

Substituent-controlled donor binding and local reactivity in N-heterocyclic carbene copper amide complexes: a DFT study

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Abstract

Context: Carbene-metal-amide (CMA) complexes provide compact two-coordinate coinage-metal platforms in which an amide donor, a carbene acceptor, and a d^{10} metal bridge are coupled within the same molecular scaffold. The present work examines whether para-substitution of the amide-bound aryl fragment can serve as a ground-state design handle to modulate donor-acceptor polarization, local reactivity, and neutral donor binding in N-heterocyclic carbene copper amide complexes. The parent complex is predicted to be a true bent minimum with an amide-rich donor manifold, a carbene-centered acceptor region, and Cu(I)-like d^{10} character. Condensed Fukui analysis identifies the carbene side as the preferred electron-accepting domain and the amido fragment as the dominant electron-donating region. Explicit small-molecule tests further show that weak CH_3CN coordination is tolerated, O-protonation is perturbative, and N-protonation disrupts the original CMA scaffold. In the donor-bound substituted series, the p- CF_3 derivative gives a slightly tighter and more persistent CH_3CN adduct than the p-OMe derivative, whereas p-OMe produces the softer donor-acceptor framework.

Methods: Geometry optimizations, harmonic frequency analyses, single-point refinements, frontier-orbital calculations, Mulliken population analyses, natural bond orbital calculations, and finite-difference Fukui-function evaluations were carried out using Q-Chem 5.4 at the $\omega\text{B97X-D/def2-TZVP}$ level in the gas phase. Global conceptual-DFT descriptors were derived from frontier-orbital energies, and local Fukui indices were obtained from the Mulliken charges of neutral, N+1, and N-1 states on the parent geometry.

Introduction

Two-coordinate carbene-metal-amide (CMA) complexes have become a chemically distinctive class of coinage-metal donor-acceptor compounds because they combine an amide donor, a carbene acceptor, and a low-coordinate d^{10} metal bridge in a compact architecture that is unusually responsive to ligand electronics and deformation [1–4, 8, 10, 21–24]. Their relevance has been driven largely by photophysical applications, including thermally activated delayed fluorescence, efficient organic light-emitting diodes, and charge-transfer emitters based on copper, gold, and related coinage-metal scaffolds [2–9, 21–24].

Despite this progress, the available literature remains more developed for device-centered behavior and excited-state interpretation than for substituent-resolved ground-state design. This imbalance matters because synthesis-guided molecular screening requires more than a qualitative statement that an amide ligand is a donor and an N-heterocyclic carbene is an acceptor. It requires an internally consistent map connecting geometry, metal-ligand bonding, charge distribution, local reactivity, and the response of the same scaffold to simple donor or protonation probes.

The gap is therefore not the absence of CMA calculations in general, but rather the limited availability of compact ground-state workflows that isolate a single chemically coherent scaffold and quantify how substituent editing propagates through the carbene-Cu-amide pathway. Recent design-rule studies have shown that amide modification can tune orbital overlap, excitation energies, and charge-transfer balance in CMA luminophores [7, 13, 21–24]. However, those studies do not fully answer which substituent patterns

stabilize a given copper CMA framework at the ground-state level, how Cu-N(amido) and Cu-C(carbene) interactions should be interpreted from local electronic-structure descriptors, or how substituent changes are reflected in chemically meaningful probe reactions.

The present study addresses this need through a focused density functional theory investigation of NHC-Cu(amide-Ar-X) complexes in which the para substituent on the amide-bound aryl fragment is the principal design variable. The objective is intentionally narrower than a broad high-throughput survey: the aim is to determine how electron-donating and electron-withdrawing para substituents reshape structural persistence, frontier-orbital polarization, Cu-ligand bonding character, condensed Fukui reactivity, and donor-adduct formation while the underlying copper coordination framework is held constant.

This framing is well matched to molecular modeling because it converts a set of raw quantum-chemical outputs into an interpretable design sequence. First, the parent CMA structure is validated as a minimum. Second, the electronic organization of the parent scaffold is interpreted using frontier orbitals, Mulliken charges, and NBO descriptors. Third, global and local conceptual-DFT indices are used to assign the dominant donor and acceptor domains. Fourth, CH₃CN binding and protonation models are used as small perturbation tests of scaffold robustness. Fifth, p-CF₃ and p-OMe derivatives are compared in the donor-bound manifold to determine how para-substituents tune donor capture. By linking these layers, the study seeks to provide a practical ground-state design rationale for future synthesis, photophysical testing, and excited-state modeling of copper CMA derivatives.

Computational methods

All calculations were performed with Q-Chem 5.4 [11, 12]. Unless otherwise stated, geometry optimizations, harmonic frequency calculations, and single-point refinements were performed using the long-range-corrected ω B97X-D functional with the def2-TZVP basis set in the gas phase [13, 14]. This level of theory was selected because it combines range separation with empirical dispersion treatment and is suitable for the weak donor association and intramolecular donor-acceptor polarization examined here.

The accepted computational workflow included only jobs that successfully terminated from the final calculation branch. For the parent NHC-Cu(amide) complex, the sequence consisted of geometry optimization, harmonic frequency analysis, single-point refinement on the optimized structure, and a dedicated NBO calculation. The optimized parent structure was accepted as a true minimum only after confirming the absence of imaginary vibrational frequencies.

Frontier-orbital energies and Mulliken charges were extracted from the completed single-point outputs. Mulliken populations were used to track charge redistribution within the donor-acceptor framework [17], whereas chemical-locality bonding and metal-character assignments were based primarily on NBO analysis [15, 16]. Particular attention was paid to the natural electron configuration of copper and to whether the Lewis/NBO partition supported conventional shared-electron descriptions for Cu-N(amido) and Cu-C(carbene) contacts.

Global conceptual-DFT descriptors were derived from the parent HOMO and LUMO energies using the Koopmans-type approximation [18–20]. The ionization potential and electron affinity were estimated as $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$, respectively. The chemical potential, global hardness, global softness, and electrophilicity index were then calculated as $\mu = -(I + A)/2$, $\eta = (I - A)/2$, $S = 1/(2\eta)$, and $\omega = \mu^2/(2\eta)$, respectively.

Local reactivity descriptors were obtained by additional single-point calculations for the $N + 1$ and $N - 1$ electron states of the parent complex on the neutral optimized geometry. Condensed Fukui functions were evaluated from Mulliken charges using the finite-difference definitions $f^+ = q(N) - q(N + 1)$, $f^- = q(N - 1) - q(N)$, and $\Delta f = f^+ - f^-$ [19, 20].

Small-molecule reactivity was probed using explicit adduct and protonation models. Neutral donor association was examined by optimizing a CH_3CN -bound adduct of the parent CMA complex, followed by frequency analysis and single-point refinement. Proton response was assessed using O- and N-protonated variants of the parent scaffold. Substituent effects were evaluated by optimizing CH_3CN adducts of p- CF_3 and p-OMe derivatives of the same NHC-Cu(amide-Ar-X) framework. Comparative analysis focused on Cu-N(amido), Cu-C(carbene), Cu-N(CH_3CN), C-Cu-N angle, minimum vibrational frequency, frontier-orbital energies, and HOMO-LUMO gap.

Results and discussion

The results are organized as a connected modeling argument rather than as isolated calculations. The parent complex first establishes the structural and electronic baseline. Conceptual-DFT and Fukui analyses then convert that baseline into local reactivity assignments. Finally, explicit donor-binding and protonation models test the robustness of the same scaffold under chemically simple perturbations.

Ground-state structural integrity of the CMA scaffold

The optimized ground-state geometry of the parent CMA complex is presented in Fig. 1. Figure 1 should appear here.

Geometry optimization preserved the expected low-coordinate CMA motif. The copper center remained bound along the carbene-Cu-amide axis, and the accepted parent structure did not depart from the electronically meaningful scaffold that underpins donor-acceptor communication in CMA systems. This result is not merely a structural check; it establishes that subsequent reactivity and substituent trends can be interpreted within a common coordination framework rather than as artifacts of scaffold rearrangement.

The verified minimum also supports an important design inference. Para substitution on the amide-bound aryl group is sufficiently remote to avoid collapse of the core carbene-Cu-amide framework, yet remains electronically coupled enough to modulate the donor side of the complex. This balance is desirable for rational ligand fine-tuning because it allows systematic substituent editing without changing the overall

coordination architecture. The retention of a low-coordinate donor-linker-acceptor motif is consistent with prior descriptions of CMA emitters, in which performance depends on preserving the carbene-metal-amide framework while allowing controlled distortion [1, 2, 4].

Frequency verification is essential for the present comparison. Flexible organometallic systems may converge to shallow or distorted stationary points, and energetic comparisons are not meaningful unless the compared structures are genuine minima. By restricting the discussion to accepted and frequency-checked structures, the present modeling workflow provides a physically credible basis for interpreting substituent and donor-binding effects.

Substituent-controlled stabilization and donor binding

The central chemical trend is a substituent-dependent modulation of donor-adduct persistence. In the CH₃CN-bound series, both p-CF₃ and p-OMe derivatives retain the same coordination motif as the parent adduct, but the p-CF₃ system displays a slightly more compact Cu-N(MeCN) contact, whereas the p-OMe analog gives the longest Cu-N(MeCN) distance and the softest frontier-orbital profile. The differences are modest in magnitude but chemically coherent, as they occur without altering the underlying donor-bound geometry.

This ordering is consistent with an electronic interpretation in which the electron-withdrawing p-CF₃ substituent tempers the amide donor and improves the balance between the donor fragment and the carbene-centered acceptor manifold. By contrast, p-OMe increases donor-side electron richness and produces a softer donor-acceptor framework after donor coordination. The trend should not be reduced to a simple Hammett-style statement; rather, the substituent perturbs donor orbital energies, copper-mediated ligand coupling, and the degree of ground-state polarization that can be sustained without excessive destabilization of the coordinated assembly.

Frontier-orbital polarization and NBO interpretation

The frontier-orbital and NBO-informed electronic-structure summary of the parent CMA complex is presented in Fig. 2. Figure 2 should appear here.

The frontier-orbital pattern follows the expected CMA logic. The occupied frontier region is dominated by the amide donor side, whereas the low-lying acceptor region is concentrated on the carbene fragment, with copper acting as a soft electronic bridge rather than as the dominant frontier-orbital reservoir. This partition agrees with earlier CMA studies that assign donor character to the amide fragment and acceptor character to the carbene fragment while recognizing the metal as an essential mediator of donor-acceptor communication [2, 4, 7, 8, 13, 21–24].

NBO descriptors provide a local interpretation of the same electronic picture. The Cu center is best described as Cu(I)-like and d¹⁰ in character. In the parent complex, the natural electron configuration of copper is dominated by a nearly filled 3d shell, and the NBO partition does not favor a simplistic view of

strongly covalent shared-electron Cu-N(amido) and Cu-C(carbene) bonds. The metal, therefore, functions as an electronically responsive bridge that stabilizes communication between the donor and acceptor ligands without becoming the sole locus of reactivity.

This interpretation is useful for molecular design because it explains why para-substituent effects can be transmitted through the scaffold even when the main coordination motif is retained. Electron-withdrawing substitution can stabilize the donor side and improve donor-acceptor complementarity, whereas electron donation can soften the manifold and loosen donor association. Thus, the substituent effect is expressed throughout the entire polarized metal-mediated framework rather than by a purely local aryl-ring perturbation.

Global reactivity descriptors and condensed Fukui analysis

The N, N + 1, and N-1 single-point calculations enable a formal condensed Fukui analysis of the parent complex. The parent frontier-orbital values are HOMO = -0.3269 a.u. and LUMO = -0.0796 a.u., giving a HOMO-LUMO gap of 0.2473 a.u. or 6.73 eV. From these values, the calculated chemical potential is $\mu = -0.2033$ a.u., the hardness is $\eta = 0.1237$ a.u., the softness is $S = 4.042$ a.u.⁻¹, and the electrophilicity index is $\omega = 4.54$ eV.

The local indices sharpen the site assignments. The largest f^+ value is located on the carbene carbon C17, followed by the copper center and then the amido nitrogen. In contrast, the highest f^- value is observed for N(amido), followed by oxygen and copper. The dual descriptor therefore identifies the carbene side as the principal electron-accepting domain and the amido fragment as the principal electron-donating domain. This numerical result is consistent with the frontier-orbital and NBO descriptions and with previous CMA design logic [2, 7].

The global conceptual-DFT descriptors and selected condensed Fukui hotspots for the parent CMA complex are summarized in Table 1. Table 1 should appear here.

Table 1

Global conceptual-DFT descriptors and selected condensed Fukui hotspots for the parent CMA complex.

Descriptor	Value	Leading f^+ site	f^+	Leading f^- site	f^-	Dual descriptor
HOMO (a.u.)	-0.3269	C(carbene), atom 17	0.2133	N(amido), atom 3	0.1740	C17: +0.1402
LUMO (a.u.)	-0.0796	Cu, atom 16	0.1315	O, atom 2	0.1324	O2: -0.0734
Gap (eV)	6.73	N(amido), atom 3	0.1180	Cu, atom 16	0.1068	N3: -0.0559
Chemical potential, μ (a.u.)	-0.2033					
Hardness, η (a.u.)	0.1237					
Softness, S (a.u. ⁻¹)	4.042					
Electrophilicity, ω (eV)	4.54					

Response toward small molecules

Small-molecule probing reveals three chemically distinct response modes. First, neutral donor coordination by CH₃CN gives a Cu-bound adduct with Cu-N(CH₃CN) = 1.930 Å. This association is accompanied by slight elongation of the Cu-C(carbene) bond and contraction of the C-Cu-N angle. The small imaginary frequency of the parent adduct (-15.23 cm⁻¹) indicates that this structure lies on a very shallow association surface and is best interpreted as a weak, floppy donor adduct rather than as a rigid three-coordinate product.

Second, oxygen protonation preserves the essential Cu-N(amido) and Cu-C(carbene) contacts, although it reorganizes the low-coordinate copper environment. The O-protonated form, therefore, represents a perturbed but still recognizable CMA scaffold. Third, protonation at the amido nitrogen is substantially more disruptive, expanding the Cu-N(amido) distance and lengthening the Cu-C(carbene) contact sufficiently to indicate effective collapse of the original CMA framework.

These contrasting behaviors are chemically useful. Donor binding is tolerated, O-protonation is perturbative, and direct protonation of the amido donor is scaffold-destructive. The response pattern, therefore, supports a design rule: the CMA scaffold is robust toward weak neutral donor association but vulnerable to perturbations that directly neutralize or disrupt the amido donor.

Substituent effects in the CHCN adduct manifold

Substituent effects were examined by comparing parent, p-CF₃, and p-OMe CH₃CN adducts. Both substituted adducts converged as closed-shell singlet structures and, unlike the parent adduct, their

frequency calculations returned true minima with no imaginary modes. Substituent editing, therefore, does not prevent donor coordination; instead, it stabilizes the donor-bound minimum enough to remove the shallow association behavior observed for the unsubstituted reference.

Structurally, the three adducts remain closely related, but the small differences are systematic. The p-CF₃ derivative gives a slightly shorter and more compact donor-bound arrangement than p-OMe, while p-OMe gives the longest Cu-N(MeCN) contact and the smallest HOMO-LUMO gap. This indicates that p-CF₃ modestly favors tighter donor capture, whereas p-OMe softens the electronic framework after donor binding.

The implication for future CMA design is direct. Electron-withdrawing para substitution is the more favorable starting point when persistent donor association and intrinsic scaffold stabilization are desired. Electron-donating substitution may still be useful when a softer donor-acceptor manifold is targeted, but it should be used selectively because it can loosen the donor-bound geometry.

The substituent effects on CH₃CN adduct formation in the parent, p-CF₃, and p-OMe CMA complexes are summarized in Table 2. Table 2 should appear here.

Table 2 Substituent effects on CH ₃ CN adduct formation in parent, p-CF ₃ , and p-OMe CMA complexes.								
System	Cu-N(amido) / Å	Cu-C(carbene) / Å	Cu-N(MeCN) / Å	C-Cu-N / °	vmin / cm ⁻¹	HOMO / a.u.	LUMO / a.u.	Gap / eV
Parent·MeCN	1.7090	1.9078	1.9299	104.54	-15.23	-0.3024	-0.0699	6.33
p-CF ₃ ·MeCN	1.7090	1.9084	1.9318	104.44	6.03	-0.2992	-0.0661	6.34
p-OMe·MeCN	1.7077	1.9092	1.9358	104.31	15.94	-0.2878	-0.0559	6.31

Conclusions

This DFT study provides a substituent-resolved ground-state description of NHC-Cu(amide-Ar-X) CMA complexes. The parent complex is confirmed as a bent two-coordinate minimum with an amide-rich donor region, a carbene-centered acceptor region, and a Cu(I)-like d¹⁰ center that mediates donor-acceptor communication. Condensed Fukui analysis assigns the carbene side as the dominant electron-accepting domain and the amido fragment as the dominant electron-donating domain.

Small-molecule probing shows that the scaffold tolerates weak CH₃CN donor association and O-protonation but is destabilized by direct N-protonation of the amido donor. In the substituted donor-bound series, p-CF₃ gives a slightly tighter and more persistent CH₃CN adduct than p-OMe, whereas p-OMe produces a softer donor-acceptor framework. These results establish a practical design rule for this CMA platform: electron-withdrawing para substituents are favored when compact donor binding and intrinsic

scaffold persistence are desired, while electron-donating substituents should be selected when electronic softening is the intended objective.

Beyond the individual complexes studied here, the work demonstrates how a compact molecular-modeling workflow can connect validated minima, local electronic-structure descriptors, conceptual-DFT indices, and explicit probe reactions into a coherent screening rationale for future copper CMA synthesis and photophysical evaluation.

Statements and Declarations

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Author contributions: Frans Augusthinus Asmuruf conceived the study, supervised the computational workflow, analyzed the data, and drafted the manuscript. Darwanta contributed to research design, interpretation, and manuscript revision. Yuliana Ruth Yabansabra, Lodwyk Nomenzen Krimadi, and Nada Pertiwi Papriani contributed to data organization, computational checking, and manuscript review. All authors read and approved the final manuscript.

Data availability: The datasets generated and analyzed during the current study, including Cartesian coordinates, selected structural metrics, charge analyses, Fukui tables, and computational output summaries, are available from the corresponding author on reasonable request and may be supplied as Online Resource files during submission.

Ethics approval: Not applicable.

Consent to participate: Not applicable.

Consent for publication: Not applicable.

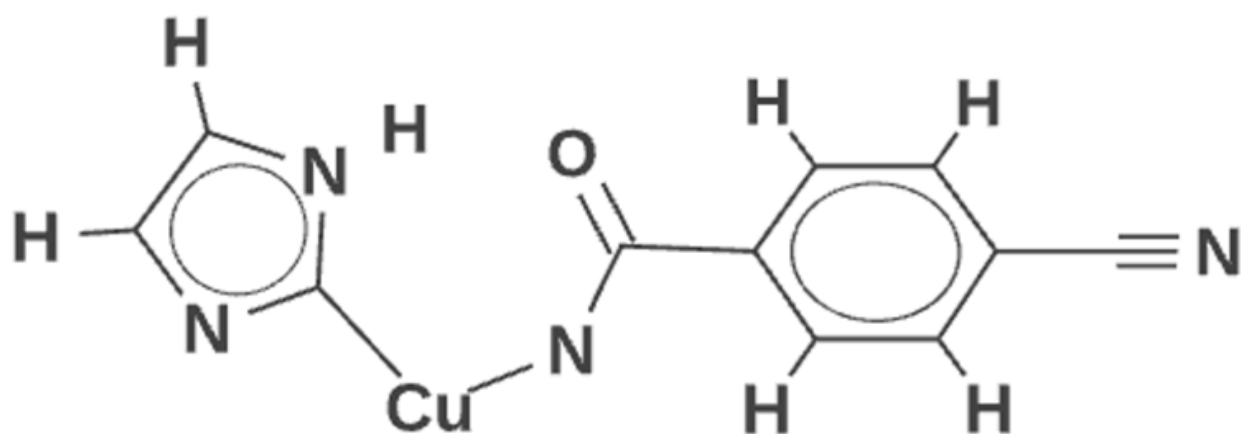
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Figures



Validated minimum (0 imaginary frequencies)

Cu-N=1.719 Å. Cu-C= 1.841 Å. <C-Cu-N=110.33° Cu---O=3.33 Å

Figure 1

Optimized ground-state structure of the parent CMA complex. The validated minimum retains a bent two-coordinate Cu center with Cu-N(amido) = 1.719 Å, Cu-C(carbene) = 1.841 Å, C-Cu-N = 110.33°, and a long nonbonding Cu...O contact of 3.33 Å. Insert the optimized molecular-structure image before submission.

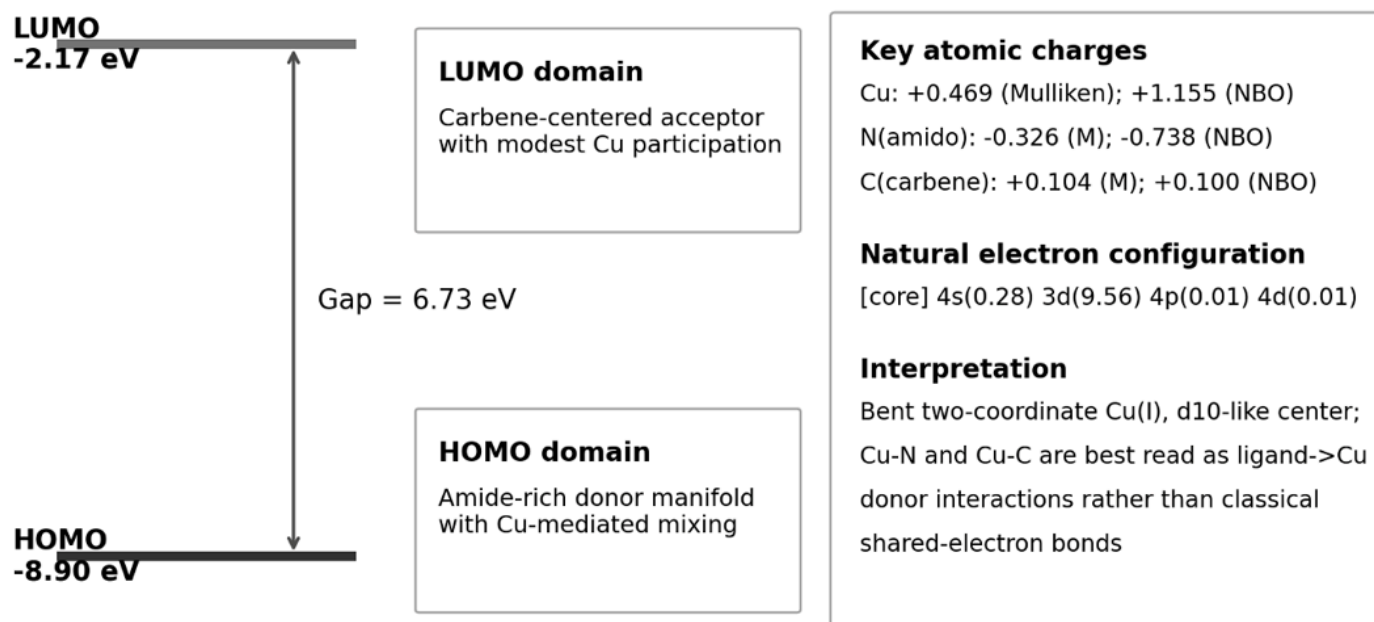


Figure 2

Electronic-structure summary of the parent CMA complex from the single-point and NBO outputs. The HOMO is donor-rich on the amide side, the LUMO is centered on the carbene acceptor fragment, and the Cu center remains Cu(I)-like and d¹⁰ in character.