

# Chemical Science

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## Chemical Science

## ARTICLE

Taming Monomeric  $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$  Complex with SilyleneNasrina Parvin,<sup>a</sup> Shiv Pal,<sup>a</sup> Jorge Echeverría,<sup>\*b</sup> Santiago Alvarez<sup>\*b</sup> and Shabana Khan<sup>\*a</sup>Received 00th January 20xx,  
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Previous theoretical and experimental endeavors suggested that  $[\text{Cu}(\text{C}_6\text{H}_6)]^+$  prefers  $\eta^1/\eta^2$  mode over  $\eta^6$  mode due to the augmented repulsion between the benzene ring and metal d-electrons. Nevertheless, the use of silylene as a neutral ligand has led to the isolation of the first monomeric copper cation,  $[\{\text{PhC}(\text{NtBu})_2\text{SiN}(\text{SiMe}_3)_2\}\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+[\text{SbF}_6]^-$  (**3**) where copper atom is bound to the benzene ring in unsupported  $\eta^6$  fashion. However, the use of IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in place of silylene results in the formation of  $[\text{IPr-Cu}(\eta^2\text{-C}_6\text{H}_6)]^+[\text{SbF}_6]^-$  (**6**), where the copper atom is bound to the benzene ring in  $\eta^2$  mode. The discrepancy in hapticities is also reflected when hexamethylbenzene is employed as the arene ring. The silylene supported copper cation continues to bind in  $\eta^6$  mode in **2** while NHC copper cation displays  $\eta^3$  bonding mode in **5**. DFT calculations are carried out to understand how the use of silylene led to  $\eta^6$  binding mode and why IPr afforded  $\eta^2$  binding mode.

## Introduction

Synthetic chemists often find fascination in isolating a compound that has been theoretically predicted as well as observed in the gas phase but never realized under laboratory condition. However, access to such compounds often poses formidable synthetic challenge. One such moiety is  $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$ . It is well evident from literature that group 11 metal-arene complexes strongly prefer the  $\eta^2$  binding mode.<sup>1,2</sup> Armentrout and coworkers reasoned that the preference of  $\eta^2$  bonding mode over  $\eta^6$  is due to the increase of repulsion between the metal d-electrons and the benzene ligand in the latter.<sup>3</sup> Cu-arene complexes with  $\eta^6$  bonding mode have also been reported albeit in small number, when using tethered arene rings in order to create cavity between the two arene rings by diminishing the repulsion.<sup>4</sup> These experimental results were further computationally supported by Guo and coworkers, who found that in the gas phase free  $\text{Cu}^+$  may form  $\eta^6$  type of complexation with benzene but in the condensed phase the propensity of  $\text{Cu}^+$  to form  $\eta^2$  complexes with benzene drastically increases in presence of a counter-anion.<sup>5</sup>

A major breakthrough in this research was recently achieved by Hayton and coworkers, who isolated two half sandwich complexes  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Cu}(\text{PR}_3)]^+[\text{PF}_6]^-$  (R=Ph, OPh)

where the  $\text{C}_6\text{Me}_6$  ring is bound to the Cu ion in  $\eta^6$  coordination mode.<sup>6</sup> However, they have also theoretically showed that when benzene is employed instead of hexamethylbenzene as an arene,  $\eta^2$  mode is preferred, and hence surmised that the preference for  $\eta^6$  mode over  $\eta^2$  mode is exclusively due to steric repulsion between Me groups and  $\text{PR}_3$  units. Additionally, they calculated the relative energies for  $[\text{Cu}(\text{C}_6\text{H}_6)]^+$  in gas as well as condensed phases and found the preference for  $\eta^2$  mode in both phases but more in condensed phase, as previously predicted by Guo et al. These studies consequently lead to the question: Is it even possible to isolate  $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$  in the condensed phase?

It is apparent now that one of the main factors responsible for the success or failure in the synthesis of  $[\text{Cu}(\eta^6\text{-arene})]^+$  is the ligand with appropriate substituent. Being better  $\sigma$ -donor than phosphines, silylenes are recently found to gain widespread interest as ligands for transition metals.<sup>7</sup> For this challenging work, we turned our attention towards  $[\text{PhC}(\text{NtBu})_2\text{SiN}(\text{SiMe}_3)_2]^8$  supported copper bromide complex,  $[\{\text{PhC}(\text{NtBu})_2\}\text{Si}\{\text{N}(\text{SiMe}_3)_2\}]_2\text{Cu}_2\text{Br}_2$  (**1**).<sup>9</sup> An appealing facet of  $[\text{PhC}(\text{NtBu})_2\text{SiN}(\text{SiMe}_3)_2]$  is that it accepts electron density from the metal as evidenced in its coinage metal complexes.<sup>9,10</sup> We postulate that such back-donation can diminish the electrostatic repulsion between metal d-electrons and arene rings that may facilitate the formation of  $\eta^6$  mode. This potential has been duly realized through the isolation and characterization of an unprecedented  $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$  complex. For a direct systematic comparison, we carried out the same reactions with *N*-heterocyclic carbene in place of **1**. Our results are reported herein.

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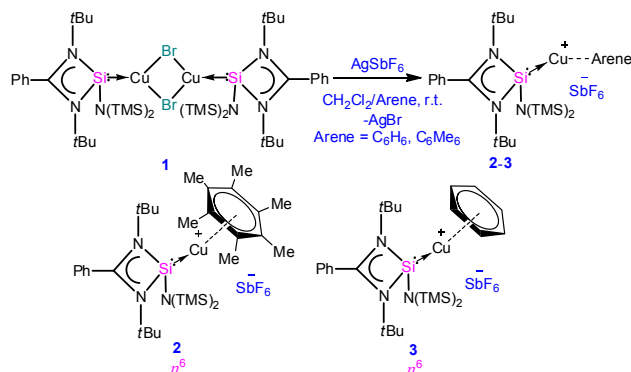
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†Electronic Supplementary Information (ESI) available: Experimental details of **2**, **3**, **5** and **6**, their single crystal X-ray data, and details of theoretical calculations are given in the supplementary material.



## Results and discussion

A simple synthetic protocol was designed to generate the desired copper cations. To check the credentials of **1** as a ligand, we commenced by probing the reaction of **1** with  $\text{AgSbF}_6$  in presence of hexamethylbenzene with the assumption that it would furnish  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Cu}]^+$  analogous to Hayton's results. Gratifyingly, the abstraction of bromide ion from dichloromethane solution of **1** with  $\text{AgSbF}_6$  in presence of hexamethylbenzene results in the formation of  $[\{\text{PhC}(\text{NtBu})_2\text{SiN}(\text{SiMe}_3)_2\}\text{Cu}(\eta^6\text{-C}_6\text{Me}_6)]^+[\text{SbF}_6]^-$  (**2**) (see S1 in supporting information for experimental details).



Scheme 1. Syntheses of complexes **2** and **3**.

The molecular structure of **2** is shown in Figure 1, which revealed the  $\eta^6$  mode of the arene ring. The Si atom adopts distorted tetrahedral geometry with the Si  $\rightarrow$  Cu bond length of 2.219(1) Å, which is in well accordance with that in **1** [2.222(2) Å].<sup>10</sup> The Cu–C(arene) bond lengths varies from 2.310(4) to 2.449(5) Å reflecting an unsymmetrical binding of the Cu with respect to the ring. The C–C bond lengths in the arene ring are more or less same ranging from 1.408(6) to 1.420(6) Å. The distance between the Cu atom and the centroid of the arene ring is 1.920 Å.

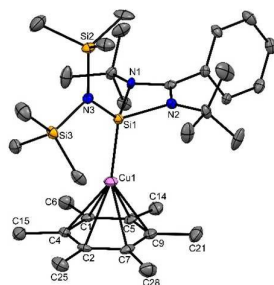


Figure 1. The molecular structure of **2** (ellipsoids are shown at the probability level of 50%). Counter anion  $\text{SbF}_6^-$  and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Si1–Cu1 2.219(1), Si1–N1 1.837(3), Si1–N2 1.834(3), Cu1–C1 2.449(5), Cu1–C2 2.372(4), Cu1–C4 2.443(5), Cu1–C5 2.407(4), Cu1–C7 2.318(4), Cu1–C9 2.310(4), C1–C4 1.408(6), C4–C2 1.414(5), C2–C7 1.420(6), C7–C9 1.410(6), C9–C5 1.409(6), C5–C1 1.414(6).

Next, we turned our endeavours towards our primary objective of isolating  $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$ . Similar synthetic protocol was adopted to access  $[\{\text{PhC}(\text{NtBu})_2\text{SiN}(\text{SiMe}_3)_2\}\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+[\text{SbF}_6]^-$  (**3**). The complex **3** crystallizes in the monoclinic space group,  $P2_1/n$ . The molecular structure of **3** (Figure 2) reveals the  $\eta^6$  coordination mode of benzene to the Cu center. The Cu–C<sub>benzene</sub> bond distances range between 2.342(9) to 2.477(8) Å, with an average of 2.404 (mean) Å, which is longer than those reported for  $[\text{Cu}(\eta^6\text{-C}_6\text{Me}_6)]^+$ .<sup>6</sup> Similarly, the distance between the Cu atom and centroid of benzene ring (Cu–C<sub>centroid</sub> 1.960 Å) in **3** is slightly longer than those in Hayton's  $[\text{Cu}(\eta^6\text{-C}_6\text{Me}_6)]^+$  complexes (1.800(3) and 1.775(6) Å),<sup>6</sup> but significantly shorter than those reported for the tethered Cu(arene) complexes such as Cu(I)-cyclophanes or 9,10-anthracene derived endo-cyclic Cu(I) complexes (~2.5–3.0 Å).<sup>4</sup> The  $[\text{SbF}_6]^-$  anion in the asymmetric unit shows no significant bonding interaction with the Cu<sup>+</sup> atom and the closest approach between the F atom and Cu center (Cu $\cdots$ F) is 4.96(1) Å, which rules out any possibility of interaction between them. The average C–C bond length of C<sub>6</sub>H<sub>6</sub> ligand in **3** is 1.39 Å (range 1.38(1)–1.40(1) Å) (C–C<sub>C6H6(non-bounded)}</sub>: 1.40 Å; C–C<sub>Me6C6(non-bounded)}</sub>: 1.41 Å). The Si(II) atom assumes a distorted tetrahedral geometry with the Si(II) $\rightarrow$ Cu bond length is 2.231(2) Å, which is similar to that in **1** and **2**.

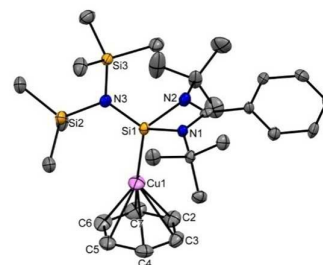
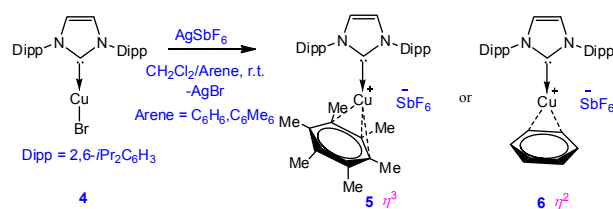


Figure 2. The molecular structure of **3** (ellipsoids are shown at the probability level of 50%). Counter anion  $\text{SbF}_6^-$  and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): N2–Si1 1.844(4), N1–Si1 1.847(5), N3–Si1 1.737(5), Cu1–Si1 2.231(2), Cu1–C2 2.454(7), Cu1–C3 2.477(8), Cu1–C4 2.413(9), Cu1–C5 2.359(9), Cu1–C6 2.342(9), Cu1–C7 2.379(8), C2–C3 1.38(1), C3–C4 1.39(1), C4–C5 1.39(1), C5–C6 1.39(1), C6–C7 1.40(1), C7–C2 1.40(1), Cu1–Centroid of benzene ring 1.960.

All analytical and spectroscopic data of **2** and **3** are consistent with the proposed structures. The binding of benzene to the Cu atom in **3** resulted in slight downfield shift of the C<sub>6</sub>H<sub>6</sub> protons ( $\delta$  7.46 ppm). The appearance of two signals for the trimethylsilyl groups in <sup>1</sup>H ( $\delta$  0.24 and 0.39 ppm) as well as <sup>29</sup>Si NMR ( $\delta$  7.21 and 7.65 ppm) of **3** indicates that they are not equivalent and the diastereotopicity arises from the bulky substituents around the Si(II) atom. The Si(II) center resonates at  $\delta$  4.41 ppm, which is marginally upfield relative to that in **1** ( $\delta$  5.72 ppm) in the <sup>29</sup>Si NMR spectrum.<sup>10</sup>

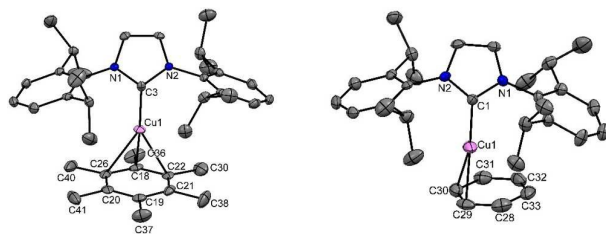




Scheme 2. Syntheses of complexes 5 and 6.

To extend the analogous chemistry with N-heterocyclic carbenes we reacted the previously reported IPr-CuBr (**4**)<sup>11</sup> with AgSbF<sub>6</sub> in presence of hexamethylbenzene and benzene which afforded [IPr-Cu(η<sup>3</sup>-C<sub>6</sub>Me<sub>6</sub>)][SbF<sub>6</sub>]<sup>−</sup> (**5**) and [IPr-Cu(η<sup>2</sup>-C<sub>6</sub>H<sub>6</sub>)][SbF<sub>6</sub>]<sup>−</sup> (**6**), respectively. Single crystal X-ray studies on **5** and **6** indicated η<sup>3</sup> and η<sup>2</sup> coordination<sup>12</sup> of Cu atom with the arene rings, respectively (Figure 3) (Please see SI for the deduction of hapticities in **5** and **6**, S3). The C<sub>IPr</sub>-Cu bond lengths in **5** and **6** are 1.890(3) and 1.886(5) Å, respectively. The Cu-C<sub>arene</sub> bond lengths in **5** range from 2.114(4) to 2.319(4) Å, while 2.129(6) and 2.217(5) Å for **6**. The methyl protons of C<sub>6</sub>Me<sub>6</sub> ring appear at δ 1.8 ppm with an integration of 18 protons.

In order to understand the different hapticities observed experimentally, the geometries of **2**, **3**, **5**, and **6** have been optimized at the DFT level (see the SI for a detailed description of the computational procedure and for the atomic coordinates of the optimized structures).

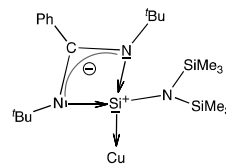


**Figure 3.** Molecular structure of **5** and **6** (ellipsoids are shown at the probability level of 50%). Counter anion SbF<sub>6</sub><sup>−</sup> and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): **5**: N1-C3 1.353(4), N2-C3 1.356(4), Cu1-C3 1.890(3), Cu1-C18 2.114(4), Cu1-C22 2.289(4), Cu1-C26 2.319(4); Cu1-C21 2.678(4), Cu1-C20 2.715(4), Cu1-C19 2.894(4). **6**: C1-N1 1.356(7), C1-N2 1.349(6), C1-Cu1 1.886(5), Cu1-C29 2.129(6); Cu1-C30 2.217(5), Cu1-C28 2.456(6), Cu1-C31 2.621(5), Cu1-C33 2.813(6), Cu1-C32 2.892(6).

The hapticities and the most relevant bond distances, calculated at the B3LYP-D3 level, are shown in Table 1, together with the experimental values. It can be seen that the experimental Cu-L (L = Si, C) distances are reproduced within 0.02 Å and the Cu-arene ones within 0.1 Å. The η<sup>6</sup> coordination in the silylene complexes is well reproduced by our calculations. The hapticities for other cases for which η<sup>1</sup>, η<sup>2</sup> and η<sup>3</sup> coordinations can be hard to distinguish are deduced from the values of the distance ratios of the three shortest Cu-C<sub>arene</sub> distances (d<sub>1</sub> < d<sub>2</sub> < d<sub>3</sub>), p<sub>1</sub> (d<sub>2</sub>/d<sub>1</sub>) and p<sub>2</sub> (d<sub>3</sub>/d<sub>1</sub>).<sup>12</sup> For the carbene complexes, the calculated hapticity is η<sup>3</sup> for **5** and η<sup>2</sup> for **6**, as indicated by the corresponding values of p<sub>1</sub> and p<sub>2</sub>. It is worth mentioning here that carbene complexes evolve to

η<sup>3</sup>/η<sup>2</sup> when starting the optimization from a η<sup>3</sup> geometry, whereas silylene complexes behave conversely.

We have performed an NBO analysis of the benzene complexes **3** and **6** to try to rationalize their different behavior in terms of arene coordination. Second order perturbation analysis revealed that bonding between Cu and the carbene ligand is a donor-acceptor interaction from the carbene lone pair to an empty Cu orbital (nC→nCu\*, E = 109.1 kcal/mol). Cu-silylene donor-acceptor interactions in **3**, however, are not clearly determined because the complex could not be decomposed into the same fragments as in **6**. On the other hand, the coordination of the benzene ring to the metal atom is associated to donor-acceptor interactions involving a mixture of s and p benzene orbitals (98 and 84 kcal/mol in **3** and **6**, respectively). Moreover, for the carbene complex there is π-back donation towards the benzene ring (nCu→πC-C\*, E = 19.3 kcal/mol). Another relevant result is that the atomic charge at the donor atoms are -0.06 for C<sub>IPr</sub> in **6**, but +1.26 for the Si atom in **3**. These values are consistent with the zerovalent nature of the carbenoid carbon atom and the formal positive charge of the Si atom in the zwitterionic Lewis structure of the ligand (Scheme 3), calculated to be +1.18 for the free ligand. The calculated charge at Si in **3** is thus the result of a formal positive charge increased by σ donation, partially compensated by π back-donation from Cu.



Scheme 3. Zwitterionic form of the silylene ligand.

The presence of H...H attractive interactions<sup>13</sup> involving the arene's hydrogen atoms on one side, and those of the <sup>t</sup>Pr and SiMe<sub>3</sub> groups of the carbene and silylene ligands on the other side, might also have some saying on the different stabilities of the η<sup>6</sup> coordination in the two cases. The optimized complexes present numerous dihydrogen contacts between the arene and the silylene ligand at distances in the range 2.3 – 2.5 Å (consistent with C...C distances of 3.5 – 3.9 Å in the crystal structures). Such intramolecular interactions have been shown to stabilize otherwise unstable systems, as for example in the case of molecules with very long C-C bonds<sup>14</sup> or the *cis* form of a substituted azobenzene.<sup>15</sup>



## ARTICLE

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**Table 1.** Optimized geometrical parameters of the four molecules under study. The dispersion-corrected B3LYP-D3 method and the 6-31G\* basis set for N and Cu and 6-311+G\* for H and C were employed. The numbers given in parentheses are the Cu-arene distance ratios  $\rho_1$  and  $\rho_2$ .

Molecule	Hapticity ( $\rho_1$ , $\rho_2$ )	Cu-L (Å)	Shortest Cu-C <sub>arene</sub> (Å)
<b>2</b>	exp. $\eta^6$	2.219	2.310
	calcd. $\eta^6$	2.206	2.298
<b>3</b>	exp. $\eta^6$	2.231	2.342
	calcd. $\eta^6$	2.209	2.272
<b>5</b>	exp. $\eta^3$ (1.05, 1.09)	1.890	2.114
	calcd. $\eta^3$ (1.08, 1.13)	1.886	2.078
<b>6</b>	exp. $\eta^2$ (1.04, 1.15)	1.886	2.129
	calcd. $\eta^2$ (1.01, 1.33)	1.887	2.105

We have performed NCI (non covalent interactions) calculations,<sup>16</sup> (see NCI maps of **2**, **3**, **5** and **6** in the SI, S4), observing regions of attractive non-covalent interactions between the hydrogen atoms at the benzene and the methyl groups from the silylene in **3** (also in the hexamethylbenzene complex **2**) and between the benzene hydrogens and the carbene *i*Pr groups in **6**. Indeed, an AIM analysis of **3** discloses a bond path between the H atoms of the coordinated C<sub>2</sub>H<sub>2</sub> moiety of benzene and those of the *i*Pr groups of the carbene, with an electron density at the bond critical point of 0.003 au, similar to previously reported dihydrogen interactions.<sup>17</sup>

**Table 2.** Energy decomposition analysis (EDA) into electrostatic ( $\Delta E_{\text{elect}}$ ), dispersion ( $\Delta E_{\text{disp}}$ ), polarization ( $\Delta E_{\text{pol}}$ ), charge transfer ( $\Delta E_{\text{CT}}$ ) and Pauli repulsion ( $\Delta E_{\text{Pauli}}$ ) terms for compounds **3**, **6** and **6'**, corrected for the BSSE. The interaction is defined between the C<sub>6</sub>H<sub>6</sub> ring and the Cu(*i*Pr) and Cu(silylene) fragments, respectively; energies in kcal/mol.

Cpd.	$\Delta E_{\text{int}}$	$\Delta E_{\text{elect}}$	$\Delta E_{\text{disp}}$	$\Delta E_{\text{pol}}$	$\Delta E_{\text{CT}}$	Total	$\Delta E_{\text{Pauli}}$	
							C <sub>6</sub> H <sub>6</sub> :L	C <sub>6</sub> H <sub>6</sub> :Cu
<b>3</b> ( $\eta^6$ )	-23.3	-51.7	-15.4	-25.0	-27.5	96.4	10.6	85.8
<b>6'</b> ( $\eta^6$ )	-17.4	-70.6	-22.0	-27.0	-32.8	134.9	37.5	97.4
<b>6</b> ( $\eta^2$ )	-38.9	-36.4	-15.0	-19.7	-23.0	55.4	7.2	48.2

To further test the relative influence of steric repulsions and noncovalent interactions on the hapticity of the coordinated arenes we have carried out an energy decomposition analysis (EDA) for **3** and **6** (Table 2), as well as for the hypothetical complex **6'** in which the benzene is forced to be coordinated in a  $\eta^6$  mode. In this constrained model complex, which is not a minimum of the potential energy surface, the Cu-C<sub>arene</sub> distances were set to be those of **3**. In general, the interaction energy and its decomposition was evaluated between two molecular fragments: the C<sub>6</sub>H<sub>6</sub> ring and the Cu(*i*Pr) and Cu(silylene) fragments, respectively. It can be seen that the results for **6'** indicate a much stronger Pauli repulsion between the two ligands than in **3**, that is relieved by its slippage to an  $\eta^2$  coordination. Even if slippage reduces also the stabilizing components, the balance yields more favorable interaction energy due to the dramatic decrease of the Pauli repulsion term. An EDA analysis of the interaction between benzene and the complementary ligands in the absence of the Cu centre for the three compounds of Table 2 allow us to estimate a Pauli term that calibrates the part of the steric

repulsion that comes from benzene-ligand interactions, and we can also roughly estimate the benzene-Cu repulsion as the difference between the total and the benzene-ligand Pauli terms. The important Pauli repulsion between the  $\eta^6$ -C<sub>6</sub>H<sub>6</sub> molecule and the Cu ion can be attributed to the interaction between the occupied  $\pi(e_{1g})$  orbitals of benzene and the  $d_{xz}$  and  $d_{yz}$  orbitals of Cu. Hence, the smaller repulsion in  $\eta^6$ -**3** compared to  $\eta^6$ -**6'** must be also attributed to the longer Cu-Si/C<sub>carbene</sub> distance in the former case (2.21 Å in **3** vs. 1.89 Å in **6'**). Clearly, slippage of the benzene ring from the  $\eta^6$  coordination in **6'** to the  $\eta^2$  mode in **6** results in a significant decrease in both the benzene-carbene and benzene-copper Pauli repulsions, and explains the preference for the  $\eta^2$  mode in the latter, in contrast with the preference of the  $\eta^6$  coordination for **3**.

The dispersion interaction contributes significantly to the bonding between the C<sub>6</sub>H<sub>6</sub> ring and the CuL fragments (L = {PhC(NtBu)<sub>2</sub>SiN(SiMe<sub>3</sub>)<sub>2</sub>} and *i*Pr for **3** and **6**, respectively), and overweights in both cases the benzene-ligand steric repulsions, contributing some 5-8 kcal/mol to the bonding between the benzene and the CuL fragment. It must be noted that the dispersion contribution is similar in the two cases and has therefore a negligible effect on the hapticity.

## Conclusions

This study was set out to synthesize the first copper cation bound to the benzene ring in an unsupported  $\eta^6$  mode. The silylene supported copper cation was found to be bound with both benzene and hexamethylbenzene in an  $\eta^6$  mode. DFT calculations revealed that the positive charge on silylene favors back-donation from the Cu atom, thus relieving the repulsions between the benzene  $\pi$ -system and the Cu d-electrons. Furthermore, the long Cu-Si bond distance places the *t*Bu substituents of the silylene at a longer distance of the arene hydrogens, thereby significantly reducing the steric repulsion that prevents the  $\eta^6$  coordination in the case of the NHC complexes. We conclude that, to favor an  $\eta^6$  coordination mode, the complementary ligands must have a  $\pi$ -acceptor character, with a third row donor atom to minimize steric repulsions, and with a relatively small cone angle. Based on those principles, we have carried out test calculations on the so far unprepared [(C<sub>6</sub>H<sub>6</sub>)Cu(CN)] and [(C<sub>6</sub>H<sub>6</sub>)Cu(CO)]<sup>+</sup> complexes that disclose an  $\eta^6$  coordination in both cases, similar in their bonding parameters to those in compound **3** reported herein.

## Conflicts of interest

There are no conflicts to declare.

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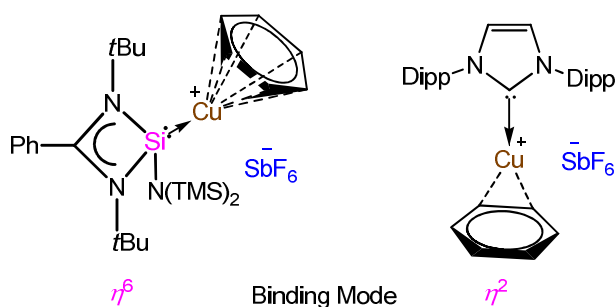
## Notes and references

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## TOC

for

**Taming Monomeric  $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$  Complex with Silylene**Nasrina Parvin,<sup>a</sup> Shiv Pal,<sup>a</sup> Jorge Echeverría,<sup>\*b</sup> Santiago Alvarez<sup>\*b</sup> and Shabana Khan<sup>\*a</sup>

Realization of hitherto elusive unsupported  $\eta^6$  binding mode of benzene to copper(I) cation employing silylene as a ligand. The back-donation from  $\text{Cu} \rightarrow \text{Si}(\text{II})$  diminishes the repulsion between d-electrons and benzene ring and enforces the  $\eta^6$  binding mode.

