

## Communication

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# Dicopper $\mu$ -Oxo, $\mu$ -Nitrosyl Complex from the Activation of NO or Nitrite at a Dicopper Center

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Supporting Information Placeholder

**ABSTRACT:** Treatment of a dicopper(I,I) complex with nitric oxide produces a dicopper  $\mu$ -oxo,  $\mu$ -nitrosyl complex [LCu<sub>2</sub>( $\mu$ -O)( $\mu$ -NO)]<sup>2+</sup>, representing the first structurally characterized  $\mu$ -oxo,  $\mu$ -nitrosyl metal complex. This compound can also be synthesized from the reaction of nitrite with a [LCu<sup>II</sup>Cu<sup>I]</sup><sup>3+</sup> synthon. Full characterization of the thermal-sensitive [LCu<sub>2</sub>( $\mu$ -O)( $\mu$ -NO)]<sup>2+</sup> complex with IR, EPR, and X-ray crystallography suggests a localized mixed-valent Cu<sup>III</sup>, Cu<sup>II</sup>, O<sup>2-</sup>, NO<sup>-</sup> formulation. The [Cu<sub>2</sub>( $\mu$ -O)( $\mu$ -NO)]<sup>2+</sup> core efficiently oxidizes exogenous substrates, such as phosphine, cyclohexadienes, and isochroman to afford phosphine oxide, benzene, and 1-isochromanone. Since both nitrite and nitric oxide are proposed oxidants in denitrifying methane oxidation, the oxidative reactivity of [Cu<sub>2</sub>( $\mu$ -O)( $\mu$ -NO)]<sup>2+</sup> core is potentially relevant to anaerobic methane oxidation observed in methanotrophic archaea.

The interconversion of nitric oxide (NO•) and nitrite (NO $_2^-$ ) at biological metal centers has important implications in neurotransmission and vasodilation.1 For example, the hemea<sub>3</sub>/Cu<sub>B</sub> site in cytochrome c oxidase (CcO) reduces NO<sub>2</sub><sup>-</sup> to NO• (Scheme 1A) under hypoxic conditions, triggering a series of biochemical responses leading to cellular O<sub>2</sub> restoration.<sup>2,3</sup> The heme-a<sub>3</sub>/Cu<sub>B</sub> site can also detoxify NO• by promoting the reductive coupling of two NO• molecules to form nitrous oxide (N<sub>2</sub>O), leaving behind a Fe<sup>III</sup>-O-Cu<sup>II</sup> moiety (Scheme 1A). Similar reductive coupling of NO• occurs at heme/non-heme<sup>4</sup> and flavodiiron<sup>5</sup> NO reductases (NOR, Scheme 1B). Based on modeling studies, it appears that bimetallic centers can promote the coupling of adjacent nitrosyl ligands to form hyponitrite (-O-N=N-O-) preceding the release of N<sub>2</sub>O. For instance, reductive coupling of two {CuNO}<sup>11</sup> moieties generates a fully characterized dicopper(II,II) hyponitrite that releases N<sub>2</sub>O to form copper(II) nitrite ([Cu<sup>II</sup>]-NO<sub>2</sub>), presumably through a dicopper(II,II)  $\mu$ -oxo complex (Scheme 1C).<sup>6-8</sup>

A common intermediate shared in the interconversion of NO• and  $NO_2^-$  is the bimetallic  $\mu$ -oxo (M-O-M) motif, which could be generated from either reductive coupling of two NO• molecules or activation of the O-N bond in  $NO_2^-$  (Scheme 1A and 1B).<sup>2</sup> Owing to our interests in the oxidative reactivity of  $NO_2^-$ , we were curious if a dicopper(II,II)  $\mu$ -oxo could be formed from the activation of  $NO_2^-$  at a dicopper center in a manner similar to heme-a<sub>3</sub>/Cu<sub>B</sub> site.<sup>2</sup> Given that dicopper(II,II)  $\mu$ -oxo core is proposed as the active site

for methane selective monooxygenation in Cu-ZSM-5,<sup>9,10</sup> nitritederived dicopper  $\mu$ -oxo species could be synthetically useful in oxidation/oxygenation reactions. Additionally, activation of NO<sub>2</sub><sup>-</sup> toward C-H hydroxylation is mechanistically and functionally relevant to anaerobic methane oxidation observed in denitrifying archaea, a metabolic process that couples reduction of nitrite with methane oxidation:  $3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O_{11}$  Although the biochemical mechanism for denitrifying methane oxidation is still under investigation, the involvement of particulate methane monooxygenase (pMMO) – an enzyme that contains copper active sites<sup>12-16</sup> – has been proposed.<sup>17,18</sup>



In this report, we describe a new nitrite activation mechanism that can be harnessed for oxidative reactivity. Cleavage of an O-NO bond at a dicopper(I,II) center provides an unprecedented dicopper(II,III)  $\mu$ -oxo,  $\mu$ -nitrosyl complex ([Cu<sub>2</sub>( $\mu$ -O)( $\mu$ -NO)]<sup>2+</sup>, Scheme 1D). This complex can also be prepared from the reaction of dicopper(I,I) with NO•. The [Cu<sub>2</sub>( $\mu$ -O)( $\mu$ -NO)]<sup>2+</sup> core is reminiscent of the active species in methane-oxidizing copperexchanged zeolite,<sup>19–23</sup> and cleanly oxidizes phosphine, cyclohexadienes, and isochroman to afford phosphine oxide, benzene, and 1-isochromanone respectively. Such oxidative reactivity of NO<sub>2</sub><sup>-</sup> at dicopper centers represents a strategy

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**Figure 1.** Synthesis of  $Py_4DMB$  ligand (L), **1**-BArF<sub>4</sub> and **1**-phenylacetylene-BArF<sub>4</sub>. Solid-state structure of **1**-phenylacetylene-BArF<sub>4</sub> with thermal ellipsoids shown at 50% probability level. Two BArF<sub>4</sub> anions and all hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Cu-Cu 2.8249(5) Å, Cu-O (average) 2.757 Å.

available to Nature to utilize  $NO_2^-$  and  $NO_2^-$  as oxidants under anaerobic conditions.

To template a dicopper complex with a close Cu-Cu distance,<sup>24</sup> we linked four pyridine ligands using a rigid 1,2-dimethoxylbenzene (DMB) linker. The Py<sub>4</sub>DMB ligand (1,2-bis(di(pyridin-2yl)methoxy)benzene, L) could be prepared from dipyridylchloromethane and catechol in 67% yield (Figure 1). Insertion of copper(I) ions to L proceeds upon treatment of L with two equivalents of  $[Cu^{I}(MeCN)_{4}]BAr^{F_{4}}$  (BAr<sup>F\_{4}</sup> = tetrakis(3,5bis(trifluoromethyl)phenyl)borate) or [Cu<sup>I</sup>(MeCN)<sub>4</sub>]OTf (OTf = trifluoromethanesulfonate), affording yellow powders with the <sup>1</sup>H and <sup>13</sup>C NMR signals expected for [LCu<sup>1</sup><sub>2</sub>(MeCN)<sub>2</sub>][BAr<sub>4</sub><sup>F</sup>]<sub>2</sub> (1-BAr<sup>F</sup><sub>4</sub>) in 81% yield or  $[LCu^{I}_{2}(MeCN)_{2}][OTf]_{2}$  (1-OTf) in 86% yield respectively. Complex 1-BAr $F_4$  can be stored as a solid at -40 °C without decomposition up to several months. Over prolonged periods in solution, however, [LCu<sup>I</sup><sub>2</sub>(MeCN)<sub>2</sub>]<sup>2+</sup> abstracts an aryl group from BAr<sup>F</sup><sub>4</sub> to form [LCu<sup>I</sup><sub>2</sub>(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)]BAr<sup>F</sup><sub>4</sub> (Figure S45), which is structurally reminiscent of the dicopper  $\mu$ -aryl complexes reported by Tilley et. al. 25,26 To confirm the binucleating nature of 1,  $[LCu^{I}_{2}(phenylacetylene)][BAr^{F}_{4}]_{2}$  (1•phenylacetylene-BAr<sup>F</sup><sub>4</sub>) was prepared in 87% yield by treating 1 with one equivalent of phenylacetylene, which was used to mimic a bridging  $\pi$  donor.<sup>27</sup> The X-ray structure of 1•phenylacetylene-BArF<sub>4</sub> showed a Cu-Cu distance of (2.8249(5) Å) and long Cu-O distances (average 2.757 Å), indicating minimal Cu-O interaction.

46 Treatment of 1-BAr<sup>F</sup><sub>4</sub> with four equivalents of NO• in acetone 47 resulted in the formation of a dark green complex, which quickly converted to a red species 2-BAr<sup>F</sup><sub>4</sub> (Figure 2 left,  $\lambda_{max} = 515$  nm;  $\epsilon$ 48 = 2300  $M^{-1}cm^{-1}$ ) at -40 °C. Similar UV-Vis spectroscopic features 49 were observed when 1-OTf was treated with NO• (Figure S19). 50 Formation of 1 eq N<sub>2</sub>O per dicopper complex was detected in 98% 51 yield with GC analysis of the reaction headspace (Figure S62-S65). 52 The reaction of 1-OTf and NO• was monitored with low-53 temperature solution IR spectroscopy. A new band at 1554 cm<sup>-1</sup> 54 assigned to 2-OTf grew in at -40 °C and was found to be sensitive 55 to <sup>15</sup>N labeling ( $\Delta v NO_{14N-15N} = -30 \text{ cm}^{-1}$ , Figure S50). The 1554 56 cm<sup>-1</sup> N-O stretch was persistent up to -40 °C, matching the 57



Figure 2. Reaction scheme (top) and corresponding UV-Vis spectra (left) for the formation of  $2\text{-BAr}^{\text{F}}$  (-40 °C, 0.75 mM [Cu<sub>2</sub>], acetone). Right: frozen EPR spectrum and simulation of 2 (THF, 20 K, 0.5 mM).

thermostability of **2**-OTf and **2**-BAr<sup>F</sup><sub>4</sub> observed by UV-Vis spectroscopy. The vNO of **2**-OTf is comparable to that of dicopper(II,II)  $\mu$ -nitrosyl complexes  $[(XYL-O)Cu^{II}_2(\mu$ -NO<sup>-</sup>)]^{2+} (1536 cm<sup>-1</sup>)^{28} and lower than that of the mixed-valent  $[Cu^{IC}u^{II}(\mu$ -NO•)] (1670 cm<sup>-1</sup>)<sup>2+,29</sup>

X-ray diffraction analysis of single crystals of 2-BArF<sub>4</sub> grown from a mixture of THF and pentane showed a dicopper  $\mu$ -oxo,  $\mu$ -nitrosyl complex  $[LCu_2(\mu-O)(\mu-NO)][BAr^F_4]_2$  (Figure 3). Although it is difficult to distinguish  $\mu$ -O<sup>2-</sup> ligand from  $\mu$ -OH<sup>-</sup> ligand crystallographically, further EPR spectroscopy study supports the assignment of  $\mu$ -O<sup>2-</sup> (vide infra). The structure of **2**-BAr<sup>F</sup><sub>4</sub> suggested that the coupling of two {CuNO}<sup>11</sup> resulted in the formation of N<sub>2</sub>O and a presumed [Cu<sup>II</sup>-O-Cu<sup>II</sup>]<sup>2+</sup> species, which was then trapped by another equivalent of NO•. Complex 2-BAr<sup>F</sup><sub>4</sub> is the first structurally characterized  $\mu$ -oxo,  $\mu$ -nitrosyl metal complex. The  $\mu$ -nitrosyl ligand is disordered over two positions (see supporting information). In the major occupancy site (60 %), the N-O bond distance is 1.154(19) Å slightly shorter than that in  $[(XYL-O)Cu^{II}_2(\mu-NO^-)]^{2+}(1.176(1) \text{ Å})$ , the only other structurally characterized dinuclear copper nitrosyl complex.<sup>28</sup> Each copper center also coordinates to one THF solvent molecule with a long Cu-O bond (Cu-O 2.395(6) and 2.406(9) Å), completing a pseudosquare pyramidal geometry. The Cu-Cu distance is 2.844(2) Å, shorter than that observed in  $[(XYL-O)Cu^{II}_{2}(\mu-NO^{-})]^{2+}$  (3.140(1) Å).<sup>28</sup> Close examination of the structural parameters of 2-BAr<sup>F</sup><sub>4</sub>



**Figure 3.** Solid-state structure (150 K) of **2**-BAr<sup>F</sup><sub>2</sub> with thermal ellipsoids was shown at 30% probability level. Two BAr<sup>F</sup> anions, the minor components of disorder, and all H atoms are omitted for clarity.

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indicates the  $[Cu_2(\mu-O)(\mu-NO)]^{2+}$  core is unsymmetric. Specifically, both the  $\mu$ -nitrosyl and  $\mu$ -oxo are closer to Cu2 (Cu2-N1 1.987(13) Å; Cu2-O1 1.869(8) Å) than Cu1 (Cu1-N1 2.030(12) Å; Cu1-O1 1.892(8) Å), hinting at a valence localized electronic structure.<sup>30</sup> We also synthesized and crystalized 2-OTf by treating 1-OTf with NO•. X-ray diffraction data of 2-OTf show that the  $[Cu_2(\mu-O)(\mu-NO)]^{2+}$  core is bisected by a mirror plane that goes through both coppers (Figure S49) and crystallographically overlays the  $\mu$ -oxo with the  $\mu$ -nitrosyl, which somewhat limits the insights into the precise bond metrics. Nonetheless, 2-OTf also shows an unsymmetric  $[Cu_2(\mu-O)(\mu-NO)]^{2+}$  core (Cu1-O(NO) =10 1.943(5) Å; Cu2-O(NO) = 1.927(5) Å) and likewise suggests a 11 valence-localized electronic structure. 12

Further evidence for the valence-localized  $[Cu_2(\mu-O)(\mu-NO)]^{2+}$ core was obtained by EPR analysis. A frozen solution EPR spectrum of 2-BAr<sup>F</sup><sub>4</sub> in THF at 20 K (Figure 2 right) displayed an axial signal ( $g_x = g_y = 2.055$ ,  $g_z = 2.270$ ) with major hyperfine couplings to one  $^{63/65}$ Cu (I = 3/2) nucleus (A<sub>z</sub>(Cu) = 520 MHz). The additional superhyperfine structures around 325 mT could be modeled in several ways (see supporting information). No difference is observed between the EPR spectra of 2-BAr<sup>F</sup><sub>4</sub> and  $^{15}\text{NO-labeled}\ \textbf{2-BAr}^{F_4}$  (Figure S58), indicating that the N atom on  $\mu$ -NO contributes little to the superhyperfine structures. The EPR features of **2**-BAr<sup>F</sup><sub>4</sub> is very similar to that of  $[Cu^{III}Cu^{II}(\mu - OH)]^{4+}$ complex,<sup>31</sup> the only other reported mixed-valent dicopper(II,III) complex. The S = 1/2 EPR spectrum lends further support to the assignment of a  $\mu$ -O<sup>2-</sup> instead of a  $\mu$ -OH<sup>-</sup> ligand, since both  $[Cu^{II}(\mu-OH)(\mu-NO^{-})Cu^{II}]^{2+}$ and  $[Cu^{I}(\mu-OH)(\mu-NO\bullet)Cu^{II}]^{2+}$ species are likely to be EPR silent due to the antiferromagnetic coupling of two Cu d<sup>9</sup> centers or Cu d<sup>9</sup> and NO• centers.<sup>32</sup> Together, solution IR, frozen EPR, and X-ray crystallography data for complex 2 indicate a Cu<sup>II</sup>, Cu<sup>III</sup>, O<sup>2-</sup>, NO<sup>-</sup> formulation.



Figure 4. Reaction scheme (left) and corresponding UV-Vis spectra (right) (-40 °C, 0.75 mM [Cu<sub>2</sub>], 1:1 THF:acetone) for the synthesis of 2-OTf via activation of NO<sub>2</sub><sup>-</sup>.

In light of the seminal findings by Tolman<sup>33-36</sup> and Karlin,<sup>6-8</sup> a [Cu<sup>II</sup>-O-Cu<sup>II</sup>]<sup>2+</sup> species produced by {CuNO}<sup>11</sup> coupling is expected to react with NO• to form [Cu<sup>II</sup>]-NO<sub>2</sub> or mixed-valent [Cu<sup>II</sup>(NO<sub>2</sub>)Cu<sup>I</sup>]<sup>2+</sup> (Scheme 1C).<sup>37,38</sup> It is therefore surprising that the  $[LCu_2(\mu-O)(\mu-NO)]^{2+}$  core could support a nitrosyl and oxo ligand at the same time without reductively eliminating NO<sub>2</sub><sup>-</sup>. Given that the elimination of  $NO_2^-$  is not favored in 2, we envisioned that a  $[Cu_2(\mu-O)(\mu-NO)]^{2+}$  species could be accessed from the activation of NO<sub>2</sub><sup>-</sup> by Cu(II) and Cu(I) templated by L (Figure 4). To generate a [LCu<sup>I</sup>Cu<sup>II</sup>]<sup>3+</sup> synthon, we first prepared a  $Cu^{II}$  precursor [LCu<sup>II</sup>][OTf]<sub>2</sub> by treating L with Cu<sup>II</sup>OTf<sub>2</sub>. Full characterization of [LCu<sup>II</sup>][OTf]<sub>2</sub>, including UV-Vis, EPR, and Xray crystallography, is included in the supporting information. The Cu<sup>II</sup> ion in [LCu<sup>II</sup>][OTf]<sub>2</sub> occupies four pyridine donors to form a

square planar complex (Figure S46). To our delight, we found that the *in situ* generated  $[LCu^{I}Cu^{II}]^{3+}$  synthon (1 eq  $[LCu^{II}]OTf_2 + 1$ eq [Cu<sup>I</sup>(MeCN)<sub>4</sub>]OTf]) reacted with  $TBANO_2$ (TBA tetrabutylammonium) in a 1:1 mixture of acetone and THF solvent (chosen to maximize the solubility of [LCu<sup>II</sup>]OTf<sub>2</sub>) at -40 °C to afford the  $[LCu_2(\mu-O)(\mu-NO)]^{2+}$  core as identified by a strong band at 515 nm (Figure 4 right). The formation of  $[LCu_2(\mu-O)(\mu-NO)]^{2+}$ was also confirmed with solution IR study (Figure S52). A plot of the yield of 2-OTf vs. different equivalent of TBANO<sub>2</sub> shows a maximum at one equivalent TBANO2 per [LCuICuII]3+, indicating a 1:1 stoichiometry (Figure S26-S27). Interestingly, addition of TBANO<sub>2</sub> to the dicopper(I,I) complex **1**-OTf did not produce any change in the UV-Vis spectroscopy (Figure S28-S29). The lack of reaction between 1-OTf and NO<sub>2</sub><sup>-</sup> is perhaps due to the low Lewis acidity of Cu(I) compared to Cu(II). Typically, the activation of NO<sub>2</sub><sup>-</sup> is strongly influenced by the Lewis acidity while rather independent of the reducing ability of the bimetallic centers.<sup>2,3,39-41</sup>



To determine the role that the binucleating ligand L may have on the activation of  $NO_2^-$ , we prepared a mononuclear analog 3 by complexing Cu<sup>II</sup>OTf<sub>2</sub> with two equivalents of 2.2'-(phenoxymethylene)dipyridine (Scheme 2). X-ray structure of 3 indicates the interaction of copper with both axial O donors are quite weak (Figure S47, Cu1-O1(OPh) 2.522 Å, Cu1-O1A(OTf) 2.393(1) Å). Treatment of **3** with an equimolar amount of [Cu<sup>I</sup>(MeCN)<sub>4</sub>OTf] and TBANO<sub>2</sub> did not produce any spectroscopic changes expected for a  $[Cu_2(\mu-O)(\mu-NO)]^{2+}$  core (Scheme 2, Figure S30-S32). Molecular orbital considerations in Scheme 2 outline the importance of bimetallic cooperativity in the activation of the O-NO bond. The dimethoxylbenzene linker in L templates a close Cu-Cu distance (ca. 2.8 Å) and aligns the two Cu d<sub>x2-y2</sub> orbitals with the nitrite  $\pi^*$  orbital in the  $\mu$ - $\eta^2$ :  $\eta^2$ -NO<sub>2</sub> binding mode, which weakens the ON-O bond in NO<sub>2</sub><sup>-</sup>. While the  $\mu$ - $\eta^2$ : $\eta^2$ -NO<sub>2</sub> binding mode is also possible with mononuclear analog 3, the commonly observed  $\mu$ - $\eta^1$ : $\kappa^2$ -NO<sub>2</sub> binding mode is perhaps more favorable,<sup>37,38,42</sup> since it allows the soft Cu(I) to interact with N atom and the hard Cu(II) to interact with O atoms. Since the otherwise favored  $\mu$ - $\eta^1$ : $\kappa^2$ -NO<sub>2</sub> binding mode requires an intermetallic distance of at least 4.3 Å, 37, 38, 42 the binuclear L prevents the formation of the inactive  $\mu$ - $\eta^1$ : $\kappa^2$ -NO<sub>2</sub> sink, therefore making the O-NO bond cleavage reactivity somewhat unique to the linked bimetallic system.

Given that NO<sub>2</sub><sup>-</sup> and NO• are proposed as active oxidants in denitrifying methane oxidation,<sup>18</sup> we are interested if the [Cu<sub>2</sub>( $\mu$ -O)( $\mu$ -NO)]<sup>2+</sup> core derived from NO<sub>2</sub><sup>-</sup> and NO• could engage in oxidative reactions, such as oxygen atom transfer (OAT), hydrogen atom abstraction (HAA), and C-H hydroxylation. As followed by UV-Vis and NMR spectroscopy, we found that the complex **2**-OTf readily transferred an oxygen atom to tricyclohexylphosphine (PCy<sub>3</sub>) to afford tricyclohexylphosphine oxide (OPCy<sub>3</sub>) in quantitative yield. Reactions of **2**-OTf with hydrogen atom donor 1,3-cyclohexadiene (BDE = 74.3 kcal/mol) and 1,4cyclohexadiene (BDE = 76.0 kcal/mol)<sup>43</sup> at -40 °C furnished benzene in 43% and 86% yield respectively. Finally, treatment of **2**-OTf with isochroman<sup>44,45</sup> at -40 °C gave oxidized product 1isochromanone in 78% yield, assuming the formation of each 1isochromanone consumed two equivalents of **2**-OTf (Scheme 3). These results point to the ability of **2** to perform hydroxylation reaction through sequential HAA and radical rebound sequence.

Scheme 3.



In summary, we illustrate that activation of NO• and NO<sub>2</sub><sup>-</sup> at dicopper centers provides a dicopper(II,III)  $\mu$ -oxo,  $\mu$ -nitrosyl complex that engages in a range of oxidative reactivity, such as OAT, HAA, and C-H hydroxylation. Given that dicopper sites in proteins/enzymes could participate in the oxidation/oxygenation of many biological substrates, our findings suggest a new anaerobic pathway to access a dicopper  $\mu$ -oxo moiety that may engage in challenging biochemical oxidation processes. The unique geometry of LCu<sub>2</sub> prevents the reductive coupling of  $\mu$ -oxo and  $\mu$ -nitrosyl to form NO<sub>2</sub><sup>-</sup>. Conversely, there is enough thermodynamic driving force to break the O-NO bond of nitrite at Cu<sup>II</sup> and Cu<sup>I</sup> supported by L. We expect that NO<sub>2</sub><sup>-</sup> could serve as a nucleophilic oxyl (O<sup>-</sup>) donor (NO<sub>2</sub><sup>-</sup>  $\rightarrow$  NO• + O<sup>-</sup>) to a large class of bimetallic complexes to form synthetically useful bimetallic  $\mu$ -oxo complexes. This will be the subject of our future study.

#### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Experimental details, and characterization data for complex 1-BAr<sup>F</sup><sub>4</sub>, 1•phenylacetylene-BAr<sup>F</sup><sub>4</sub>, 1-OTf, 2-BAr<sup>F</sup><sub>4</sub>, 2-OTf, LCu<sup>II</sup>(OTf)<sub>2</sub>, and 3 including X-ray crystallographic data for 1•phenylacetylene-BAr<sup>F</sup><sub>4</sub> (1905396), [LCu<sup>I</sup><sub>2</sub>(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)]BAr<sup>F</sup><sub>4</sub> (1905393), 2-BAr<sup>F</sup><sub>4</sub>(1905394), 2-OTf (1905395), LCu<sup>II</sup>OTf<sub>2</sub> (1905397), and 3 (1905392).

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#### Notes

The authors declare no competing financial interests.

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