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Structural and theoretical investigation into a copper(I)–arene complex with an unsupported η^6 interaction**

Ashley M. Wright, Benjamin J. Irving, Guang Wu, Anthony J. H. M. Meijer, Trevor W. Hayton*

Abstract. Addition of PR_3 ($\text{R} = \text{Ph}$ or OPh) to $[\text{Cu}(\eta^2\text{-Me}_6\text{C}_6)_2][\text{PF}_6]$ results in formation of $[(\eta^6\text{-Me}_6\text{C}_6)\text{Cu}(\text{PR}_3)][\text{PF}_6]$, 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.

The synthesis of the first metal–arene complex $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$, 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 pre-cursors 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)-catalysed cross-coupling reactions.^[14] Cu–arene complexes are also pre-cursors for catalytic alkoxylation and aminations,^[15] and are known to mediate the reactivity 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 favoured as it lessens the interaction between the filled nd 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 ($\sim 2.5\text{--}3.0$ Å) indicative of weak interactions (Chart 1).^[25, 26] Interestingly, though, the η^6 configuration is proposed to be slightly more stable than the η^2 configuration for the “naked” $[\text{Cu}(\text{C}_6\text{H}_6)]^+$ 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 pseudo-halide, 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]

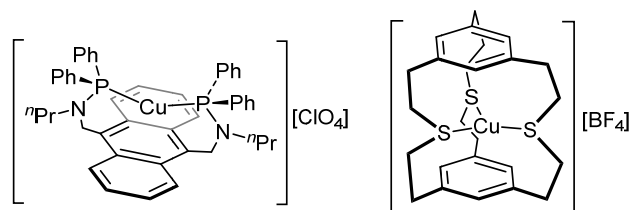
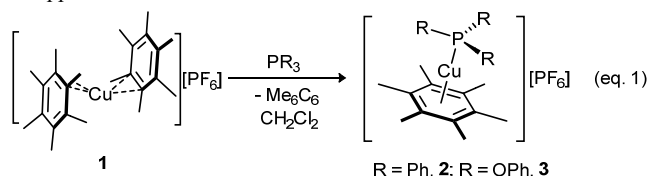


Chart 1. Known examples of $\text{Cu}(\eta^6\text{-arene})$ interactions.

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, $[\text{Cu}(\eta^2\text{-Me}_3\text{C}_6\text{H}_3)_2][\text{PF}_6]$, which was prepared by oxidation of Cu metal with $[\text{NO}][\text{PF}_6]$ in the presence of mesitylene.^[29] The hexamethylbenzene analogue, $[\text{Cu}(\eta^2\text{-Me}_6\text{C}_6)_2][\text{PF}_6]$ (**1**), was prepared in a similar fashion. As determined by X-ray crystallography, complex **1** features two Me_6C_6 ligands coordinated to Cu via 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.



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 pseudo-tetrahedral $18e^-$ Cu(I) complex. Gratifyingly, addition of 1 equiv of PR_3 ($\text{R} = \text{Ph}$, OPh) to a CH_2Cl_2 solution of **1** results in formation of the half-sandwich complexes $[(\eta^6\text{-Me}_6\text{C}_6)\text{Cu}(\text{PR}_3)][\text{PF}_6]$ ($\text{R} = \text{2, Ph}$; **3**, OPh) (eq. 1). Complexes **2** and **3** can be crystallized from CH_2Cl_2 /hexanes at -25 °C to give colourless blocks in moderate to good yields (**2**: 40%; **3**: 78%).

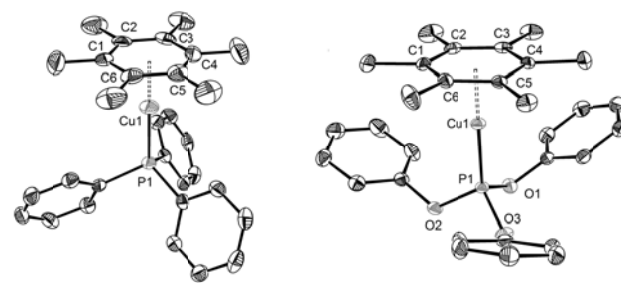


Figure 1. ORTEP drawing of $[(\eta^6\text{-Me}_6\text{C}_6)\text{Cu}(\text{PPh}_3)][\text{PF}_6]$ (**2**) (left) and $[(\eta^6\text{-Me}_6\text{C}_6)\text{Cu}(\text{P(OPh)}_3)][\text{PF}_6]$ (**3**) (right). Hydrogen atoms and a PF_6^- anion have been omitted for clarity.

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) centre bound by a $\eta^6\text{-Me}_6\text{C}_6$ ligand and a single PR_3 ligand, in an overall pseudo-tetrahedral geometry (Fig. 1). 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 (Chart 1).^[25, 26] For instance, Mascall 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 Me₆C₆ ligand in **2** is 1.411 Å (range = 1.395(7) - 1.423(7) Å), and is comparable with those of unbound Me₆C₆, suggesting that there is little net charge transfer in the Cu–arene interaction.^[9] Complex **3** features comparable C–C bond lengths for its Me₆C₆ 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 (η⁵-Cp)Cu(PPh₃) (2.116(2) Å).^[33, 34]

The binding of an arene to a metal can result in a significant shift of its ¹³C resonances.^[35] However, only small shifts are observed for the aryl carbons in **2** (131.2 ppm) vs. those of unbound Me₆C₆ (132.1 ppm). A slight down field 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 Me₆C₆ (**2**: 19.06 ppm; **3**: 16.07 ppm; free Me₆C₆: 16.71 ppm). Overall, these data are consistent with a relatively weak Cu–arene interaction.

To gain further insight into the bonding interactions in **2** and **3**, DFT calculations were performed. For comparison, the “naked” Cu–arene complexes, [Cu(C₆H₆)]⁺ and [Cu(C₆Me₆)]⁺, were also studied, as were their C₆H₆-bearing sister molecules, [(C₆H₆)Cu(PPh₃)]⁺ and [(C₆H₆)Cu(P(OPh)₃)]⁺. The optimized coordinates for all calculated species are given in the Supporting Information. The energy differences between the η⁶ and η² binding modes for the naked complexes and **2** and **3** are tabulated in Table 1. For the “naked” complexes the calculations reveal that the η² structures are generally more stable (apart from [Cu(C₆Me₆)]⁺ in the gas phase), in accordance with earlier calculations.^[27, 28] Structurally, the two η⁶ complexes feature similar geometries; however, the Cu⁺ ion in [Cu(η⁶-C₆Me₆)]⁺ is closer to the arene than in [Cu(η⁶-C₆H₆)]⁺ (Cu–C_{cent} = 1.66 Å and 1.73 Å, respectively). The two η² 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(η²-C₆Me₆)]⁺ and [Cu(η²-C₆H₆)]⁺, respectively.

Interestingly, the addition of PPh₃ or P(OPh)₃ to the [Cu(arene)]⁺ motif results in a reversal of the favored arene binding mode. The η⁶ motif becomes favoured by 8.78 and 13.83 kJ mol⁻¹ for **2** and **3** (in the gas phase), respectively (Table 1). Inclusion of solvent (CH₂Cl₂) in the calculation results in a slight destabilization of η⁶ binding mode relative to the η² mode, which we attribute to the attenuation of the electrostatic interaction due to the change in dielectric constant from vacuum to CH₂Cl₂, but the η⁶ mode is still favored. We attribute the lower stability of the η² mode to the steric clash between the CH₃ groups on Me₆C₆ and the [Cu(PR₃)]⁺ moiety. The larger ΔE(η⁶-η²) values calculated for compound **3**, which features the phenyl groups on the P(OPh)₃ moiety pointing towards the methyl groups of the Me₆C₆ ligand (see Table 1, Fig. S18), also support the notion that sterics dictate the binding mode. Moreover, we calculate that [(C₆H₆)Cu(PPh₃)]⁺, which features the smaller C₆H₆ ligand, prefers the η² motif, whereas [(C₆H₆)CuP(OPh)₃]⁺ exhibits a preference for an η¹ motif, consistent with a diminished steric clash between the C₆H₆ ring and the [Cu(PR₃)]⁺ fragment (see SI). The isolation of **1** is also consistent with this argument, as it reveals that a η² binding mode of the Me₆C₆ ligand is preferred in the absence of a phosphine co-ligand. Thus, several lines of evidence support the argument that sterics to play a dominating role in the choice of final binding mode.

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

Complex	ΔE(η ⁶ -η ²) / kJ mol ⁻¹	
	Gas phase	CH ₂ Cl ₂
[Cu(C ₆ H ₆)] ⁺	9.79	17.6 ^[a]
[Cu(C ₆ Me 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 η⁶ structure is not a stationary point, so was calculated as a restricted optimization at a fixed C_{6v} geometry [b] The η⁶ structure in this case is actually slightly off centre, i.e. η⁴. [c] The η² binding mode was calculated using a restricted optimization.

Inspection of the molecular orbitals (both for B3LYP and for a Hartree-Fock calculation, based on the DFT-optimized geometry) does not reveal a clear molecular orbital picture for the Cu–arene interaction. Moreover, the effect of solvent on the relative stabilities of the η² and η⁶ 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 CH₂Cl₂), 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 H₂ (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**: η² = 0.07 a.u., η⁶ = 0.05 a.u.; **3**: η² = 0.07 a.u., η⁶ = 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 PR₃ ligand, but is sensitive to the coordination mode: i.e., the lower electron density cutoff values for the η⁶ coordination mode indicate a less covalent interaction than the η² mode. Similar results are also observed for the ‘naked’ systems. For example, for [Cu(C₆H₆)]⁺, the maximum values of the electron densities are 0.08 a.u. for the η² mode and 0.055 for η⁶ mode. Our calculations also show that the η² motif for the ‘naked’ systems becomes relatively more stable with the introduction of the CH₂Cl₂ 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 η⁶ bound arene

Complex	Gas phase	CH ₂ Cl ₂
2 / PPh ₃ ^[c]	0.83	0.86
3 / P(OPh) ₃ ^[c]	0.78	0.81

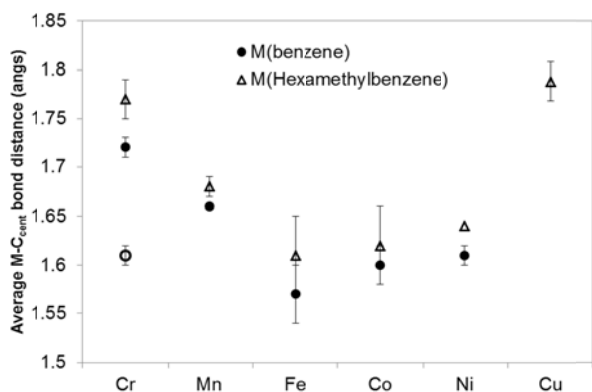


Figure 2. Average M–C_{cent} distances for 18e[−] M(η^6 -C₆R₆) complexes (R = H, closed circles, or Me, open triangles) in the Cambridge Structural Database.^[19] The open circle represents Cr(benzene)L₃-type complexes, where L is not a carbonyl ligand (9 examples).

Finally, the isolation of complexes **2** and **3** allows for a structural comparison with other first row M(η^6 -arene) complexes. A search of the Cambridge Structural Database reveals the existence of 77 18e[−] η^6 -C₆R₆ (R = H or Me) complexes of the first row transition metals (Cr to Ni). Figure 2 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 3d¹⁰ 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.

In summary, we have isolated and structurally characterized the first copper complex with an unsupported η^6 arene interaction. This completes the series of known unsupported [M(η^6 -C₆R₆)]⁺ 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(η^6 -arene) compounds. Despite this structural difference, density functional theory calculations reveal the Cu⁺-arene interaction is largely electrostatic in nature, while 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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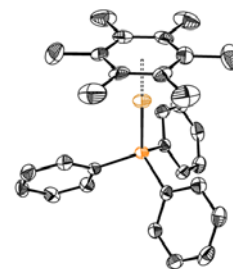
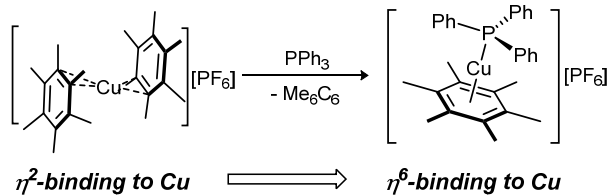
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Copper arenes

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