Taming a monomeric [Cu(η⁶-C₆H₆)]⁺ complex with silylene†‡

Nasrina Parvin,a Shiv Pala, Jorge Echeverria,b Santiago Alvarezb, and Shabana Khanb,*

Previous theoretical and experimental endeavors suggested that [Cu(C₆H₆)]⁺ prefers the η⁵/η⁶ mode over the η⁶ 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, [{PhC(NBu)₂SiN(SiMe₃)₂}Cu(η⁶-C₆H₆)]⁺[SbF₆]⁻ (3), where a copper atom is bound to the benzene ring in an unsupported η⁶ fashion. However, the use of IPr (1,3-bis[2,6-disopropylphenyl]imidazol-2-ylidene) in place of silylene results in the formation of [IPr·Cu(η⁵-C₆H₆)]⁺[SbF₆]⁻ (6), where the copper atom is bound to the benzene ring in the η⁵ mode. The discrepancy in hapticities is also reflected when hexamethylbenzene is employed as the arenne ring. The silylene supported copper cation continues to bind in the η⁵ mode in 2 while the NHC copper cation displays an η⁵ bonding mode in 5. DFT calculations are carried out to understand how the use of silylene led to the η⁶ binding mode and why IPr afforded the η⁵ bonding 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 conditions. However, access to such compounds often poses a formidable synthetic challenge. One such moiety is [Cu(η⁶-C₆H₆)]⁺. It is well evident from the literature that group 11 metal–arene complexes strongly prefer the η⁶ binding mode.² Armentrout and coworkers reasoned that the preference of the η² bonding mode over η⁵ is due to the increase of repulsion between the metal d-electrons and the benzene ligand in the latter.³ Cu–arene complexes with the η⁶ bonding mode have also been reported albeit in small numbers, when using tethered arene rings in order to create a cavity between the two arene rings by diminishing the repulsion.⁴ These experimental results were further computationally supported by Guo and coworkers, who found that in the gas phase Cu⁺ may form η⁶ type of complexation with benzene but in the condensed phase the propensity of Cu⁺ to form η⁵ complexes with benzene drastically increases in the presence of a counter-anion.⁵

A major breakthrough in this research was recently achieved by Hayton and coworkers, who isolated two half sandwich complexes [{η²-C₆Me₆}Cu(PR₃)]²[P₄F₁₀] (R = Ph, OPh) where the C₆Me₆ ring is bound to the Cu ion in the η⁶ coordination mode.⁶ However, they have also theoretically shown that when benzene is employed instead of hexamethylbenzene as an arenne, the η² mode is preferred, and hence surmised that the preference for the η⁶ mode over the η⁵ mode is exclusively due to steric repulsion between Me groups and PR₃ units. Additionally, they calculated the relative energies for [Cu(C₆H₆)]⁺ in gas as well as condensed phases and found the preference for the η⁵ mode in both phases but more in the condensed phase, as previously predicted by Guo et al. These studies consequently lead to the question: is it even possible to isolate [Cu(η⁶-C₆H₆)]⁺ in the condensed phase?

It is apparent now that one of the main factors responsible for the success or failure of the synthesis of [Cu(η⁵-arene)]⁺ is the ligand with an appropriate substituent. Being better σ-donors than phosphines, silylenes have recently been found to attract widespread interest as ligands for transition metals.⁷ For this challenging work, we turned our attention towards a [PhC(NBu)₂SiN(SiMe₃)₂]⁸ supported copper bromide complex, [{PhC(NBu)₂SiN(SiMe₃)₂}Cu₂Br₂ (1)].⁸ An appealing facet of [{PhC(NBu)₂SiN(SiMe₃)₂}Cu₂Br₂ (1)] is that it accepts electron density from the metal as evidenced in its coinage metal complexes.⁹,¹⁰ We postulate that such back-donation can diminish the electrostatic repulsion between metal d-electrons and arene rings, which may facilitate the formation of the η⁶...
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 our investigation by probing the reaction of 1 with AgSbF$_6$ in the presence of hexamethylbenzene with the assumption that it would furnish [Cu($\eta^6$-C$_6$H$_6$)]$^+$ analogous to Hayton’s results. Gratifyingly, the abstraction of bromide ions from a dichloromethane solution of Hayton’s results. Gratifyingly, the abstraction of bromide ions [PhC(N$_3$)$_2$] bu[s(SiMe$_3$)$_2$]Cu($\eta^6$-C$_6$H$_6$)]$^+$ [SbF$_6$]$^-$ (3). Complex 3 crystallizes in the monoclinic space group $P2_1/n$. The molecular structure of 3 (Fig. 2) reveals the $\eta^6$ coordination mode of benzene to the Cu center. The Cu–C$_6$H$_6$ bond distances range from 2.342(9) to 2.477(8) Å, with an average of 2.404 Å, which is longer than those reported for [Cu($\eta^6$-C$_6$H$_6$)]$^+$—$.^*$ Similarly, the distance between the Cu atom and the centroid of the benzene ring (Cu–C$_{centroid}$) is 1.960 Å in 3 is slightly longer than those in Hayton’s [Cu($\eta^6$-C$_6$H$_6$)]$^+$ complexes (1.800(3) and 1.775(6) Å, 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). The [SbF$_6$]$^-$ anion in the asymmetric unit shows no significant bonding interaction with the Cu$^+$ atom and the closest approach between the F atom and the Cu center (Cu–F) is 4.96(1) Å, which rules out any possibility of interaction between them. The average C–C bond length of the C$_6$H$_6$ ligand in 3 is 1.39 Å (range 1.38(1)–1.40(1) Å). The Si(n) atom assumes a distorted tetrahedral geometry with a Si–C bond length of the C$_6$H$_6$ ligand in 3 is 1.39 Å (range 1.38(1)–1.40(1) Å). The Si(n) atom assumes a distorted tetrahedral geometry with a Si–C bond length of 1.40 Å; C–C$_{MeC}_{6}(non-bound)$: 1.41 Å. The $SbF_6^-$ atom forms a weak interaction with the Si(n) atom. The Si(n) center resonates at δ 4.41 ppm, which is marginally upfield relative to that in 1 (δ 5.72 ppm) in the $^{29}$Si NMR spectrum (Scheme 2).$^*$

Next, we turned our endeavours towards our primary objective of isolating [Cu($\eta^6$-C$_6$H$_6$)]$^+$. A similar synthetic protocol was adopted to access [[PhC(N$_3$)$_2$]Si(SiMe$_3$)$_2$]Cu($\eta^6$-C$_6$H$_6$)]$^+$ [SbF$_6$]$^-$ (4). Complex 4 crystallizes in the monoclinic space group $P2_1/n$. The molecular structure of 4 (Fig. 2) reveals the $\eta^6$ coordination mode of benzene to the Cu center. The Cu–C$_6$H$_6$ bond distances range from 2.372(8) to 2.477(8) Å, with an average of 2.404 Å, which is longer than those reported for [Cu($\eta^6$-C$_6$H$_6$)]$^+$—$.^*$ Similarly, the distance between the Cu atom and the centroid of the benzene ring (Cu–C$_{centroid}$) is 1.960 Å.

The molecular structure of 2 is shown in Fig. 1, which revealed the $\eta^6$ mode of the arene ring. The Si atom adopts a distorted tetrahedral geometry with a Si–Cu bond length of 2.219(1) Å, which is in good accordance with that in 1 [2.222(2) Å].$^*$ The Cu–C(arene) bond lengths varies from 2.310(4) to 2.449(5) Å, reflecting a slightly unsymmetrical binding of the Cu with respect to the ring. The C–C bond lengths in the arene ring are more or less the 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.

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To extend the analogous chemistry with N-heterocyclic carbenes we reacted the previously reported iPr-CuBr \( \text{4}^{11} \) with AgSbF\(_6\) in the presence of hexamethylenbenzene and benzene, which afforded \([\text{IPr-Cu}\left(\eta^1-\text{C}_6\text{Me}_6\right)]\left[\text{SbF}_6\right]^-\) (5) and \([\text{IPr-Cu(\eta^3-\text{C}_6\text{H}_5)}]\left[\text{SbF}_6\right]^-\) (6), respectively. Single crystal X-ray studies on 5 and 6 indicated \( \eta^1 \) and \( \eta^3 \) coordination\(^{12}\) of the Cu atom with the arene rings, respectively (Fig. 3) (please see S3 in the ESI for a detailed description of the computational procedure and for the atomic coordinates of the optimized structures).

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 \( \eta^1 \) coordination in the silylene complexes is well reproduced by our calculations. The hapticities for other cases for which \( \eta^1, \eta^2 \) and \( \eta^3 \) coordinations can be hard to distinguish are deduced from the values of the distance ratios of the three shortest Cu–arene distances \( d_1, d_2, d_3 \), \( \rho_1 \left( d_1/d_2 \right) \) and \( \rho_2 \left( d_3/d_2 \right) \).\(^{12}\) For the carbene complexes, the calculated hapticity is \( \eta^3 \) for 5 and \( \eta^1 \) for 6, as indicated by the corresponding values of \( \rho_1 \) and \( \rho_2 \). It is worth mentioning here that carbene complexes evolve to \( \eta^1/\eta^3 \) when starting the optimization from an \( \eta^3 \) 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\(\rightarrow\)nCu\(^+\), \( E = 109.1 \) kcal mol\(^{-1}\)). 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 with donor–acceptor interactions involving a mixture of s and p benzene orbitals (98 and 84 kcal mol\(^{-1}\) in 3 and 6, respectively). Moreover, for the carbene complex there is a \( \pi \)-back donation towards the benzene ring (nC\(\rightarrow\pi\text{Cu}^+\), \( E = 19.3 \) kcal mol\(^{-1}\)). Another relevant result is that the atomic charge on the donor atoms is \(-0.06\) for C\(_{\text{IPr}}\) in 6, but +1.26 for the Si atom in 3. These values are consistent with the zero-valent nature of the carbenoid carbon atom and the formal positive charge of the Si atom in the zwitterionic Lewis structure of the silylene ligand (Scheme 3), calculated to be +1.18 for the free ligand. The calculated charge on Si in 3 is thus the result of a formal positive charge increased by \( \sigma \) donation, partially compensated by \( \pi \) back-donation from Cu.

The presence of H–H attractive interactions,\(^{13}\) involving the arene’s hydrogen atoms on one side, and those of the \(^1\text{Pr} \) and SiMe\(_3\) groups of the carbene and silylene ligands on the other side, might also have some effect on the different stabilities of the \( \eta^1 \) coordination in the two cases. The optimized complexes present numerous dihydrogen contacts between the arene and the silylene ligand at distances in the range of 2.3–2.5 Å (consistent with C–H distances of 3.5–3.9 Å in the crystal structure).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Hapticity ((\rho_1, \rho_2))</th>
<th>Cu–L (Å)</th>
<th>Shortest Cu–arene (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Exp. ( \eta^6 )</td>
<td>2.219</td>
<td>2.310</td>
</tr>
<tr>
<td></td>
<td>Calcd. ( \eta^6 )</td>
<td>2.206</td>
<td>2.298</td>
</tr>
<tr>
<td>3</td>
<td>Exp. ( \eta^6 )</td>
<td>2.231</td>
<td>2.342</td>
</tr>
<tr>
<td></td>
<td>Calcd. ( \eta^6 )</td>
<td>2.209</td>
<td>2.272</td>
</tr>
<tr>
<td>5</td>
<td>Exp. ( \eta^6(1.05, 1.09) )</td>
<td>1.890</td>
<td>2.114</td>
</tr>
<tr>
<td></td>
<td>Calcd. ( \eta^6(1.08, 1.13) )</td>
<td>1.886</td>
<td>2.078</td>
</tr>
<tr>
<td>6</td>
<td>Exp. ( \eta^6(1.04, 1.15) )</td>
<td>1.886</td>
<td>2.129</td>
</tr>
<tr>
<td></td>
<td>Calcd. ( \eta^6(1.01, 1.33) )</td>
<td>1.887</td>
<td>2.105</td>
</tr>
</tbody>
</table>

**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 \( \rho_2 \).
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\textsuperscript{34} or the cis form of a substituted azobenzene.\textsuperscript{15}

We have performed NCI (non-covalent interaction) calculations\textsuperscript{34} (see the NCI maps of 2, 3, 5 and 6 in ESI, S4\textdagger), observing regions of attractive non-covalent interactions between the hydrogen atoms of the benzene and the methyl groups of the silylene in 3 (also in the hexamethylbenzene complex 2) and between the benzene hydrogens and the carbene p’r groups in 6. Indeed, AIM analysis of 3 discloses a bond path between the H atoms of the coordinated C\textsubscript{6}H\textsubscript{6} moiety of benzene and those of the p’r groups of the carbene, with an electron density at a bond critical point of 0.003 au, similar to previously reported dihydrogen interactions.\textsuperscript{17}

To further test the relative influence of steric repulsions and non-covalent interactions on the hapticity of the coordinated arenes we have carried out 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 an \( \eta^6 \) mode. In this constrained model complex, which is not a minimum of the potential energy surface, the Cu–C\textsubscript{arene} distances were set to those of 3. In general, the interaction energy and its decomposition was evaluated between two molecular fragments: the C\textsubscript{6}H\textsubscript{6} ring and the Cu(IPr) and Cu(silylene) fragments, respectively.

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>( \Delta E_{\text{int}} )</th>
<th>( \Delta E_{\text{elect}} )</th>
<th>( \Delta E_{\text{disp}} )</th>
<th>( \Delta E_{\text{pol}} )</th>
<th>( \Delta E_{\text{CT}} )</th>
<th>( \Delta E_{\text{Pauli}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 (( \eta^1 ))</td>
<td>–23.3</td>
<td>–51.7</td>
<td>–15.4</td>
<td>–25.0</td>
<td>–27.5</td>
<td>96.4</td>
</tr>
<tr>
<td>6’ (( \eta^6 ))</td>
<td>–17.4</td>
<td>–70.6</td>
<td>–22.0</td>
<td>–27.0</td>
<td>–32.8</td>
<td>134.9</td>
</tr>
<tr>
<td>6 (( \eta^6 ))</td>
<td>–38.9</td>
<td>–64.6</td>
<td>–15.0</td>
<td>–19.7</td>
<td>–23.0</td>
<td>55.4</td>
</tr>
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</table>

and explains the preference for the \( \eta^2 \) mode in the latter, in contrast with the preference for the \( \eta^6 \) coordination in 3.

The dispersion interaction contributes significantly to the bonding between the C\textsubscript{6}H\textsubscript{6} ring and the CuL fragments (L = {PhC(NtBu)\textsubscript{2}Si[SiMe\textsubscript{3}]\textsubscript{2}} and IPr for 3 and 6, respectively), and outweighs in both cases the benzene–ligand steric repulsions, contributing some 5–8 kcal mol\textsuperscript{–1} 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 therefore has a negligible effect on the hapticity.

**Conclusions**

This study was undertaken 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 tBu substituents of the silylene at a longer distance from 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 these principles, we have carried out test calculations on the so far unprepared \([\text{C}_6\text{H}_6]\text{Cu(CN)}\) and \([\text{C}_6\text{H}_6]\text{Cu(CO)}\) complexes that disclose an \( \eta^6 \) coordination in both cases and similar bonding parameters to those in compound 3 reported herein.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

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**Table 2** Energy decomposition analysis (EDA) of 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\textsubscript{6}H\textsubscript{6} ring and the Cu(IPr) and Cu(silylene) fragments, respectively; energies are given in kcal mol\textsuperscript{–1}.

\( \Delta E_{\text{int}} \) and \( \Delta E_{\text{Pauli}} \) are given in kcal mol\textsuperscript{–1} and include BSSE corrections.

Determining the distances between the occupied \( \pi_\text{CuL} \) orbitals of benzene and the \( \text{d}_{xz} \) and \( \text{d}_{yz} \) orbitals of Cu.

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>( \Delta E_{\text{int}} )</th>
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<td>–19.7</td>
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Notes and references


