Aryl Group Transfer from Tetraarylborato Anions to an Electrophilic Dicopper(I) Center and Mixed-Valence μ-Aryl Dicopper(I,II) Complexes

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Supporting Information Placeholder

ABSTRACT: The synthesis of discrete, cationic binuclear μ-aryl dicopper complexes $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ar})DPFN]X$, (Ar = C_6H_5, 3,5-$(CF_3)_2C_6H_3$, C_6F_5; DPFN = 2,7-bis(fluoro-di-(2-pyridyl)methyl)-1,8-naphthyridine; X = BAr_4^-, $NTf_2^- = N(SO_2CF_3)_2^-$), was achieved by treatment of a dicopper complex ($[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-NCCH}_3)DPFN]X$ (X = PF_6^-, NTf_2^-) with tetraarylborates. Structural characterization revealed symmetrically-bridging aryl groups, while ^{1}H NMR spectroscopy evidenced the same structure in solution at 24 °C. Electrochemical investigation of the resulting arylcopper complexes revealed reversible redox events that led to the synthesis and isolation of a rare mixed-valence organocopper complex, $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})DPFN](NTf_2)_2$, in high yield. The solid-state structure of the mixed-valence μ-phenyl complex exhibits inequivalent copper centers, despite a short Cu$\cdots$Cu distance. Electronic and variable-temperature electron paramagnetic resonance spectroscopy of the mixed-valence μ-phenyl complex suggest that the degree of spin localization is temperature dependent, with a high degree of spin localization observed at lower temperatures. Electronic structure calculations agree with the experimental results and suggest the spin is localized almost entirely on one metal center.

Introduction

Organometallic copper complexes have found significant utility in organic synthesis and transition-metal mediated catalysis.[1] As a result, much effort has been devoted to the synthesis, isolation, and characterization of stable organocopper complexes that can help to elucidate mechanisms or serve as improved reagents and catalysts.[2,3] Historically, these complexes have primarily been anionic organocuprates of the form $[CuR_2]^-$ (where R = alkyl or aryl groups) or neutral $[CuR]_n$ species.[4,5] Moreover, most of the isolated, structurally characterized organocopper complexes contain copper(I),[2] and proposed reaction mechanisms often feature anionic or neutral organocopper(I) intermediates.[6,7] More recently, organocopper(III) intermediates have also been invoked for carbon-carbon and carbon-heteroatom bond forming reactions.[7,8] Less commonly, organocopper(II) species have been suggested as intermediates in a few catalytic reactions, including the Meerwein Arylation,[9] Chan–Lam–Evans coupling,[10] alkene amination,[11] as well as C–H bond activation.[12–14] However, complexes of this type have rarely been isolated and structurally characterized.[2] The very few reported Cu(II) and Cu(III) arylcopper complexes all incorporate the aryl moiety into a multi-dentate ligand, such as azacalix[1]arene[3]pyridines, and contain only one copper center.[12,14–16]

Similarly, despite the large body of known chemistry for neutral and anionic arylcopper complexes and aggregates,[2,4] cationic organocopper complexes are uncommon,[14] and to our knowledge, only one cationic μ-aryl copper(I) complex has been reported to date.[17]

This study focuses on dicopper complexes supported by a rigid dinucleating ligand that holds two copper centers in close proximity (Figure 1). The $[Cu_2(DPEN)]^{2+}$ fragment (DPEN = 2,7-bis(1,1-dipyridylethyl)-1,8-naphthyridine) has been shown to bind various two-electron donors in a bridging position to yield unusual types of three-center two-electron bonds.[18] For example, acetonitrile adopts a highly unusual symmetrically-bridging geometry in $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-NCCH}_3)(DPEN)]^{2+}$. Calculations indicate that the copper centers cooperate to provide a delocalized acceptor orbital composed of sigma-type, copper-centered orbitals overlapping in an angled manner (Figure 1).[18] This report describes a related, unexpectedly electrophilic dicopper(I) complex that abstracts aryl groups (even $-C_6F_5$) from tetraarylborato anions. Notably, the products are rare examples of cationic arylcopper complexes. Moreover, investigations of the $Cu^I_2(\mu\text{-phenyl})$ analog reveal that the unusual bonding arrangement allows access to an oxidized species formally containing copper(II) — the corresponding mixed-valence $Cu_2(I,II)(\mu\text{-phenyl})$ complex.
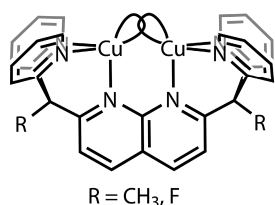
Figure 1. General structure of a naphthyridine-based dinucleating ligand supporting two Cu centers with qualitative molecular orbitals.

## Synthesis of a Dinuclear Copper Complex

The complexes described herein utilize the fluorinated ligand 2,7-bis(R-di-(2-pyridyl)methyl)-1,8-naphthyridine (DPFN, Figure 1 where R = F). The reported synthesis of DPFN gave a low yield (9%) over the last two steps,[19] which led to attempts to improve the procedure's efficiency. Notably, deprotonation of dipyridylmethane and use of the resulting carbanion in a nucleophilic aromatic substitution reaction with 2,7-dichloro-1,8-naphthyridine was achieved with NaH in THF, to generate 2,7-bis(di-(2-pyridyl)methyl)-1,8-naphthyridine (DPMN) that upon oxidation with Selectfluor provided DPFN in good yield (63%, eq 1).
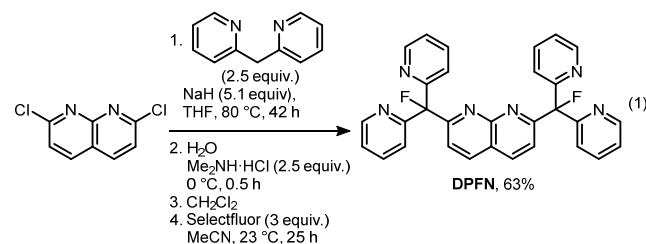
Addition of DPFN to 2.05 equivalents of $[Cu(NCCH_3)_4]PF_6$ in THF precipitated an orange powder of $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}NCCH_3)DPFN](PF_6)_2$ (**1**) (89% yield), analogous to the dinuclear copper complex of DPEN.[18] Single crystal X-ray diffraction (SI figure SC1) indicates that in the solid-state, the two copper atoms are separated by 2.4725(5) Å and are slightly further apart than in the DPEN complex (2.4457(4) Å). Meanwhile the bridging acetonitrile molecule is bound similarly in both complexes (Cu1–N7: 1.959(2), Cu2–N7: 1.992(2) in the DPFN complex, compared to 2.004(3) and 1.979(3) with DPEN).

Anion Activation to Give Cationic Bridging Aryl Complexes

In an attempt to increase its solubility in less polar solvents, complex **1** was treated with 2 equivalents of sodium tetraphenylborate ($NaBPh_4$). Surprisingly, the originally orange mixture became dark green. Layering pentane over a solution of the product afforded crystals, and X-ray diffraction revealed the product to be $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}Ph)DPFN]BPh_4 \cdot 3(o\text{-}C_6H_4F_2)$ (**2**$\cdot$3(o-C$_6$H$_4$F$_2$)), presumably resulting from arylation by the borate anion (eq 2). An additional product in the reaction mixture, identified by ^{1}H and ^{11}B{^{1}H} NMR spectroscopy, was BPh_3.
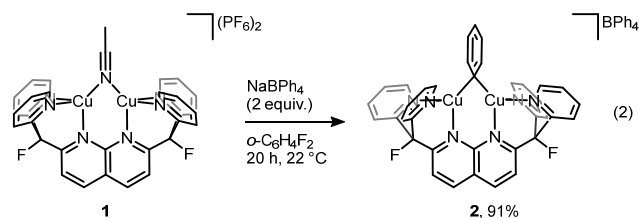
The solid-state structure of **2** (Figure 2) exhibits a nearly symmetrically bridging phenyl ligand. The copper–carbon distances Cu1–C31 and Cu2–C31 are 2.023(2) and 2.016(2) Å; respectively, and the phenyl moiety does not bend preferentially toward either copper center: ∢C34–C31–Cu1 and C34–C31–Cu2 are 144.4(1) and 143.0(1)°, respectively. In addition, the Cu⋯Cu distance (2.3927(5) Å) is significantly shorter than that observed for the acetonitrile complex, as might be expected for replacement of a neutral with an anionic bridging ligand. Meanwhile, the bridging aryl is nearly hexagonal with internal angles between 114.3(2) and 123.0(2)° and bond lengths between 1.376(4) and 1.416(3) Å, consistent with aromatic C–C bonds.[20] The narrowest angle (∢C32–C31–C36: 114.3(2)°) is found at the *ipso*-carbon, as are the longest bonds (C31–C32: 1.415(3) and C31–C36 1.416(3) Å), presenting a geometry similar to those found in the phenyl groups that constitute the co-crystallized tetraphenylborato anion.

To the best of our knowledge, the only previously reported, cationic μ-aryl complex of copper to be crystallographically characterized is $[Cu_3Ph_2(PMDTA)_2][Cu_5Ph_6]$ (PMDTA = *N, N, N′, N″, N″*-pentamethyldiethylenetriamine), which was synthesized in an attempt to isolate a monomeric form of phenylcopper and in room temperature solution, appears to convert to $(CuPh)_4\cdot(DMS)_2$ and free PMDTA.[17] However, the solid-state structure of this copper complex could be determined crystallographically at 130 K and exhibits two equivalent μ-phenyl groups. Compared to the tricopper cation, **2** exhibits a shorter Cu⋯Cu distance (for the tricopper cation, Cu⋯Cu = 2.444(1) Å), while the Cu–C distances in **2** are slightly longer than those in the tricopper cation (2.006(7) and 1.989(5) Å).
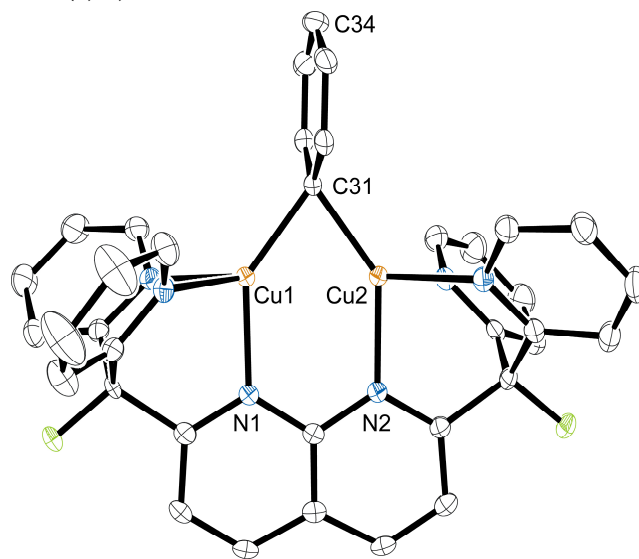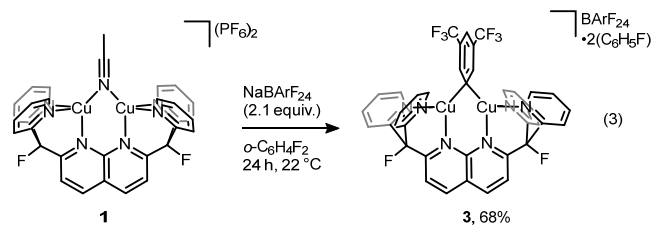

Figure 2. Solid-state structure of **2** as determined by single crystal X-ray diffraction. Three co-crystallizing o-C$_6$H$_4$F$_2$ molecules, one BPh$_4^-$ ani-

on, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

The solution behavior of **2** was investigated by ^{1}H NMR spectroscopy. At 24 °C low concentration (*ca.* 0.2 mM), the spectrum is consistent with the solid-state structure on the NMR time-scale; the NMR resonances are sharp and exhibit well-resolved ^{1}H-^{1}H couplings. In addition, ^{13}C{^{1}H} NMR spectroscopy, corroborated with HSQC and HMBC experiments, locate the *ipso*-carbon shift of **2** at 143.7 ppm. This resonance is upfield of that observed for the *ipso*-carbon of $[Cu_3Ph_2(PMDTA)_2]^+$ (150.3 ppm), and upfield of the range observed for neutral $[PhCu]_n$ (n = 1, 3, or 4) aggregates (146.8 – 151.0 ppm).[21]

The aryl-group transfer that results in **2** implies that this dicopper center acts as an electrophile, in accepting a nucleophilic phenyl group from the BPh$_4$ anion. Tetraphenylborate activation was unexpected as others have reported stable copper complexes containing open coordination sites or acetonitrile ligands in the presence of BPh$_4^-$,[22] tetrakis[(3,5-trifluoromethyl)phenyl]borate (BArF$_{24}^-$),[23] and tetrakis(pentafluorophenyl)borate (BArF$_{20}^-$).[24] Only one previous example of BPh$_4^-$ activation by a putative copper complex could be found in the literature. In a reaction that resulted in phosphorous–carbon bond formation, Knight and coworkers observed that addition of CuCl to the tetraphenylborate salt of an N-heterocyclic phosphenium ligand at 50 °C resulted in net aryl transfer to the electrophilic phosphorous atom.[25]

While phenyl transfer from BPh$_4^-$ to transition metal centers is somewhat uncommon,[26,27] transfer from tetraarylborates containing electron-withdrawing aryl groups is rarer. These weakly-coordinating anions are generally considered significantly more resistant to coordination and cleavage of the carbon–boron bond.[28] Only a handful of noble metal complexes have been reported to abstract an aryl group from $[BArF_{24}]^-$ [29–31] while Ag$^+$ (in non-coordinating solvents)[32] and a diiron complex (heated at 70 °C for 72 h)[33] similarly activated BArF$_{20}^-$. To determine whether the dicopper dication would react with such an electron-deficient tetraarylborate, complex **1** was treated with 2.1 equivalents of Na$[BArF_{24}]$ in *o*-C$_6$H$_4$F$_2$. Over the course of 1 d at 22 °C, the reaction mixture turned dark orange-brown, and layering pentane over a fluorobenzene solution of the product afforded crystals of $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}(3,5\text{-trifluoromethyl})phenyl))DPFN]BArF_{24}\cdot2(C_6H_5F)$ ($3\cdot2C_6H_5F$) (eq 3) in good yield (68%).

To determine whether a presumably even less reactive tetraarylborate might be a competent anion, complex **1** was also treated with 2 equivalents of K$[BArF_{20}]$ in *o*-C$_6$H$_4$F$_2$. After 24 h at 22 °C, no activation of the BArF$_{20}^-$ anion was observed by ^{1}H and ^{19}F NMR spectroscopy (Figures S1-2). However, upon heating the mixture at 100 °C for 2 d, resonances consistent with formation of a new dicopper complex and pentafluorophenyl abstraction were observed by ^{1}H and ^{19}F NMR spectroscopy (Figure S3), including the formation of B(C$_6$F$_5$)$_3$. The resulting bridging aryl complex, $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-pentafluorophenyl})DPFN]BArF_{20}$ (**4**), was isolated in good yield (73%) (eq 4).
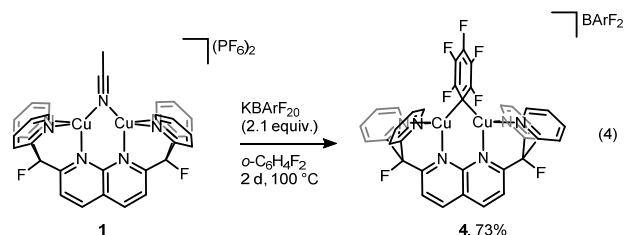
Given the observed reactivity of tetraarylborato anions in this system, further investigations of the aryl dicopper cations used the bis(trifluoromethanesulfonyl)imide (triflimide, NTf$_2^-$) anion. Employing tetrakis(acetonitrile)copper(I) triflimide as a copper(I) source, $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-NCCH}_3)DPFN](NTf_2)_2$ (**5**) was synthesized in THF and isolated in high yield (91%). Addition of 0.98 equiv. of NaBPh$_4$ to **5** in *o*-C$_6$H$_4$F$_2$ afforded $[Cu_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})DPFN](NTf_2)$ (**6**), also in high yield (97% based on the dicopper complex).

To determine whether the bridging aryl could be exchanged *via* a C–H bond activation process, **6** was treated with pentafluorobenzene (150 equiv.). Upon heating, slow exchange of the μ-phenyl for μ-pentafluorophenyl was observed, with 85% yield (99% conversion) achieved after 35 d at 110 °C (eq 5) as determined by ^{19}F NMR spectroscopy. Concomitant formation of C$_6$H$_6$ was also observed by ^{1}H NMR spectroscopy.
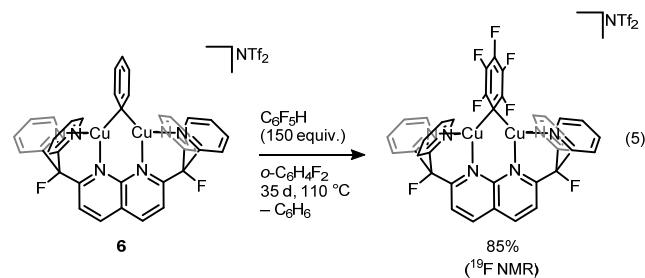
The solid-state structure of **3** (SI figure SC2) is similar to that of **2**; the aryl ligand symmetrically bridges the two copper centers and the Cu···Cu distance is 2.3966(8) Å. Once again, proton NMR spectra display sharp, well-defined resonances consistent with the solid-state structure. With the aid of a ^{13}C -^{1}H HMBC experiment, the *ipso*-carbon resonance was located at 147.1 ppm.

This aryl exchange suggests that the μ-phenyl complex persists even at high temperatures and is also capable of activating aromatic C–H bonds.

Mixed-Valence Arylcopper Complexes

Cyclic voltammetry of **6** revealed a single reversible redox process ($E°$ = –14 mV vs $[Cp_2Fe]^{0/1+}$, i_a/i_c = 1.02 ΔE_p = 106 mV, Figure 3), between other irreversible oxidation and reduction features (Figure S4). Moreover, this redox event is reversible over a range of scan rates, from 10 to 1000 mV/s (Figure S5), as is confirmed by the plots of cathodic and anodic peak currents of this couple versus the square root of scan rate (Figure S6). Under similar conditions, DPFN and **5** do not exhibit reversible reduction-oxidation couples (Figure S7), which suggests that the reversible couple observed for

6 is not solely attributable to the DPFN ligand or to DPFN-ligated Cu(I) metal centers.
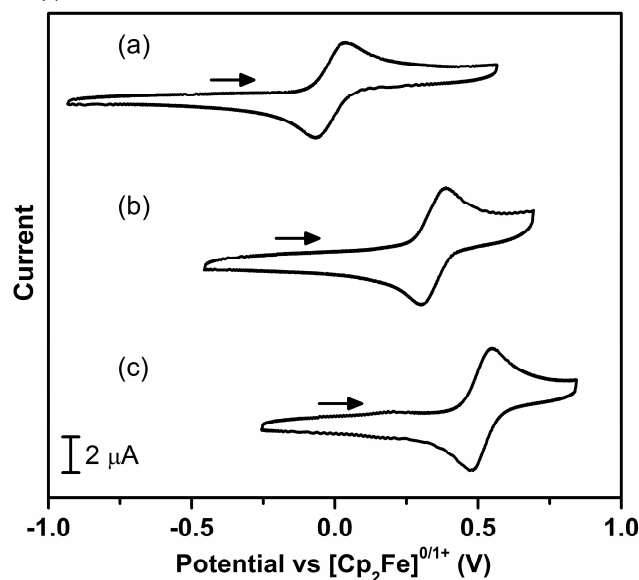

Figure 3. Cyclic voltammograms of 0.5 mM solutions of **6** (a), **3** (b), and **4** (c) in o-C$_6$H$_4$F$_2$ with 0.1 M [^{n}Bu$_4$N][PF$_6$] supporting electrolyte. The arrows indicate the initial potentials and scanning directions. Scan rate: 100 mV/s.

Similar redox processes were observed for **3** and **4** at 347 and 516 mV vs [Cp$_2$Fe]$^{0/1+}$, respectively (Figure 3). These progressively more positive oxidation potentials are consistent with the electron-withdrawing nature of the bridging (3,5-trifluoromethyl)phenyl and perfluorophenyl groups. Both redox events for **3** and **4** were also reversible, with i_a/i_c ratios close to 1 (**3**: 1.12 , **4**: 1.18, at 100 mV/s) and small ΔE_p values (**3**: 0.084 mV, **4**: 0.070 mV, at 100 mV/s), and they remained reversible over a variety of scan rates (Figures S8-11). In addition, as with **6**, irreversible oxidation and reduction events bounded the reversible feature (Figures S12-13).

Electrochemical characterizations of organocopper complexes are rare, and the oxidation of organocopper(I) complexes often leads to short-lived species.[34] These short lifetimes are commonly attributed to an inherent instability of organocopper(II) species.[2,34] However, the chemical reversibility of the redox processes observed for **3**, **4,** and **6** suggested that the products might be persistent enough to isolate. Thus, **6** was treated with AgNTf$_2$ (1.02 equiv.) in o-C$_6$H$_4$F$_2$ (eq 5). Layering diethyl ether over an o-C$_6$H$_4$F$_2$ solution of the dark orange product afforded crystalline [Cu$_2$(μ-η^1:η^1-Ph)DPFN](NTf$_2$)$_2$ (**7**) in high yield (90%).

(6)
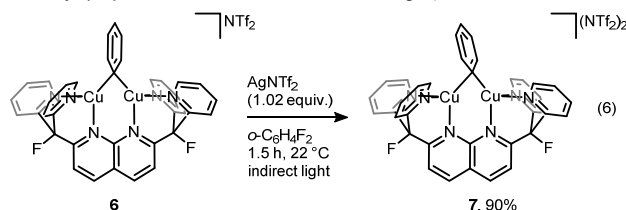
X-ray quality crystals were grown by vapor diffusion of diethyl ether into an o-C$_6$H$_4$F$_2$ solution of **7** at –35 °C. The solid-state structure of **7** (Figure 4) reveals that the bridging phenyl ligand is now bound unsymmetrically, rather than symmetrically as in **2**. From an average copper–carbon bond length of 2.020 Å in **2**, one

copper–carbon bond (Cu1–C31) has lengthened to 2.077(5) Å while the other (Cu2–C32) has contracted to 1.940(6) Å (Table 1). Similarly, from an average C34–C31–Cu angle of 143.7° in **2**, the phenyl group is significantly tilted, with angles of 119.9(2) and 167.5(3)°. Meanwhile, the Cu···Cu distance has shortened only slightly, to 2.3809(5) Å.
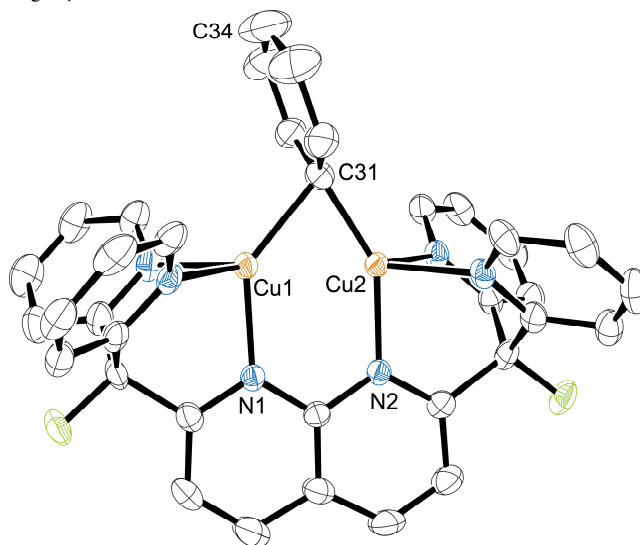

Figure 4. Solid-state structure of **7** as determined by single crystal X-ray diffraction. Two NTf$_2^-$ anions and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

Table 1. Selected Distances, Bond Lengths, and Angles for the [Cu$_2$(μ-η^1:η^1-Ph)DPFN]$^{+/++}$ Cation and Dication

Distance (Å) or Angle (°)	Cation	Dication
Cu···Cu	2.3927(5)	2.3809(5)
Cu1–C31	2.023(2)	2.077(5)
Cu2–C31	2.016(2)	1.940(6)
Cu1–N1	2.095(2)	2.030(4)
Cu2–N2	2.074(2)	1.977(4)
C34–C31–Cu1	144.4(1)	119.9(2)
C34–C31–Cu2	143.0(1)	167.5(3)

In addition, while in complex **2** both copper centers exhibit similar bond lengths to the naphthyridine nitrogen atoms, in **7** these distances have shortened and diverged, to 2.030(4) and 1.977(4) Å, respectively. This unsymmetric binding of the bridging phenyl group, at least at low temperatures and in the solid-state, suggests that the unpaired electron might be at least partially localized on one copper center, and that complex **7** might be best described as spin-localized, Cu$_2$(I,II), rather than delocalized (Cu$_2$(1.5,1.5)). This localization appears to exist despite a Cu···Cu distance in **7** that is shorter than those observed in many spin-delocalized copper complexes (2.4 to 2.9 Å), which would ostensibly suggest that the electron hole could be delocalized.[35–37]

Similar unsymmetric binding of an unsupported bridging phenyl group between two first-row transition metals was previously observed by Beck and Johnson.[38] Addition of Ph$_3$SiH to [(^{i}Pr$_3$P)$_2$Ni]$_2$(μ-η^1:η^1-N$_2$) generated a dinickel complex, [(^{i}Pr$_3$P)Ni]$_2$(μ-C$_6$H$_5$)(μ-SiHPh$_2$). In the solid-state, the two nickel

4

centers are separated by 2.408(1) Å, which is slightly longer than the Cu···Cu distance observed in **7**. Compared to **7**, the dinickel complex has a significantly smaller difference between the two Ni–C_{ipso} bonds (1.958(7) and 1.892(5) Å), but a larger difference between the C_{para}–C_{ipso}–M angles (109.1(3)° and 173.3(3)°).

On the basis of the crystallographically-determined solid-state structure, two hypotheses could be developed. First, the unsymmetrical binding mode for the phenyl group in **7** might simply be a consequence of crystal packing forces. Alternatively, this bent structure could result from an electronic preference and possibly represent one of two equivalent, energetic minima that could be in rapid equilibrium in solution (eq 6).

$$\text{Cu}^A \diagup \diagdown \text{Cu}^B \rightleftharpoons \text{Cu}^A \diagdown \diagup \text{Cu}^B \qquad (6)$$
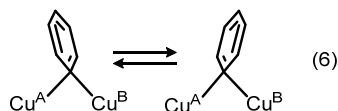
Assuming spin localization, formal oxidation states can be assigned based on bond distances. Significantly shorter bonds to Cu2, from both the *ipso*-carbon (C31) and its naphthyridine nitrogen (N2), suggest that it can be assigned as Cu(II). As a result Cu1, which appears to interact slightly more with the π-system of the bridging phenyl, can be assigned as Cu(I).

Regardless of the degree of spin localization, complex **7** is a rare example of a persistent mixed-valence organocopper complex, and to our knowledge represents the first discrete, isolable example. Numerous attempts to isolate mixed-valence organocopper species have been unsuccessful, and such short-lived species have only been studied spectroscopically or electrochemically.[34] In addition, **7** is an organocopper complex in which the Cu(II)-bound hydrocarbyl is not a component of a multi-dentate ligand. In comparison, most Cu(II) and Cu(III) organocopper species rely on incorporating the hydrocarbyl moiety into a rigid polydentate ligand (*e.g.* N-confused porphyrin derivatives, azacalix[1]arene[3]pyridines, or tris(2-pyridylthio)methane) or using very electron-withdrawing organic perfluorocarbyls that stabilize high oxidation states (*i.e.* –CF_3).[2,3] In fact, the few reported high-valent (Cu(II) or Cu(III)) arylcopper species all incorporate the aryl moiety into a polydentate ligand.[14,39–41] Upon heating at 60 °C in THF-d_8 over 2 d, **7** decomposes to a mixture diamagnetic and paramagnetic products, with the production of benzene (ca. 0.2 equiv.), and no evidence of C_6H_5D, as determined by ${}^1H$, ${}^2H$, and ${}^{19}F$ NMR spectroscopy, was obtained.

Spectroscopy of a Mixed-Valence Organocopper Complex

Mixed-valence dicopper coordination complexes and biological active sites have been well-documented,[35,42–49] but such species are quite rare in organocopper chemistry. In spectroscopic investigations of these coordination complexes, particular attention has been devoted to characterization of the degree of electron delocalization between the copper centers, which could help distinguish between the two aforementioned hypotheses. To more fully characterize the nature of the possibly distinct copper centers and spin localization in **7**, various spectroscopic studies were conducted.

Despite the paramagnetism exhibited by **7**, in THF-d_8 at 23 °C, distinct two fluorine resonances at –78.98 and –172.66 ppm (vs $CFCl_3$) are observed by ${}^{19}F$ NMR spectroscopy (Figure S14). Integration suggests the former resonance can be assigned to NTf_2^- while the latter can be assigned to the complexed ligand. The ligand resonance's appearance as a broad singlet is consistent with both hypotheses: the phenyl group adopting a symmetric bridging mode in solution or rapidly interconverting between two bent structures on the NMR timescale. Upon cooling a solution of **7** to –78 °C, both resonances shifted slightly upfield and broadened, but neither resolved into separate peaks (Figure S15).

Upon addition of increasing quantities of **6** to **7,** the broad resonance at –172.66 ppm sharpened and shifted upfield, approaching the ${}^{19}F$ ligand resonance of **6**, which suggests that self-exchange of an electron occurs (Figures S16-19).[50–52] Unfortunately, as has been observed for other dicopper systems with fast exchange,[36] the self-exchange rate could not be accurately measured as the broadening attributable to exchange was comparable with the errors in our linewidth estimates (Figure S19).

Many mixed-valence complexes exhibit characteristic intervalence charge transfer (IVCT) bands. An electronic spectrum of a solution of **7** revealed an intense near-IR (NIR) absorption not observed in **6** (Figure 5), tentatively assigned to IVCT. To analyze the band, the UV-Visible-NIR spectrum of **7**, between 5952 and 25380 cm^{-1}, was fit to a sum of Gaussian curves, and a minimum of four curves were required to provide a satisfactory fit (Figure S20). The Gaussian-shaped NIR band is centered around 11086 cm^{-1} (902 nm) and is relatively low in intensity (ε_{max} = 2477 $M^{-1}·cm^{-1}$) compared to reported IVCT bands,[53] and broad (FWHM: 3409 cm^{-1}), suggesting that the complex is electronically at least partially localized, or Class II according to the Robin-Day classification scheme.[53–55] Employing the theoretical framework developed by Hush, the IVCT band parameters can be used to estimate the ground-state delocalization parameter (α^2).[45,55] For **7** in THF, $\alpha^2 \approx$ 0.057, which is also consistent with a Class II designation and supports the second hypothesis.
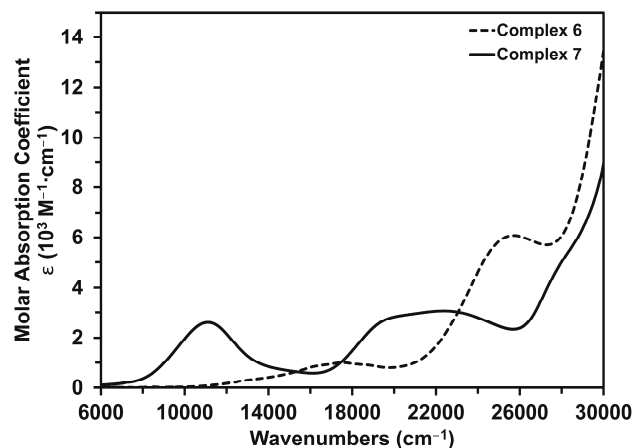

Figure 5. UV-Visible-Near IR spectra of THF solutions of **6** and **7**.

Another well-known characteristic of electronic localization in mixed valence complexes is IVCT band solvatochromism.[56] A deconvolution of the UV-Visible-NIR spectrum of **7** in o-$C_6H_4F_2$ located the IVCT band centered at 10966 cm^{-1} (912 nm) (Figure S21). Compared to the band observed in THF (902 nm), there is a small shift to lower energy, which is opposite of that expected by Hush's theory for the effect of solvent polarity on IVCT band ener-

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gies.[55] The close Cu···Cu distance may explain why solvatochromism is not observed; Hush's theory only predicts solvatochromism if the distance between metal centers is significantly greater than their respective radii, which is not the case in **7**.

Dicopper complexes can also be classified as either Class I, II, or III based on the temperature dependence of their respective *cw* EPR spectral signatures. In particular, Class II dicopper complexes present temperature-dependent EPR spectra.[42,43] The spectra acquired at lower temperatures typically consist of four peaks, indicating that the unpaired electron spin (S = 1/2) is localized primarily on the Cu(II) ion (nuclear spin I = 3/2) in the dicopper Cu(I)Cu(II) complex. At higher temperatures, the EPR spectra of a Class II complex often exhibits seven peaks, consistent with delocalization of the electron spin between both of Cu ions. In contrast, Class III dicopper complexes, sometimes denoted as average-valence or Cu(1.5)Cu(1.5), display EPR spectra typically consisting of seven hyperfine peaks at both low and high temperature.[35,46,48]

Thus, to examine the extent and possible temperature-dependence of spin localization, the electronic structure of **7** was directly probed with variable-temperature continuous-wave (*cw*) X-band EPR spectroscopy. The EPR spectrum of a frozen sample of **7** in THF in the temperature range of 4 - 150 K displayed four distinct peaks centered at g ~ 2 (Figure S22). Similar EPR spectra were obtained for a frozen solution of **7** in 1:1 o-$C_6H_4F_2$/diethyl ether (Figure S23). A spectral simulation of an electron spin (S = 1/2) with electron-nuclear hyperfine interactions for a single Cu center (nuclear spin I = 3/2) provided an excellent fit of the experimental EPR spectrum of **7** in THF at 100 K (Figure 6). The hyperfine parameters employed in the numerical simulation are in good agreement with parameters previously reported for dicopper complexes.[42,43,57]
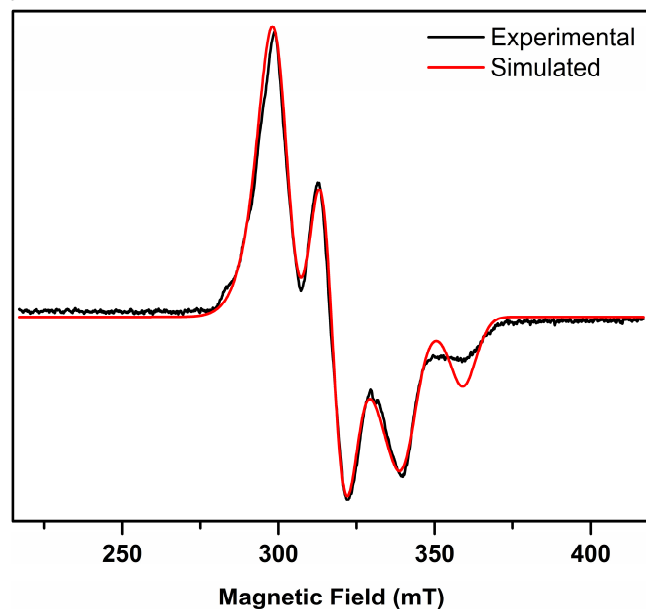

Figure 6. The experimental (black trace) and simulated (red trace) *cw* EPR spectra of **7** in THF at 100 K. The numerical simulation was obtained with g values of g_1 = 2.032, g_2 = 2.096, g_3 = 2.159 and principal hyperfine components of A_1^{Cu} = 191.9, A_2^{Cu} = 65.8, A_3^{Cu} = 29.6 10^{-4} T.

At temperatures between 150 and 260 K, the four peaks observed in the EPR spectrum of **7** (Figure 6) merged into a single resonance that persisted to 295 K (Figure S24). However, compared to the spectrum of **7** at 100 K, the spectrum recorded at 240 K displayed a larger number of hyperfine peak splittings (Figure 7). The appearance of additional hyperfine structure in the EPR spectrum of **7** at 240 K suggests partial delocalization of the unpaired electron spin over the two copper centers in the complex. Using the hyperfine interaction parameters obtained from the simulation of the spectrum collected at 100 K, numerical simulations of isotropic spectra suggest that the EPR spectrum of **7** at 240 K is a combination of spectra with four and seven-line patterns due to the presence of a mixture of spectrally distinct species with the electron spin on either one or two Cu centers, respectively (Figure S25). In addition, it was observed that the EPR spectrum of **7** at 240 K is inhomogeneously broadened, likely as a result of unresolved hyperfine interactions and/or fluxional behavior, such as flipping of the bridging phenyl between the metal centers. Previously reported mixed-valence dicopper complexes possess more rigid core structures in comparison with **7**, whose μ-phenyl ligand is potentially conformationally flexible and can alter the symmetry of the dicopper core.

The low-temperature EPR spectra with four peaks and increased hyperfine structure at higher temperatures displayed by **7** are characteristic of a Class II Cu(I)Cu(II) complex. Moreover, the observed coupling to only one copper center in the solid state and at low temperatures further supports the second hypothesis, that the phenyl tilting is driven by an electronic effect.
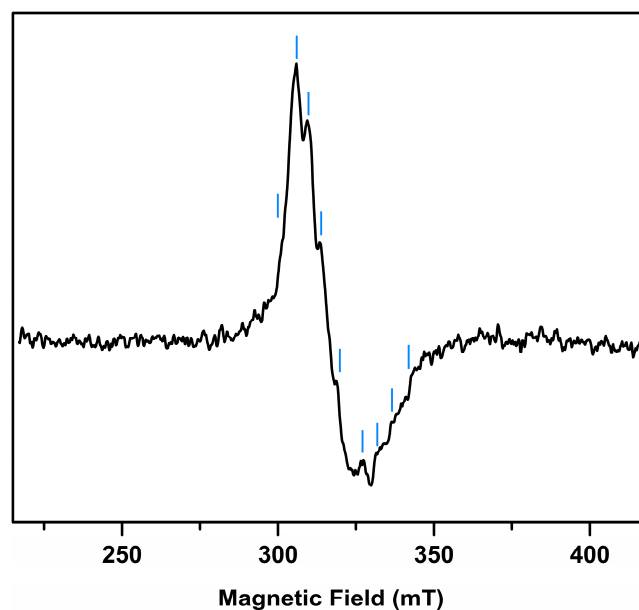

Figure 7. The experimental *cw* EPR spectrum of **7** in THF at 240 K. The blue vertical lines highlight the peak splittings due to hyperfine interactions with one and two Cu nuclei.

Electronic Structure Calculations

The spin localization observed by *cw* EPR spectroscopy prompted exploration of the electronic structure of complex **7**. Initial DFT calculations suggested significant spin delocalization, inconsistent with the spectroscopic results. Previous analyses have documented a tendency of DFT calculations to artificially stabilize delocalized states, compared to localized states, when calculating spin density.[58,59] Specifically, unpaired spin density often suffers from over-delocalization due to the "self-interaction error" (or "delocalization error") which arises from the use of an approximate exchange-correlation functional.[60,61] As a result, while reasonable energies and structures can typically be calculated from DFT approaches, electron localization cannot in general be reliably obtained.

The use of a range-separated hybrid functional, which utilizes an attenuator that smoothly transitions the Coulomb potential from a fraction of Hartree-Fock (HF) exchange (also referred to as "exact exchange") at short-range to full HF exchange at long range, partially mitigates this delocalization problem and can lead to better performance.[62] Indeed, optimization of the crystallographically-determined structure of the dication of **7** with the range-separated ωB97X-D functional[63] in the 6-31+G** basis set, reproduces the observed structure closely, but analysis of the unpaired spin density shows it to be highly delocalized (35% on Cu1 and 29% on Cu2). However, a calculation of the unpaired spin density using HF theory or SF-CAS[64] shows the spin almost completely localized on one metal center (1.1% on Cu1 and 95% on Cu2, Figure 8). This localization is consistent with both the estimate of the ground-state delocalization parameter ($\alpha^2 \approx 0.057$) from the analysis of the IVCT band parameters and the observation of coupling to only one Cu center by low-temperature EPR spectroscopy.
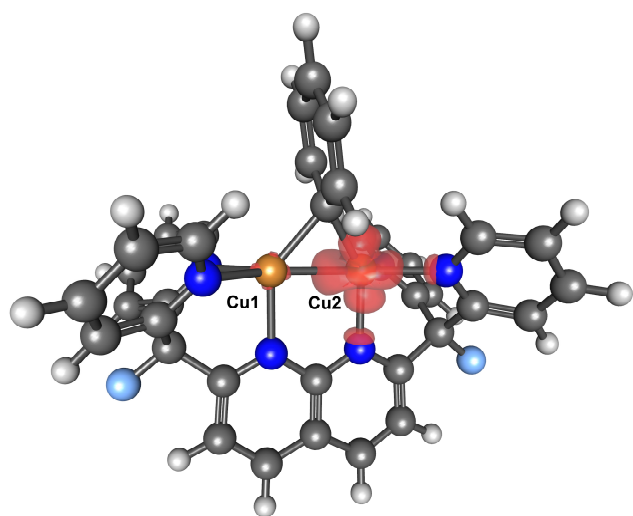

Figure 8. Spin-density map calculated using SF-CAS, visualized with an isosurface of 0.002, which encapsulates all spin density up to 0.2%.

To demonstrate that the difference is attributable to the delocalization error of DFT, the unpaired spin localization was calculated employing several long-range-corrected DFT functionals with an increasing fraction of short-range HF exchange, along with a standard hybrid functional, B3LYP, which uses a fixed amount (20%) of HF exchange at all ranges of the Coulomb operator (Figures S26-27). These results show that an increasing amount of HF exchange,

and concomitant decrease in the self-interaction error, produces electron spin density that is more localized.

Concluding Remarks

The aforementioned results demonstrate unexpected electrophilicity of a first-row metal complex and merge two historically distinct concepts in copper chemistry: organocopper complexes and mixed-valence dicopper species. An unusually electrophilic dicopper complex with a labile, bridging acetonitrile ligand was found to abstract an aryl group from a range of tetraarylborato anions and kinetically stabilize the aryl moiety as a bridging ligand. The resulting μ-aryl groups bind symmetrically, and the cations' solid-state structures appear to persist in solution. Surprisingly, the arylcopper complexes exhibited chemically reversible redox couples, and the oxidized product of the phenylcopper complex could be synthesized, isolated, and structurally and spectroscopically characterized. It is an example of both a discrete mixed-valence and Cu(II)-containing organocopper complex. Its solid-state structure suggests spin localization despite a Cu···Cu distance that is shorter than that reported in most spin-delocalized complexes. Analysis of a well-resolved NIR band and variable-temperature EPR spectroscopy evidence that the spin localization is temperature-dependent, consistent with previously reported dicopper Class II coordination complexes. The high degree of spin localization observed by EPR at low temperatures, and estimated by analysis of the IVCT transition, is also consistent with electronic structure calculations of unpaired spin density. This localization could be enabled by the conformationally-flexible μ-phenyl group.

This work establishes the structure of mixed-valence organocopper complexes, and we expect that this class of compounds could provide new synthetic targets for the development of reagents and catalysts that might exhibit yet undiscovered reactivity. Moreover, they could serve as intermediates in reactions that were previously only partially explained by mononuclear copper complexes or binuclear complexes containing only Cu(I) or Cu(II).[10,65]

ASSOCIATED CONTENT

Supporting Information

Experimental details, supplementary figures and tables, and crystallographic figures and data are available free of charge on the ACS Publications website at DOI: XXX. CIF files can also be obtained free of charge from the Cambridge Crystallographic Data Centre under reference numbers 1473702, 1473703, 1473705, 1473706, 1473704, 1473701.

Full experimental details and spectroscopic data (PDF)

X-ray crystallographic data for **1**·2.5($C_6H_5NO_2$), **2**·3(*o*-$C_6H_4F_2$), **3**·3(*o*-$C_6H_4F_2$), **5**·*n*(*o*-$C_6H_4Cl_2$), **6**·2.5(C_6H_5F), and **7**·*n*(*o*-$C_6H_4F_2$) (CIF)

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Notes

The authors declare no competing financial interest.

7

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homo- and mixed-valence organocopper: discrete, isolable, structurally-characterized