azides bearing electron donating groups afford better yields (IX and X) than those with electron withdrawing ones (XI and XII). Replacement of benzyl azide with the naphthylmethyl moiety has little effect on the yield except in the case of VII. It is to be noted here that the exploitation of naphthylmethyl azide in homogeneous click chemistry is not known, and the formation of triazole with the naphthylmethyl group is only accessed in a heterogeneous manner.²⁴ The drop



Scheme 5 General reaction scheme and substrate scope for triazole synthesis using 2. ^aReaction conditions: azide (0.2 mmol), alkyne (0.2 mmol), and toluene (2 mL) at room temperature. ^bHeating at 50 °C. ¹H NMR spectroscopy was used to determine the conversion yield of the products. See Table S1 (ESI†) for the reaction optimization details.

of yield for trimethylsilyl alkynes (**IV** and **VIII**) was also noted with a Stalke's multinuclear Si(π)–Cu catalyst. In fact, the performance of 2 is better than Stalke's catalysts in terms of catalyst loading (0.5 mol% *vs.* 1 mol%) and the reaction time. For comparison purpose, we have also used 5 as a catalyst in the CuAAC reaction and the related results are provided in the ESI† (Scheme S2).

In summary, we report for the first time free toluene and *m*-xylene coordinated monomeric cationic copper(1)-silylene/IPr complexes. Replacement of silylene with NHC as a ligand led to the isolation of NHC supported copper-toluene and xylene complexes too. Further we also showed the reactivity of these complexes with strong donor ligands which led to the isolation of the first dicoordinate copper complex **8** supported by mixed tetrelylenes. We also used **2** and **5** as catalysts in the copper-catalyzed azide-alkyne cycloaddition (CuAAC) reactions and found that **2** is very efficient for a variety of substrates.

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Conflicts of interest

There are no conflicts to declare.

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