Copper Arenes

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A Copper(I)–Arene Complex With an Unsupported η^6 Interaction**

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Abstract: *Addition of PR_3 (R = Ph or OPh) to $[Cu(\eta^2\text{-}Me_6C_6)_2][PF_6]$ results in the formation of $[(\eta^6\text{-}Me_6C_6)Cu(PR_3)][PF_6]$, the first copper–arene complexes to feature an unsupported η^6 arene interaction. A DFT analysis reveals that the preference for the η^6 binding mode is enforced by the steric clash between the methyl groups of the arene ligand and the phenyl rings of the phosphine co-ligand.*

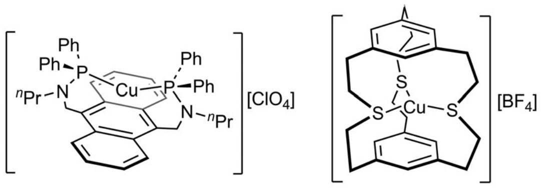


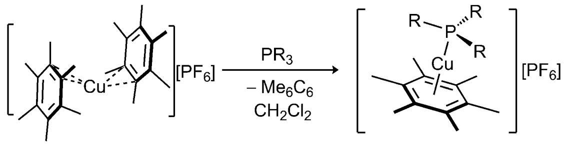
Figure 1. Known examples of Cu(η^6-arene) interactions.

The synthesis of the first metal–arene complex $Cr(\eta^6\text{-}C_6H_6)_2$, nearly 100 years ago by Hein and co-workers,[1] was an important milestone in the development of organometallic chemistry.[2–4] Since its discovery, metal–arene complexes have been isolated for most of the transition metal elements,[5–10] and these species have found use in a wide variety of applications. For example, the binding of an arene to a metal activates the ring toward nucleophilic addition, and also renders the ring protons more acidic, making these species synthetically useful.[11] In addition, metal–arene complexes have found utility as both catalyst precursors and common starting materials.[12,13] These points are well illustrated by the chemistry of the coinage metals. For example, Cu–arene species are thought to play a role in copper(I)-catalyzed cross-coupling reactions.[14] Cu–arene complexes are also precursors for catalytic alkoxylation and amination reactions,[15] and are known to mediate the reaction of Cu^I with oxygen.[16,17]

Group 11 metal–arene complexes strongly prefer the η^2 binding mode.[12,18–23] This binding mode is favored as it lessens the interaction between the filled *n*d orbitals with the filled arene π orbitals.[24] Consistent with this analysis, the only reported Cu arene complexes that contain the η^6 binding mode feature tethered arene rings and long $Cu–C_{cent}$ distances ($\approx 2.5–3.0$ Å) indicative of weak interactions (Figure 1).[25,26] Interestingly, though, the η^6 configuration is proposed to be slightly more stable than the η^2 configuration for the "naked" $[Cu(C_6H_6)]^+$ fragment in the gas phase, but the difference between the η^6 and η^2 modes is less than 1 kJ mol^{-1}.[27] Inclusion of a counterion, such as a halide or pseudohalide, to the Cu coordination sphere was calculated to increase the stability of the η^2 mode over η^6,[28] which led to the proposal that the unsupported η^6-arene–copper interaction is unlikely to be observed in the condensed state.[28]

Herein, we report the synthesis and structural characterization of the first Cu^I–arene complexes that feature unsupported η^6 interactions, demonstrating that complexes of this type are, in fact, isolable.

We previously reported the synthesis of the copper–arene sandwich complex, $[Cu(\eta^2\text{-}Me_3C_6H_3)_2][PF_6]$, which was prepared by oxidation of Cu metal with [NO][PF$_6$] in the presence of mesitylene.[29] The hexamethylbenzene analogue, $[Cu(\eta^2\text{-}Me_6C_6)_2][PF_6]$ (**1**), was prepared in a similar fashion. As determined by X-ray crystallography, complex **1** features two Me_6C_6 ligands coordinated to Cu through η^2 interactions. The Cu–C bond lengths are 2.092(2) and 2.192(2) Å, and are comparable with those previously reported for η^2-arene,[13,22,30] alkyne,[31] and alkene[32] complexes of copper.



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R = Ph, **2**; R = OPh, **3**

(1)

With **1** in hand, we postulated that substitution of one Me_6C_6 ligand with a 2e σ-donor ligand would result in a η^2 to η^6 ring slip to generate a pseudotetrahedral 18e$^-$ Cu^I complex. Gratifyingly, addition of 1 equiv of PR_3 (R = Ph, OPh) to a CH_2Cl_2 solution of **1** results in formation of the half-sandwich complexes $[(\eta^6\text{-}Me_6C_6)Cu(PR_3)][PF_6]$ (R = **2**, Ph; **3**, OPh) [Eq. (1)]. Complexes **2** and **3** can be crystallized from

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CH_2Cl_2/hexanes at −25 °C to give colorless blocks in moderate to good yields (**2**: 40 %; **3**: 78 %).

Single crystals of **2** and **3** suitable for X-ray crystallography were grown from a dilute CH_2Cl_2/hexane solution at −25 °C. Both complexes feature a copper(I) center bound by a η^6-Me_6C_6 ligand and a single PR_3 ligand, in an overall pseudotetrahedral geometry (Figure 2). The η^6 coordination mode of the Me_6C_6 ligand is exemplified by the narrow range of Cu−C_{aryl} bond lengths (**2**: 2.284(5)–2.293(5) Å; **3**: 2.253(1)–2.300(1) Å) and short Cu–C_{cent} distances (**2**: 1.800(3) Å; **3**: 1.775(6) Å). Notably, these Cu–C_{cent} distances are significantly shorter than those previously reported for the tethered Cu^I–η^6-arene interactions (Figure 1).[25,26] For instance, Mascal and co-workers reported a Cu^I cyclophane complex that features a Cu–C_{cent} distance of 2.97 Å.[25] Similarly, Zhang and co-workers reported a Cu^I complex, supported by 9,10-bis{*N*,*N*-propyl-*N*-(diphenylphosphino)aminomethyl}anthracene, which features a Cu–C_{cent} distance of 2.50 Å.[26] Finally, the average C−C bond length of the Me_6C_6 ligand in **2** is 1.411 Å (range = 1.395(7)–1.423(7) Å), and is comparable with those of unbound Me_6C_6, suggesting that there is little net charge transfer in the Cu–arene interaction.[9] Complex **3** features comparable C−C bond lengths for its Me_6C_6 ligand (1.416(1)–1.421(2) Å). The Cu−P bond lengths in **2** (2.158(2) Å) and **3** (2.1242(4) Å) are similar to those of (η^5-Cp)Cu(PPh_3) (2.116(2) Å).[33,34]

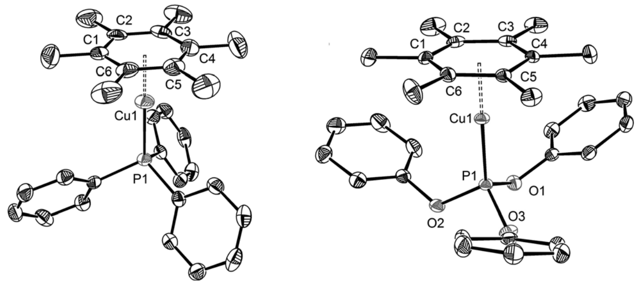

Figure 2. ORTEP drawing of [(η^6-Me_6C_6)Cu(PPh_3)][PF_6] (**2**) (left) and [(η^6-Me_6C_6)Cu(P(OPh)$_3$)][PF_6] (**3**) (right). Hydrogen atoms and a PF_6 anion have been omitted for clarity. Ellipsoids are shown at 50% probability.

The binding of an arene to a metal can result in a significant shift of its ^{13}C resonances.[35] However, only small shifts are observed for the aryl carbons in **2** (131.2 ppm) versus those of unbound Me_6C_6 (132.1 ppm). A slight downfield shift of the aryl carbon is observed for **3** (149.2 ppm). Additionally, the methyl carbon resonances in **2** and **3** do not differ significantly from those observed for unbound Me_6C_6 (**2**: 19.06 ppm; **3**: 16.07 ppm; free Me_6C_6: 16.71 ppm). Overall, these data are consistent with a relatively weak Cu–arene interaction.

Table 1: Calculated relative energies for different binding modes of **2** and **3**.

Complex	$\Delta E(\eta^6-\eta^2)$ [kJ mol^{-1}]	
	Gas phase	CH_2Cl_2
$[Cu(C_6H_6)]^+$	9.79	17.6[a]
$[Cu(C_6Me_6)]^+$	−3.99	4.51
2/PPh_3[c]	−8.78	−7.19[b]
3/P(OPh)$_3$[c]	−13.83	−12.16

[a] The η^6 structure is not a stationary point, so it was calculated as a restricted optimization at a fixed C_{6v} geometry. [b] The η^6 structure in this case is actually slightly off center, that is, η^4. [c] The η^2 binding mode was calculated using a restricted optimization.

To gain further insight into the bonding interactions in **2** and **3**, DFT calculations were performed. For comparison, the "naked" Cu–arene complexes, $[Cu(C_6H_6)]^+$ and $[Cu(C_6Me_6)]^+$, were also studied, as were their C_6H_6-bearing sister molecules, $[(C_6H_6)Cu(PPh_3)]^+$ and $[(C_6H_6)Cu(P(OPh)_3)]^+$. The optimized coordinates for all calculated species are given in the Supporting Information (SI). The energy differences between the η^6 and η^2 binding modes for the naked complexes and **2** and **3** are tabulated in Table 1. For the "naked" complexes the calculations reveal that the η^2 structures are generally more stable (apart from $[Cu(C_6Me_6)]^+$ in the gas phase), in accordance with earlier calculations.[27,28] Structurally, the two η^6 complexes feature similar geometries; however, the Cu^+ ion in $[Cu(\eta^6\text{-}C_6Me_6)]^+$ is closer to the arene than in $[Cu(\eta^6\text{-}C_6H_6)]^+$ (Cu–C_{cent} = 1.66 Å and 1.73 Å, respectively). The two η^2 structures are also similar, but the distance between Cu^+ and the C=C bond has increased to 1.89 Å and 1.92 Å for $[Cu(\eta^2\text{-}C_6Me_6)]^+$ and $[Cu(\eta^2\text{-}C_6H_6)]^+$, respectively.

Interestingly, the addition of PPh_3 or P(OPh)$_3$ to the $[Cu(arene)]^+$ motif results in a reversal of the favored arene binding mode. The η^6 motif becomes favored by 8.78 and 13.83 kJ mol^{-1} for **2** and **3** (in the gas phase), respectively (Table 1). Inclusion of solvent (CH_2Cl_2) in the calculation results in a slight destabilization of the η^6 binding mode relative to the η^2 mode, which we attribute to the attenuation of the electrostatic interaction due to the change in dielectric constant from vacuum to CH_2Cl_2, but the η^6 mode is still favored. We attribute the lower stability of the η^2 mode to the steric clash between the CH_3 groups on Me_6C_6 and the $[Cu(PR_3)]^+$ moiety. The larger $\Delta E(\eta^6-\eta^2)$ values calculated for compound **3**, which features the phenyl groups on the P(OPh)$_3$ moiety pointing toward the methyl groups of the Me_6C_6 ligand (see Table 1, Figure S18), also support the notion that sterics dictate the binding mode. Moreover, we calculate that $[(C_6H_6)Cu(PPh_3)]^+$, which features the smaller C_6H_6 ligand, prefers the η^2 motif, whereas $[(C_6H_6)CuP(OPh)_3]^+$ exhibits a preference for a η^1 motif, consistent with a diminished steric clash between the C_6H_6 ring and the $[Cu(PR_3)]^+$ fragment (see SI). The isolation of **1** is also consistent with this argument, as it shows that a η^2 binding mode of the Me_6C_6 ligand is preferred in the absence of a phosphine co-ligand. Thus, several lines of evidence support the argument that sterics do play a dominating role in the choice of final binding mode.

Inspection of the molecular orbitals (both for B3LYP and for a Hartree–Fock calculation, based on the DFT-optimized geometry) does not give a clear molecular orbital picture for the Cu–arene interaction. Moreover, the effect of solvent on the relative stabilities of the η^2 and η^6 binding modes, along with the importance of sterics in determining the hapticity, suggest a significant electrostatic component to the interaction. Thus, to elucidate the bonding interaction further, the complexes were studied using a Mulliken partitioning scheme, permitting the Mulliken charges of the Cu^+ ions in **2** and **3** to be calculated. The calculated Cu^+ charges for **2** and **3** are 0.86 and 0.81 (in CH_2Cl_2), respectively (Table 2). Both of these values are close to 1, which supports a largely electrostatic bonding interaction with very little covalency. The electrostatic bonding arrangement is further supported by analysis of the total electron density isosurfaces of **2** and **3** (see SI for details).[36] We used H_2 (0.24 a.u.) and LiF (0.005 a.u.) as benchmarks for covalent and ionic bonding, respectively (see SI). The calculated values for **2** and **3** (in vacuo) are: **2**: $\eta^2 = 0.07$ a.u., $\eta^6 = 0.05$ a.u.; **3**: $\eta^2 = 0.07$ a.u., $\eta^6 = 0.05$ a.u. Notably, these values are similar to that calculated for LiF, which supports the conclusion that arene binding in **2** and **3** is largely electrostatic. These data also suggest that the character of the Cu–arene interaction is insensitive to the choice of PR_3 ligand, but is sensitive to the coordination mode: i.e., the lower electron density cutoff values for the η^6 coordination mode indicate a less covalent interaction than the η^2 mode. Similar results are also observed for the 'naked' systems. For example, for $[Cu(C_6H_6)]^+$, the maximum values of the electron densities are 0.08 a.u. for the η^2 mode and 0.055 for the η^6 mode. Our calculations also show that the η^2 motif for the 'naked' systems becomes relatively more stable with the introduction of the CH_2Cl_2 solvent into the calculation, which indicates that the binding between naked Cu^+ and the arene is also largely electrostatic in character, in accordance with previous results.[27,28]

Table 2: Mulliken charges on the central Cu^+ ion for complexes **2** and **3** with a η^6 bound arene.

Complex	Gas phase	CH_2Cl_2
2/PPh_3	0.83	0.86
3/$P(OPh_3)$	0.78	0.81

Finally, the isolation of complexes **2** and **3** allows for a structural comparison with other first-row $M(\eta^6$-arene) complexes. A search of the Cambridge structural database reveals the existence of 77 $18e^-$ η^6-C_6R_6 (R = H or Me) complexes of the first-row transition metals (Cr to Ni). Figure 3 depicts the average $M–C_{cent}$ distance for each element for this series of complexes. Most importantly, **2** and **3** feature the longest $M–C_{cent}$ distances, which supports our contention that the Cu–arene interaction is weak and predominantly electrostatic in nature, a consequence of the contracted nature of the $3d^{10}$ shell. This contention is further supported by the observed decrease in $M–C_{cent}$ distances on moving from Cu to Fe. This decrease can be rationalized by the better energy match of the 3d orbitals with the arene π^* orbitals as one moves from right to left across the row, which permits a more effective back-bonding interaction.

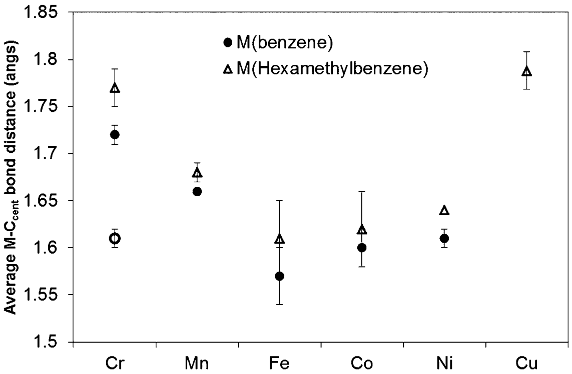

Figure 3. Average $M–C_{cent}$ distances for $18e^-$ $M(\eta^6$-$C_6R_6)$ complexes (R = H, closed circles, or Me, open triangles) in the Cambridge Structural Database.[19] The open circle represents Cr(benzene)L_3-type complexes, in which L is not a carbonyl ligand (9 examples).

In summary, we have isolated and structurally characterized the first copper complexes with an unsupported η^6 arene interaction. This completes the series of known unsupported $[M(\eta^6$-$C_6R_6)]^+$ first-row transition metal complexes. These copper–arene complexes have much shorter $Cu–C_{cent}$ distances (≈ 1.80 Å) than those previously reported for $Cu(\eta^6$-arene) compounds. Despite this structural difference, density functional theory calculations show that the Cu^+–arene interaction is largely electrostatic in nature, whereas the preference for the η^6 binding mode is enforced by the steric clash between the methyl groups of the arene ligand and the phenyl rings of the phosphine co-ligand.

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