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# 1 Tuning Inner-Sphere Electron Transfer in a Series of Copper/ 2 Nitrosoarene Adducts

3 Mohammad S. Askari, Farshid Effaty, Federica Gennarini, Maylis Orio, Nicolas Le Poul,\*  
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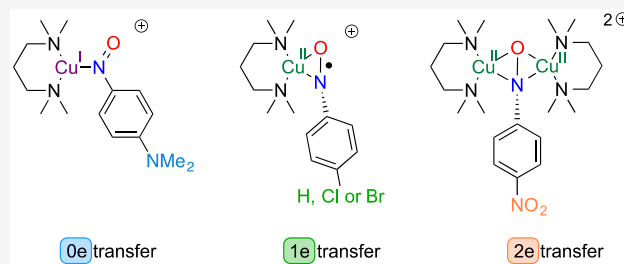


Article Recommendations



Supporting Information

5 **ABSTRACT:** A series of copper/nitrosoarene complexes were  
6 created that mimic several steps in biomimetic O<sub>2</sub> activation by  
7 copper(I). The reaction of the copper(I) complex of *N,N,N',N'*-  
8 tetramethylpropylenediamine with a series of para-substituted  
9 nitrosobenzene derivatives leads to adducts in which the nitro-  
10 soarene (ArNO) is reduced by zero, one, or two electrons, akin to  
11 the isoivalent species dioxygen, superoxide, and peroxide, respec-  
12 tively. The geometric and electronic structures of these adducts were  
13 characterized by means of X-ray diffraction, vibrational analysis,  
14 ultraviolet–visible spectroscopy, NMR, electrochemistry, and  
15 density functional theory (DFT) calculations. The bonding mode of the NO moiety depends on the oxidation state of the  
16 ArNO moiety:  $\kappa\text{N}$  for ArNO, mononuclear  $\eta^2\text{-NO}$  and dinuclear  $\mu\text{-}\eta^2\text{:}\eta^1$  for ArNO<sup>•-</sup>, and dinuclear  $\mu\text{-}\eta^2\text{:}\eta^2$  for ArNO<sup>2-</sup>. <sup>15</sup>N  
17 isotopic labeling confirms the reduction state by measuring the NO stretching frequency (1392 cm<sup>-1</sup> for  $\kappa\text{N}$ -ArNO, 1226 cm<sup>-1</sup> for  
18  $\eta^2$ -ArNO<sup>•-</sup>, 1133 cm<sup>-1</sup> for dinuclear  $\mu\text{-}\eta^2\text{:}\eta^1$ -ArNO<sup>•-</sup>, and 875 cm<sup>-1</sup> for dinuclear  $\mu\text{-}\eta^2\text{:}\eta^2$  for ArNO<sup>2-</sup>). The <sup>15</sup>N NMR signal  
19 disappears for the ArNO<sup>•-</sup> species, establishing a unique diagnostic for the radical state. Electrochemical studies indicate reduction  
20 waves that are consistent with one-electron reduction of the adducts and are compared with studies performed on Cu–O<sub>2</sub> analogues.  
21 DFT calculations were undertaken to confirm our experimental findings, notably to establish the nature of the charge-transfer  
22 transitions responsible for the intense green color of the complexes. In fine, this family of complexes is unique in that it walks  
23 through three redox states of the ArNO moiety while keeping the metal and its supporting ligand the same. This work provides  
24 snapshots of the reactivity of the toxic nitrosoarene molecules with the biologically relevant Cu(I) ion.



## 25 ■ INTRODUCTION

26 The interaction of nitrosoarenes (ArNO) with metal centers  
27 has drawn much attention because of its relevance to biological  
28 pathways<sup>1–7</sup> and catalytic C–N bond formation processes.<sup>8–12</sup>  
29 Chemists now have a good understanding of the geometric  
30 structure of transition metal/nitrosoarene complexes.<sup>13,14</sup> In  
31 addition, ArNO species are redox-noninnocent ligands,<sup>15–17</sup>  
32 which portends a large landscape of electronic structures and  
33 reactivity types upon interaction with redox-active metal ions.  
34 Because ArNO species are isoivalent with O<sub>2</sub>, the reduction  
35 of ArNO by a transition metal is akin to the reduction of O<sub>2</sub> to  
36 the superoxide ion (O<sub>2</sub><sup>•-</sup>, 1e reduction) or the peroxide ion  
37 (O<sub>2</sub><sup>2-</sup>, 2e reduction). Therefore, metal/ArNO adducts are  
38 often regarded as surrogates for metal/O<sub>2</sub> adducts. In  
39 particular, and with relevance to the present paper, the  
40 activation of O<sub>2</sub> by Cu(I) centers is paramount in the  
41 biological world. This process fuels enzymes such as  
42 dopamine- $\beta$ -hydroxylase, tyrosinase, and particulate methane  
43 monooxygenase, to name but a few.<sup>18,19</sup> This has inspired  
44 numerous biomimetic studies in which an electron-rich Cu(I)  
45 species is reacted with O<sub>2</sub>.<sup>20–22</sup> Without protection of the  
46 protein backbone, however, the ensuing Cu/O<sub>2</sub> complexes are

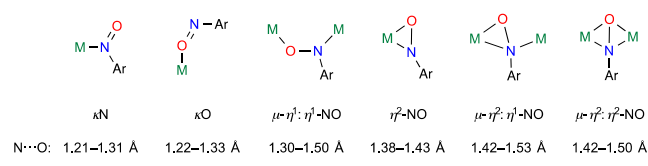
usually too oxidative to be stable above –60 °C. By contrast, 47  
Cu/ArNO adducts have been shown to have geometric and 48  
electronic structures very similar to those in Cu/O<sub>2</sub> adducts 49  
but were advantageously characterized at ambient temper- 50  
ature.<sup>17,23–25</sup> 51

Owing to the asymmetric structure of ArNO in comparison 52  
with that of O<sub>2</sub>, the structural variety of metal/nitrosoarene 53  
complexes exceeds that of metal/O<sub>2</sub> compounds. Some of the 54  
main bonding modes of ArNO to metal ions are shown in 55  
Scheme 1,<sup>13,14</sup> with the most common one being through the 56 s1  
N atom ( $\kappa\text{N}$ ). The other bonding modes are thought to be 57  
more prevalent when the ArNO moiety is reduced to the 58  
mono- or dianion. 59

The NO bond length in metal/ArNO complexes depends on 60  
the bonding mode, nature, and oxidation state of the metal and 61  
the supporting ligands but alone is insufficient to characterize 62

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### Scheme 1. Some Bonding Modes in Metal/Nitrosoarene Complexes, with Typical NO Bond Lengths<sup>13</sup>



63 the degree of reduction of the ArNO moiety, as was already  
64 shown with metal/O<sub>2</sub> adducts.<sup>26</sup> A few studies have scrutinized  
65 the electronic structure on metal/ArNO complexes, particu-  
66 larly the oxidation state of the ArNO moiety, by means of  
67 techniques such as X-ray absorption spectroscopy or vibra-  
68 tional analysis with isotopic labeling (Scheme 2 for group 10  
69 and 11 complexes). Their main conclusions are the following:  
70 (i) In the majority of mononuclear  $\kappa\text{N}$  nitrosoarene  
71 complexes, the NO bond length, 1.209–1.31 Å, shows little  
72 or no elongation compared with that in free nitrosoar-  
73 enes,<sup>13,14,27–29</sup> unless back-bonding from the metal becomes  
74 significant.<sup>16</sup> A radical character of the  $\kappa\text{N}$ -ArNO moiety, and  
75 thus formally a 1.5 bond order, has been confirmed or inferred  
76 in a few species (Scheme 2a).<sup>16,30,31</sup>  
77 (ii) Most mononuclear  $\kappa\text{O}$  complexes with non-d<sup>10</sup>  
78 transition metals are structurally disordered,<sup>13,14,32–36</sup> and  
79 conclusive statements about the extent of back-donation and  
80 ArNO reduction cannot be made. By contrast, the non-  
81 disordered crystal structures of [(Me<sub>6</sub>tren)Cu( $\kappa\text{O}$ -PhNO)]X  
82 (X = TfO<sup>-</sup>, SbF<sub>6</sub><sup>-</sup>; Scheme 2b) show significant NO bond  
83 elongation. The radical character of the PhNO moiety (to an

arylnitrosyl radical anion) was confirmed by magnetic  
measurements and vibrational and computational studies.<sup>17,37</sup>

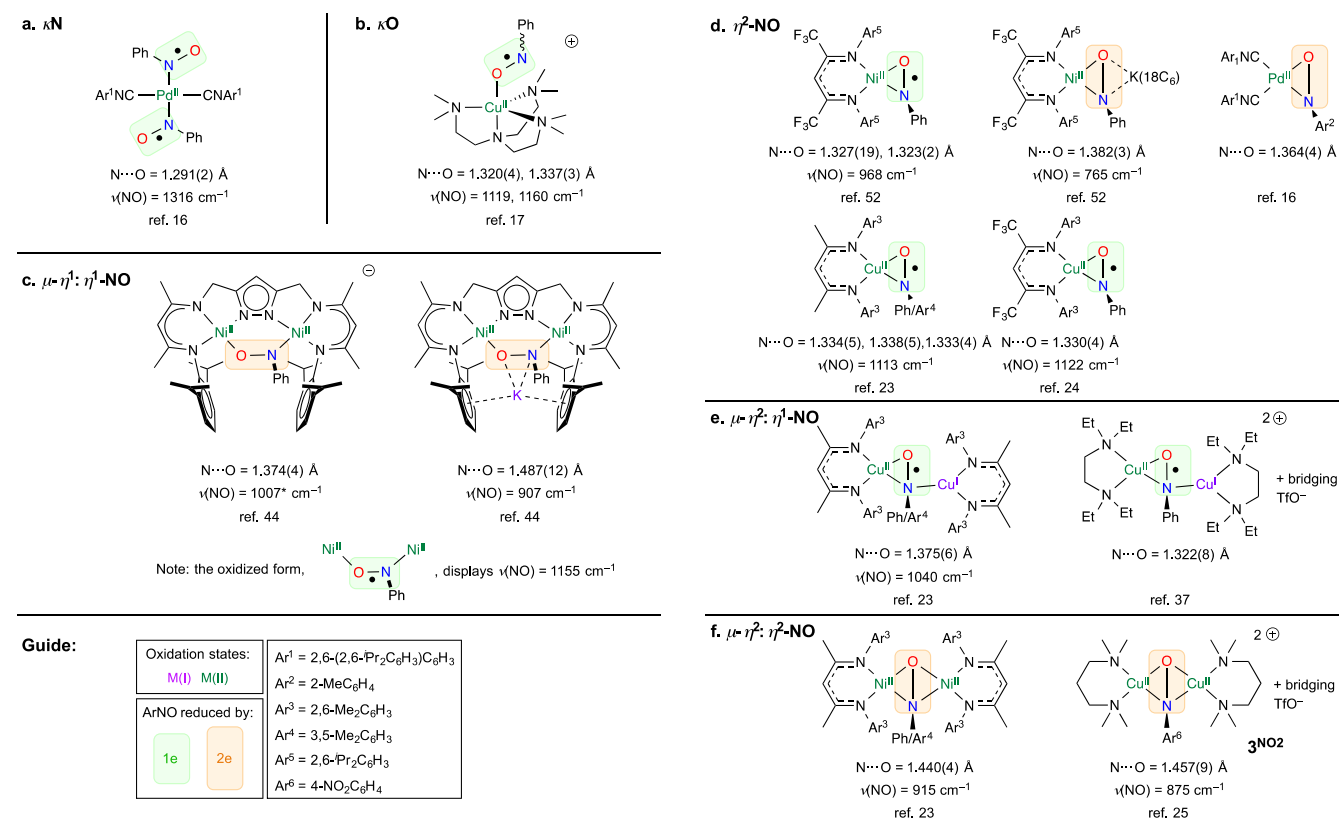
(iii) Dinuclear  $\mu\text{-}\eta^1\text{:}\eta^1$  (end-on) complexes present varying  
degrees of ArNO reduction: by 0e (NO = 1.257–1.32  
Å),<sup>28,29,38–41</sup> 1e (1.33–1.35 Å),<sup>42</sup> and 2e (1.37–1.49 Å;  
Scheme 2c).<sup>43,44</sup>

(iv) In  $\eta^2\text{-NO}$  complexes, the NO bond length (1.323–  
1.432 Å)<sup>16,23,31,45–52</sup> is significantly longer than that in free  
nitrosoarenes. 1e reduction of the ArNO moiety has been  
confirmed in Cu and Ni complexes (Scheme 2d).<sup>23,52</sup> Further  
reduction of the Ni complex led to a doubly reduced PhNO<sup>2-</sup>  
moiety.<sup>52</sup> 2e reduction of the ArNO moiety was also confirmed  
in a square-planar Pd(II) species upon reaction of a Pd<sup>0</sup> species  
with TolNO.<sup>16</sup>

(v) Alongside several ArNO<sup>2-</sup> examples (N–O = 1.40–1.53  
Å),<sup>31,53–58</sup> dinuclear  $\mu\text{-}\eta^2\text{:}\eta^1$  complexes have been found in the  
solid-state structures of Cu complexes with shorter NO bond  
lengths (1.322–1.375 Å).<sup>23,37</sup> Typically, the 1e-reduced  
ArNO<sup>•-</sup> moiety binds  $\eta^2$  to a Cu(II) center and  $\eta^1$  to a  
Cu(I) center (Scheme 2e). These species are thought to be in  
equilibrium with the mononuclear form [Cu<sup>II</sup>( $\eta^2$ -ArNO<sup>•-</sup>)] in  
solution.<sup>23,37</sup>

(vi) Dinuclear  $\mu\text{-}\eta^2\text{:}\eta^2$  complexes are quite rare, and only a  
few examples with Rh,<sup>57</sup> Zr,<sup>59</sup> Hf,<sup>59</sup> Ni,<sup>23</sup> and Cu<sup>25</sup> are  
reported in the literature. With an NO bond length in the  
range of single bonds (1.422–1.500 Å), these complexes  
possess a doubly reduced ArNO<sup>2-</sup> moiety. In the case of the  
Cu complex (Scheme 2f), this 2e reduction was made possible  
by using a very electron-poor nitrosoarene bearing a *p*-NO<sub>2</sub>  
substituent. More on this complex will be discussed below.

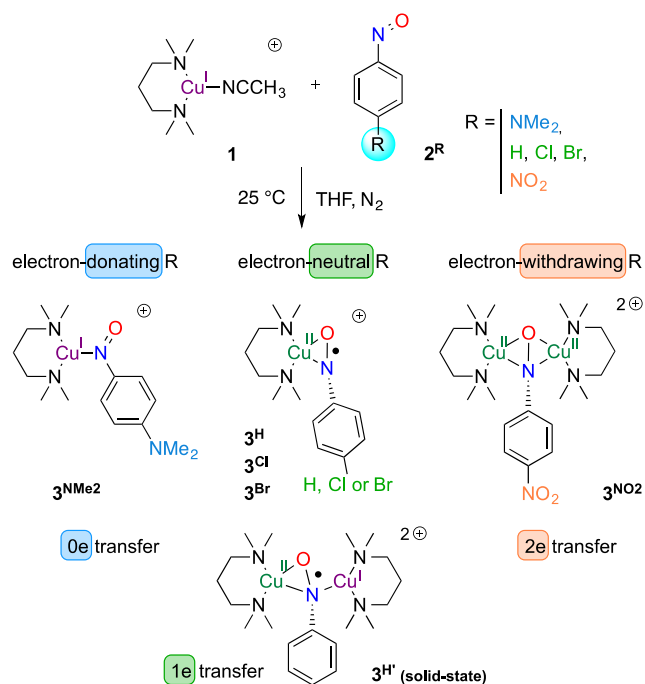
### Scheme 2. Confirmed Examples of Group 10 and 11 Complexes in Which ArNO Gets Reduced by 1e or 2e upon Reaction<sup>a</sup>



<sup>a</sup>Asterisks indicate calculated values.

114 To summarize, 1e reduction of the ArNO moiety is usually  
 115 indicated by NO bond lengths in the range 1.29–1.37 Å and  
 116 NO stretching frequencies in the range 1000–1300 cm<sup>-1</sup>  
 117 (Scheme 2). Reduction by 2e is revealed by NO bond lengths  
 118 of 1.36–1.46 Å and NO stretching frequencies below 950  
 119 cm<sup>-1</sup>. When no reduction occurs, the NO bonds are short  
 120 [1.261(4) and 1.268(4) Å for free PhNO] and the NO  
 121 stretching frequency is high (1506 cm<sup>-1</sup> for free PhNO),  
 122 although these values can be modified significantly when back-  
 123 bonding is present.<sup>16</sup> Last, 4e reduction of PhNO, with  
 124 complete NO bond cleavage, is possible with very electron-rich  
 125 metal complexes such as cobalt(I) β-diketiminato species.<sup>60</sup>  
 126 Noting that these examples comprise different supporting  
 127 ligands and metal ions, we aimed at providing a systematic  
 128 study of the degree of inner-sphere ArNO reduction by using a  
 129 single Cu(I) precursor. Thus, in the present study, we report  
 130 on adducts 3<sup>R</sup> (R = NMe<sub>2</sub>, H, Cl, Br, NO<sub>2</sub>) formed upon  
 131 intermolecular reaction of para-substituted nitrosobenzenes 2<sup>R</sup>  
 132 with the Cu(I) complex of *N,N,N',N'*-tetramethyl-1,3-  
 133 propanediamine (TMPD), **1** (Scheme 3), for which analogous  
 134 Cu/O<sub>2</sub> chemistry is known.<sup>61–63</sup>

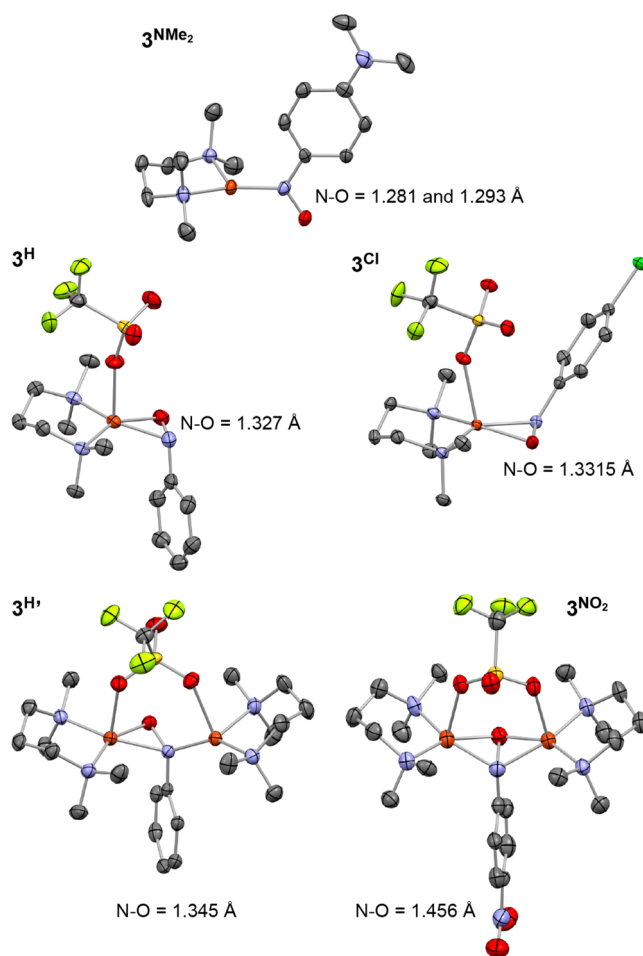
### Scheme 3. Formation of the 3<sup>R</sup> Adducts<sup>a</sup>



<sup>a</sup>With a TfO<sup>-</sup> counterion. 3<sup>NO<sub>2</sub></sup> was already reported.<sup>25</sup>

## 135 ■ RESULTS AND DISCUSSION

136 **Synthesis and Crystallography.** The slow addition of a  
 137 [(MeCN)<sub>4</sub>Cu](TfO) (MeCN = acetonitrile) solution to a  
 138 solution of TMPD and nitrosoarene, in a 1:1:1 ratio in  
 139 tetrahydrofuran (THF) at 25 °C (1:1:2 for R = NO<sub>2</sub>), results  
 140 in the formation of deeply colored complexes that remain  
 141 stable under inert conditions. Crystallization of the complexes  
 142 by the slow diffusion of pentane into the reaction mixtures at  
 143 –30 °C afforded crystals suitable for X-ray diffraction analysis.  
 144 Several binding motifs consisting of mono- and dinuclear  
 145 complexes are obtained depending on the para substituent of  
 146 the nitrosoarene (Figure 1 and Table S1).



**Figure 1.** ORTEP at 50% probability of 3<sup>NMe<sub>2</sub></sup> (one of two independent molecules), 3<sup>H</sup>, 3<sup>Cl</sup>, and 3<sup>NO<sub>2</sub></sup>, with relevant N–O bond lengths. Uncoordinated TfO<sup>-</sup> anions (3<sup>NMe<sub>2</sub></sup> and 3<sup>NO<sub>2</sub></sup>) and H atoms were omitted for clarity.

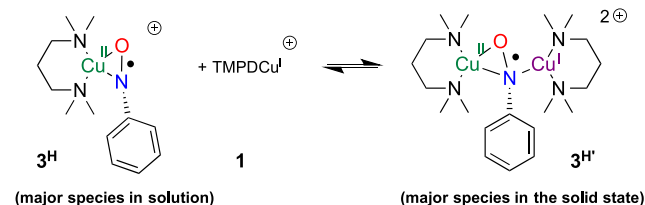
The structure of 3<sup>NMe<sub>2</sub></sup> is that of a copper(I) arylnitroso 147 complex, i.e., mere κN coordination of 1<sup>NMe<sub>2</sub></sup> onto the [TMPD-  
 Cu<sup>I</sup>]<sup>+</sup> complex **1**. The N–O bond lengths in the two 148  
 independent molecules, 1.281 and 1.293 Å, are typical for 149  
 N=O double bonds. The trigonal-planar ligand field of Cu is 150  
 consistent with a Cu(I) oxidation state. In the solid state, the 151  
 species dimerizes via two weak Cu⋯O interactions (2.242 and 152  
 2.278 Å) between two crystallographically related 3<sup>NMe<sub>2</sub></sup> 153  
 cations. This fact, coupled with the back-bonding of Cu into 154  
 the nitroso π\* orbital, could explain the slight elongation of the 155  
 N–O bond compared with a true double bond.<sup>16,37</sup> 156  
 157

Two types of crystals were obtained in the same 158  
 crystallization pot with R = H. The minor component, of 159  
 green color, is the mononuclear [TMPDCu<sup>II</sup>(η<sup>2</sup>-PhNO<sup>•-</sup>)- 160  
 (TfO)] species (3<sup>H</sup>). This complex displays an η<sup>2</sup>-NO 161  
 coordination with an elongated N–O bond of 1.327 Å, 162  
 consistent with a 1.5 bond order.<sup>23,52</sup> Cu sits in a square- 163  
 pyramidal environment with a TfO<sup>-</sup> anion as a weak axial 164  
 ligand (Cu⋯O = 2.345 Å). The brown major component, 3<sup>H</sup>, 165  
 of the formula [TMPDCu<sup>II</sup>(μ-η<sup>2</sup>:η<sup>1</sup>-PhNO<sup>•-</sup>)(μ-TfO)- 166  
 Cu<sup>I</sup>TMPD](TfO) also displays an elongated N–O bond 167  
 1.345 Å, consistent with a 1.5 bond order. One of the Cu 168  
 centers is bonded to both N and O of the PhNO moiety (Cu– 169  
 N = 2.019 Å; Cu–O = 1.853 Å), while the other is only 170  
 bonded to the N atom of PhNO (Cu–N = 1.904 Å; Cu⋯O = 171



172 2.828 Å). Species  $3^{H'}$  is therefore well described as formed  
 173 from the association of the minor green component  $3^H$  with  
 174 one molecule of **1** (Scheme 4). Such architecture and

#### Scheme 4. Mononuclear/Dinuclear Equilibrium in $3^H$ Species<sup>a</sup>



<sup>a</sup>TfO<sup>-</sup> anions are not shown.

175 association were already described in the literature.<sup>23,37</sup>  
 176 Because the mononuclear complex prevails in solution (the  
 177 solution is green, and a Job titration confirms a 1:1  
 178 stoichiometry; Figure S14), formation of the dinuclear  
 179 compound is an artifact of crystallization.

180 For  $3^{Cl}$ , only green crystals of [TMPDCu<sup>II</sup>( $\eta^2$ - $2^{Cl}$ •<sup>-</sup>)(TfO)]  
 181 were formed. The molecular structure is very similar to that of  
 182  $3^H$ , with a 1.5 N–O bond order (1.3315 Å), except that the  
 183 TfO<sup>-</sup> anion and the aromatic ring are on the same side of the  
 184 CuNO plane.

185 The complex with the most electron-poor ArNO moiety,  
 186  $3^{NO_2}$ , was characterized in a previous communication.<sup>25</sup> It is a  
 187 dinuclear species of the formula [TMPDCu<sup>II</sup>( $\mu$ - $\eta^2$ : $\eta^2$ -  
 188 PhNO<sup>2-</sup>)( $\mu$ -TfO)Cu<sup>II</sup>TMPD](TfO), where  $2^{NO_2}$  is reduced  
 189 by 2e (N–O = 1.456 Å) and both Cu centers are in the 2+  
 190 oxidation state.

191 Overall, the crystallographic study concludes on an increased  
 192 degree of electron transfer from **1** to  $2^R$  inasmuch as the *p*-R  
 193 substituent is made more electron-poor: 0e in  $3^{NMe_2}$ , 1e in  $3^H$ /  
 194  $3^{H'}$  and  $3^{Cl}$ , and 2e in  $3^{NO_2}$ . The lability of Cu complements  
 195 the self-assembly process by allowing TfO<sup>-</sup> or extra Cu(I)  
 196 coordination when necessary.

197 **IR Properties.** Vibrational analysis by IR spectroscopy was  
 198 conducted on  $2^R$  precursors and  $3^R$  complexes, where the N  
 199 atom of the nitroso moiety is either <sup>14</sup>N or <sup>15</sup>N. Synthesis of  
 200 the <sup>15</sup>N-labeled  $2^R$  precursors is provided in the Supporting  
 201 Information. Isotopic labeling enables one to isolate the  
 202 vibrations near the nitroso moiety from the rest of the  
 203 molecule. In parallel, density functional theory (DFT)  
 204 calculations were conducted to identify the nature of the  
 205 modes observed (especially NO vs CN stretches in the ArNO  
 206 moiety).

207 Comparing the IR properties of the organic precursors  $2^R$  is  
 208 tentative because they have different structures in the solid  
 209 state: monomeric for  $2^{NMe_2}$ , syn dimeric for  $2^H$ , and anti  
 210 dimeric for  $2^{Br}$  (Tables 1 and S2 and Figures S1–S6). Still, the  
 211 correlation between the experimental and calculated spectra is  
 212 excellent, providing confidence that the calculations can enable  
 213 us to locate the NO stretch accurately in the complexes.

214 Drastic changes in the NO stretching frequency are seen in  
 215  $3^R$  complexes, consistent with NO bond weakening upon  
 216 electron transfer (Tables 1 and S3 and Figures S7–S12). While  
 217 the symmetry of the complexes is different and some  
 218 complexes have multiple vibrational modes involving the NO  
 219 stretch, the NO stretching energy decreases from 1315/1392  
 220 cm<sup>-1</sup> for  $3^{NMe_2}$  to 1226 cm<sup>-1</sup> for  $3^{Br}$  to 875 cm<sup>-1</sup> for  $3^{NO_2}$ .<sup>25</sup>  
 221 This trend, supported by DFT calculations, is fully consistent

Table 1. NO Stretching Frequencies<sup>a</sup>

species	$\nu$ ( $\Delta$ )/cm <sup>-1</sup>	species	$\nu$ ( $\Delta$ )/cm <sup>-1</sup>
$2^{NMe_2}$	1365 (12), 1340 (19)	$3^{NMe_2}$	1392 (14), 1315 (6)
$2^H$ <sup>b</sup>	1388 (27)	$3^{H'c}$	1162 (10), 1133 (23)
$2^{Br}$ <sup>d</sup>	1286 (4), 1256 (24)	$3^{Br}$	1226 (6)
$2^{NO_2}$ <sup>d</sup>	1238 (20)	$3^{NO_2}$	875 (15)

<sup>a</sup>Measured at 25 °C on species labeled with <sup>14</sup>N and <sup>15</sup>N on the NO moiety. Full data are given in the Supporting Information. <sup>b</sup>Syn ArN(O)N(O)Ar dimer. <sup>c</sup>Contains a small amount of mononuclear species  $3^H$ . <sup>d</sup>Anti ArN(O)N(O)Ar dimer.

with reduction of the bond order upon inner-sphere electron  
 222 transfer from the Cu center(s). For mixed-valent dinuclear  
 223 species  $3^{H'}$ , the NO stretch is lowered from  $3^{Br}$  by about 70–  
 224 100 cm<sup>-1</sup>, consistent with the electron density being  
 225 delocalized onto the additional Cu(I) center.  
 226

**NMR Properties.** In CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, or acetone-*d*<sub>6</sub>  
 227 solutions, all  $3^R$  species display diamagnetic <sup>1</sup>H and <sup>13</sup>C  
 228 NMR spectra (Figures S37–S47). For  $3^H$ ,  $3^{Cl}$ , and  $3^{Br}$ , this  
 229 indicates a singlet ground state, as was observed for similar  $\eta^2$ -  
 230 ArNO complexes.<sup>23,24,37</sup> By analogy with structurally similar  
 231  $\eta^2$ -superoxocopper(II) species, this ground-state singlet is  
 232 expected to be highly delocalized.<sup>64</sup> This situation also  
 233 contrasts with the end-on topology, where end-on  
 234 superoxocopper(II) complexes have a *S* = 1 ground  
 235 state,<sup>65–68</sup> as do Cu<sup>II</sup>( $\kappa$ O-ArNO•<sup>-</sup>) complexes when Cu–  
 236 O–N–C<sub>Ar</sub> is coplanar.<sup>17</sup>  
 237

The <sup>15</sup>N NMR spectra of the <sup>15</sup>N-labeled  $3^R$  species are  
 238 most informative on the degree of electron transfer (Figure 2  
 239 12)

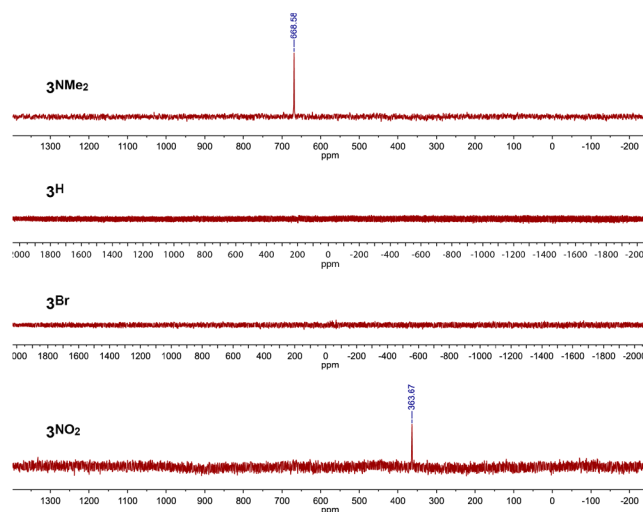


Figure 2. <sup>15</sup>N NMR data (50.7 MHz) of the  $3^R$  species (R = NMe<sub>2</sub>, H, Br, NO<sub>2</sub>), <sup>15</sup>N-enriched at the NO position, in CDCl<sub>3</sub> at 25 °C. Species  $3^H$  was made in situ by mixing equimolar amounts of [Cu(MeCN)<sub>4</sub>](TfO), and  $2^H$ .

and Table 2). For comparison, the <sup>15</sup>N NMR spectra of the  
 240 12 <sup>15</sup>N-labeled  $2^R$  species reveal a logical downfield shift of the  
 241 signal inasmuch as the R substituent becomes more electron-  
 242 poor. Cu(I) coordination on  $2^{NMe_2}$  to form  $3^{NMe_2}$  leads to an  
 243 upfield shift of the signal by 119 ppm, consistent with the  
 244 presence of a partial charge transfer from Cu(I) to the ArNO  
 245 moiety. On the other end of the series, the formation of  $3^{NO_2}$   
 246 leads to a dramatic upfield shift of the signal by 550 ppm,  
 247 consistent with the ArNO moiety being doubly reduced  
 248

Table 2.  $^{15}\text{N}$  NMR Data<sup>a</sup>

species	$\delta(^{15}\text{N})/\text{ppm}$	species	$\delta(^{15}\text{N})/\text{ppm}$
$2^{\text{NMe}_2}$	787.58	$3^{\text{NMe}_2}$	668.58
$2^{\text{H}}$	885.83	$3^{\text{H}}$	not observed
$2^{\text{Br}}$	878.67	$3^{\text{Br}}$	not observed
$2^{\text{NO}_2}$	913.23	$3^{\text{NO}_2}$	363.67

<sup>a</sup>Measured in  $\text{CDCl}_3$  at 25 °C on a 500 MHz instrument;  $\nu(^{15}\text{N}) = 50.7$  MHz.

( $\text{ArNO}^{2-}$ ) and therefore quite electron-rich. Interestingly, no  $^{15}\text{N}$  signal was observed for  $3^{\text{H}}$  and  $3^{\text{Br}}$  under the same recording conditions or with a wider acquisition window. This behavior is consistent with the radical character of the  $\text{ArNO}^{\bullet-}$  moiety in these species. A small amount of triplet character admixture in the ground-state singlet at room temperature could lead to a paramagnetic shift of the  $^{15}\text{N}$  NMR resonance outside the acquisition window (Fermi contact at  $^{15}\text{N}$ ).<sup>69</sup> Hence, the lack of a signal in a standard acquisition window can be used as a local diagnostic of radical character on N. Overall, the NMR data confirm, in solution, the assignments that were made in the solid state.

### Ultraviolet–Visible (UV–Vis) Absorption Properties.

The electronic structure of the complexes was probed by UV–vis absorption spectroscopy (Figure 3 and Table 3).

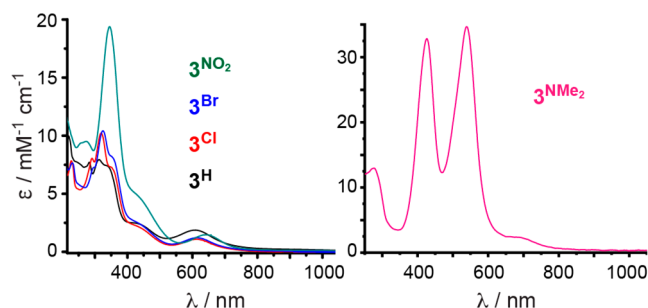


Figure 3. UV–vis spectra of  $3^{\text{R}}$  species in  $\text{CH}_2\text{Cl}_2$  at 25 °C.

Table 3. UV–Vis Data of  $3^{\text{R}}$  Complexes<sup>a</sup>

species	$\lambda_{\text{max}} (\epsilon)^b$	$\lambda_{\text{max}} (\epsilon)^b$	$\lambda_{\text{max}} (\epsilon)^b$
$3^{\text{NMe}_2}$	426 (32.8)	538 (34.7)	690 (2.3)
$3^{\text{H}}$	313 (8.0), 338 (7.4)	440 (sh)	609 (1.9)
$3^{\text{Cl}}$	319 (10.2), 350 (7.3)	440 (sh)	614 (1.1)
$3^{\text{Br}}$	325 (10.4), 350 (8.2)	440 (sh)	614 (1.2)
$3^{\text{NO}_2}$	345 (19.4)	440 (sh)	644 (1.5)

<sup>a</sup>Measured in  $\text{CH}_2\text{Cl}_2$  at 25 °C. <sup>b</sup> $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{mM}^{-1} \text{cm}^{-1}$ ).

Complexes  $3^{\text{H}}$ ,  $3^{\text{Cl}}$ , and  $3^{\text{Br}}$  display sensibly the same UV–vis spectrum, with an intense band around 330 nm and a less intense feature around 610 nm. Compound  $3^{\text{NO}_2}$  exhibits the same spectral shape, but the 345 nm band is twice as intense.

The spectrum for complex  $3^{\text{NMe}_2}$  is very different from the other four spectra. It shows two very intense bands at 426 and 538 nm, while the weaker feature is red-shifted to 690 nm. These absorptions will be analyzed in the next section.

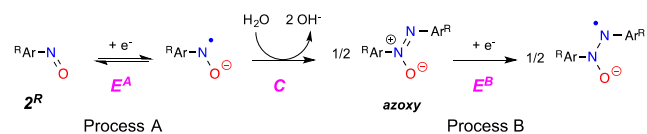
**DFT Calculations.** DFT calculations have been undertaken on the  $3^{\text{R}}$  complexes to gain insight into the nature of the species observed experimentally and to correlate their electronic structures to the experimental data. The structures of the  $3^{\text{R}}$  species were subjected to geometry optimization, and

their electronic properties were investigated. A good agreement is found upon a comparison of the molecular geometries with the X-ray crystallographic data (Figure S13). The calculated NO bond lengths are 1.243 Å for  $3^{\text{NMe}_2}$ , 1.287–1.288 Å for  $3^{\text{H}}$ ,  $3^{\text{Cl}}$ , and  $3^{\text{Br}}$ , 1.313 Å for  $3^{\text{H}'}$ , and 1.405 Å for  $3^{\text{NO}_2}$ . While these values are all underestimated (up to 0.05 Å), they lie within the typical error range of DFT and provide a fair trend along the series, being thus informative on the redox state of the  $\text{ArNO}$  moiety. The DFT-optimized structures are very close to those observed experimentally, with root-mean-square deviations of 0.543, 0.427, 0.407, 0.419, 0.444, and 0.338 from the crystal molecular structures of  $3^{\text{NMe}_2}$ ,  $3^{\text{H}}$ ,  $3^{\text{Cl}}$ ,  $3^{\text{Br}}$ ,  $3^{\text{H}'}$ , and  $3^{\text{NO}_2}$ , respectively.

Time-dependent DFT (TD-DFT) calculations were performed on the  $3^{\text{R}}$  complexes, and the predicted spectroscopic data provide calculated spectra that compare well with the experimental observations (Tables S4–S8 and Figures S15–S20). Our computations support that the UV–vis spectra of  $3^{\text{H}}$ ,  $3^{\text{Cl}}$ ,  $3^{\text{Br}}$ , and  $3^{\text{NO}_2}$  are similar and dominated by two main absorption bands of different intensities, while that of  $3^{\text{NMe}_2}$  displays two intense electronic transitions. For the latter, the band at 538 nm is assigned to a metal-to-ligand charge transfer (MLCT), and the band at 426 nm is attributed to a ligand-to-ligand charge transfer (LLCT). For both transitions, the acceptor states mainly involve the nitroso moiety (Figure S16). The electronic transitions for  $3^{\text{NO}_2}$  were already analyzed.<sup>25</sup> The 345 and 644 nm bands correspond to MLCT transitions involving the  $\mu\text{-}\eta^2\text{:}\eta^2\text{-NO}^{2-}$  moiety, in a very similar manner to the transitions in the  $(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2^{2-})\text{Cu}^{\text{II}}$  cores that mimic the active sites of oxytyrosinase and oxyhemocyanin.<sup>22</sup> For  $3^{\text{H}}$ ,  $3^{\text{Cl}}$ , and  $3^{\text{Br}}$ , the absorptions near 320 nm are due to a combination of MLCT and LLCT, with the acceptor state involving the NO moiety, while the transitions in the visible around 610 nm display a mixed character with similar contributions from the metal and the nitroso moiety in both donor and acceptor states (Figures S17–S19). Our TD-DFT calculations thus adequately reproduce the energy of the key features of the experimental spectra, which further support the geometries and electronic properties of the  $3^{\text{R}}$  complexes. Vibrational analysis also confirmed the experimental observations (vide supra). Consequently,  $3^{\text{NMe}_2}$  can be described as a Cu(I) complex, while  $3^{\text{H}}$ ,  $3^{\text{Cl}}$ , and  $3^{\text{Br}}$  are  $\text{Cu}^{\text{II}}\text{-(ArNO}^{\bullet-})$  species. The dimer  $3^{\text{H}'}$  is assigned to  $\text{Cu}^{\text{II}}\text{-Cu}^{\text{I}}\text{-(ArNO}^{\bullet-})$  species, while  $3^{\text{NO}_2}$  was previously shown to be a  $\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}$  complex with a  $\text{ArNO}^{2-}$  moiety (2e-reduced  $\text{ArNO}$ ).

**Electrochemical Studies.** Because this work aims at tuning the redox properties by simple substitution, we studied the electrochemical behavior of both precursors  $2^{\text{R}}$  and complexes  $3^{\text{R}}$  for the whole series of R substituents ( $\text{NMe}_2$ , H, Cl, Br, and  $\text{NO}_2$ ). The goal was to correlate the electrochemical properties with the reactivity (0e, 1e, or 2e transfer) observed upon reaction with the [(TMPD) $\text{Cu}^{\text{I}}$ ]<sup>+</sup> complex **1** and the H-atom-transfer (HAT) reactivity of the  $3^{\text{R}}$  complexes (see below). The data were also compared to existing records for analogous  $\text{ArNO}$  and  $\text{O}_2$  complexes. Cyclic voltammetry (CV) studies were performed at a glassy-carbon working electrode in dry  $\text{CH}_2\text{Cl}_2$  with 0.1 M  $\text{NBu}_4\text{OTf}$  as the supporting electrolyte. In what follows, all potentials are referenced to the  $\text{Fc}^{+/0}$  couple.

**Substituted Nitrosoarenes,  $2^{\text{R}}$ .** CV studies of the free nitrosoarenes,  $2^{\text{R}}$ , led to the summary in Scheme 5.  $2^{\text{H}}$  was first studied for a comparison with the literature.<sup>70–72</sup> When scanned negatively, it displays two reversible responses at  $E_{1/2}^{\text{A}}$

Scheme 5. Reduction Steps of 2<sup>R</sup> Species

340 = -1.40 V (process A) and E<sup>B</sup><sub>1/2</sub> = -1.86 V versus Fc<sup>+0</sup>  
 341 (process B) (Figure S21 and Table 4). An irreversible

Table 4. Electrochemical Data of the 2<sup>R</sup> Nitrosoarenes<sup>a</sup>

species	E <sup>A</sup> <sub>1/2</sub> (2 <sup>R</sup> )	E <sup>B</sup> <sub>1/2</sub> (2 <sup>R</sup> )	σ <sub>para</sub> <sup>b</sup>
2 <sup>NMe<sub>2</sub></sup>	-1.69 (120) <sup>c</sup>	<i>d</i>	-0.83
2 <sup>H</sup>	-1.40 (90)	-1.86 (100)	0
2 <sup>Cl</sup>	-1.32 (110)	-1.79 (90)	0.227
2 <sup>Br</sup>	-1.30 (90)	-1.75 (90)	0.232
2 <sup>NO<sub>2</sub></sup>	-0.93 (90)	-1.33 (100) <sup>e</sup>	0.78

<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M NBu<sub>4</sub>OTf at 25 °C (glassy-carbon working electrode); scan rate ν = 0.1 V s<sup>-1</sup>, E/V versus Fc<sup>+0</sup> (ΔE<sub>p</sub>/mV). <sup>b</sup>σ<sub>para</sub> Hammett parameters. <sup>c</sup>Determined at ν = 0.5 V s<sup>-1</sup>. <sup>d</sup>Not determined. <sup>e</sup>An intermediate wave at -1.17 V was observed at faster scan rates.

342 oxidation peak is also detected at 0.63 V on the backscan  
 343 after reduction at -1.90 V (Figure S22). Variation of the scan  
 344 rate ν induces a significant modification of the redox behavior  
 345 (Figure S23), which is typical of two successive electron-  
 346 transfer processes coupled to a chemical reaction, namely, an  
 347 ECE mechanism (E = electrochemical and C = chemical;  
 348 Scheme 5). In agreement with previous electrochemical  
 349 studies,<sup>70,71</sup> process A corresponds to the monoelectronic  
 350 reduction of 2<sup>H</sup> (Scheme 5), while process B corresponds to 1e  
 351 reduction of the azoxybenzene formed in situ by reaction of  
 352 the radical anion with residual water. This dimerization  
 353 hypothesis is supported by the ratio of the cathodic peak  
 354 currents, *i*<sub>pc</sub><sup>B</sup>/*i*<sub>pc</sub><sup>A</sup> ≈ 0.5 (assuming similar diffusion coefficients).  
 355 In addition, the value of E<sup>B</sup><sub>1/2</sub> is in good agreement with the  
 356 standard potential values for the azoxy species in organic  
 357 solvents.<sup>70–72</sup>

358 The processes described in Scheme 5 occur for 2<sup>R</sup> with  
 359 different para substituents (R = NMe<sub>2</sub>, H, Cl, Br, NO<sub>2</sub>) but at  
 360 different redox potentials (Figure S21 and Table 4). Under the  
 361 same experimental conditions, 2<sup>H</sup>, 2<sup>Cl</sup>, and 2<sup>Br</sup> display almost  
 362 the same redox pattern, i.e., one quasi-reversible redox system  
 363 at ca. E<sup>A</sup><sub>1/2</sub> = -1.3 V and a second one at ca. E<sup>B</sup><sub>1/2</sub> = -1.8 V. For  
 364 2<sup>NMe<sub>2</sub></sup>, E<sup>A</sup><sub>1/2</sub> is shifted negatively by ca. 300 mV with respect to  
 365 E<sup>A</sup><sub>1/2</sub> (2<sup>H</sup>), and the (2<sup>NMe<sub>2</sub></sup>)<sup>•-</sup> radical anion is relatively unstable  
 366 because process A occurs irreversibly for ν < 0.2 V s<sup>-1</sup> (Figure  
 367 S21a). For 2<sup>NO<sub>2</sub></sup>, E<sup>A</sup><sub>1/2</sub> and E<sup>B</sup><sub>1/2</sub> are shifted positively by ca. 500  
 368 mV (Figure S21b).

369 Thus, a span of +760 mV is observed for E<sup>A</sup><sub>1/2</sub> upon NMe<sub>2</sub>/  
 370 NO<sub>2</sub> substitution, consistent with the electron-donating/  
 371 withdrawing properties of the substituents. Fittingly, plots of  
 372 E<sup>A</sup><sub>1/2</sub> versus the σ<sub>para</sub> Hammett parameter follow a linear trend,  
 373 indicating that the value of the redox potential is mainly  
 374 controlled by electronic effects (Figure S29).

375 [Cu(TMPD)(ArNO)](OTf) Complexes 3<sup>R</sup>. CV studies of the  
 376 3<sup>R</sup> complexes (R = NMe<sub>2</sub>, H, Br, NO<sub>2</sub>) were performed under  
 377 the same experimental conditions as those for 2<sup>R</sup> ligands  
 378 (Figure 4 and Table 5). Adding 2<sup>R</sup> to a solution of 1 under CV  
 379 monitoring led to the same conclusions as those below (Figure  
 380 S25). All 3<sup>R</sup> complexes display a first irreversible reduction

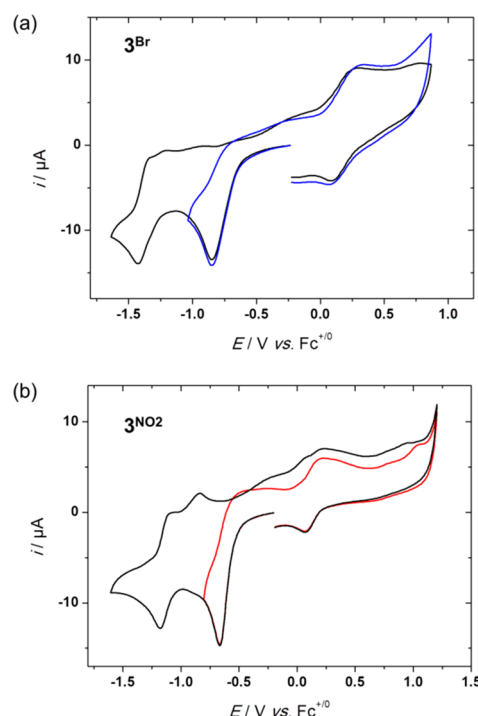


Figure 4. CV cycles at a glassy-carbon working electrode (E/V vs Fc<sup>+0</sup>; ν = 0.1 V s<sup>-1</sup>) of 3<sup>R</sup> (1.0 mM) in dry CH<sub>2</sub>Cl<sub>2</sub> and 0.1 M NBu<sub>4</sub>OTf: (a) R = Br; (b) R = NO<sub>2</sub>.

Table 5. Electrochemical Data of 3<sup>R</sup> Complexes<sup>a</sup>

	E <sup>C</sup> <sub>pc</sub> (3 <sup>R</sup> )	E <sup>D</sup> <sub>1/2</sub> (3 <sup>R</sup> )	E <sup>E</sup> <sub>1/2</sub> (3 <sup>R</sup> )	σ <sub>para</sub> <sup>b</sup>
3 <sup>NMe<sub>2</sub></sup>	-1.05	-1.75	-0.36 (140)	-0.83
3 <sup>H</sup>	-0.92	-1.45 <sup>c</sup>	0.28	0.00
3 <sup>Br</sup>	-0.82	-1.22 (180)	0.08 (130)	0.23
3 <sup>NO<sub>2</sub></sup>	-0.72	-1.17 (145)	0.11 (120)	0.78

<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M NBu<sub>4</sub>OTf at 25 °C; scan rate ν = 0.1 V s<sup>-1</sup>. E/V versus Fc<sup>+0</sup> (ΔE<sub>p</sub>/mV). <sup>b</sup>σ<sub>para</sub> Hammett parameters. <sup>c</sup>Irreversible cathodic peak.

381 peak E<sup>C</sup><sub>pc</sub> (process C) extending from -1.05 V for 3<sup>NMe<sub>2</sub></sup> to  
 382 -0.72 V for 3<sup>NO<sub>2</sub></sup> (Figure 4 and Table 5). As was the case with  
 383 process A for the 2<sup>R</sup> ligands, the redox potential is mainly  
 384 controlled by electronic effects, which is confirmed by the  
 385 linear variation of E<sup>C</sup><sub>pc</sub> versus σ<sub>para</sub> Hammett parameters (Figure  
 386 S29). Whatever the nature of R, the first system remains  
 387 irreversible at moderate scan rates (ν < 10 V s<sup>-1</sup>; Figures 4 and  
 388 S26 and S27a). This is indicative that a fast chemical reaction  
 389 occurs upon electrochemical reduction. This EC mechanism  
 390 was confirmed, for R = NO<sub>2</sub>, by the linear behavior of E<sup>C</sup><sub>pc</sub>  
 391 versus log ν (33 mV decade<sup>-1</sup>; Figure S27b) and the constancy  
 392 of the normalized current intensity (*i*<sub>pc</sub><sup>C</sup>ν<sup>-1/2</sup>) with ν (inset  
 393 Figure S27a), hence excluding an ECE process.

394 CV scanning until -1.8 V leads to the appearance of a  
 395 second system (process D) at E<sup>D</sup> (-1.75 V < E<sup>D</sup> < -1.21 V),  
 396 which is quasi-reversible or irreversible, depending on R  
 397 (Figures 4 and S31). Increasing the scan rate induces a  
 398 decrease of the relative peak currents *i*<sub>pc</sub><sup>C</sup> and *i*<sub>pc</sub><sup>D</sup> (Figure S27c,d  
 399 for 3<sup>NO<sub>2</sub></sup>), without modification of the peak potential values.  
 400 Altogether, this data set confirms that the chemical species that  
 401 is reduced reversibly through a simple electron transfer at E<sup>D</sup>  
 402 originates from the first electrochemical reduction of the 3<sup>R</sup>  
 403 complex. As shown in Table 5, the potential value at E<sup>D</sup> is



404 highly dependent on the substituting group R, meaning that  
405 the chemical species or complex contains the ArNO moiety.  
406 Possibly, reduction of the complex induces breaking of the  
407 Cu–ArNO bond, liberating  $2^R$  and explaining the similarity of  
408 the  $E^D$  and  $E^A$  values. Such a hypothesis is verified in all cases  
409 except for  $3^{NO_2}$  (Figures S28 and S30).

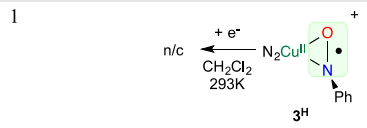
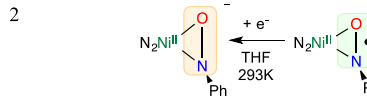
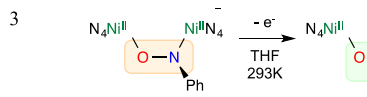
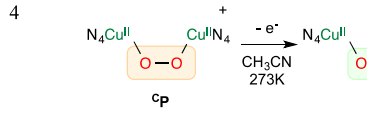
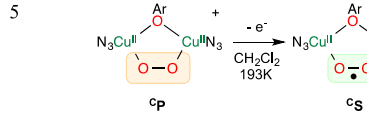
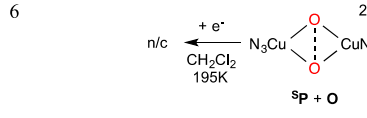
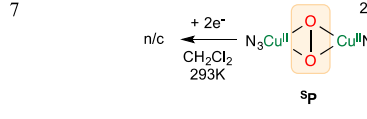
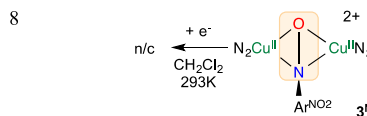
410 Exhaustive electrolyses at  $E_{pc}^C$  and coulometric measurements  
411 confirm that system C is a 1e process per mole of  $3^R$ . For  
412 example, electrochemical reduction of  $3^{NMe_2}$  leads to its  
413 disappearance, while a new wave appears at  $E_{1/2}^D$  (Figure  
414 S31), together with a significant color change of the solution  
415 (purple to orange). A new system also appears in oxidation at  
416  $-0.2$ ,  $+0.45$ , and  $+0.65$  V, suggesting a release of TMPD  
417 (Figure S25a).

418 In a general manner, 1e reduction of the  $3^R$  complexes is  
419 accompanied by fast chemical processes that lead to partial  
420 decomplexation and release of the TMPD ligand and/or  $2^R$ .  
421 The transient electron-reduced species may thus be implicated  
422 in several reactions: radical dimerization and simple decoordi-  
423 nation, which themselves seem dependent on R.  
424 On the oxidation side, a quasi-reversible system (process E)  
425 is detected at  $E_{1/2}^E$  (Table 5), with varying peak potential and  
426 intensity values as R is varied.  $E_{1/2}^E$  is in the same range as that  
427 reported by Warren et al. ( $E_{pa} = +0.48$  V in MeCN) for a  
428 similar side-on arylnitrosylcopper(II) complex with a diket-  
429 iminate ligand.<sup>23</sup>

430 The reduction data obtained for the  $3^R$  complexes can be  
431 compared with the few redox processes reported for Ni<sub>n</sub>/  
432 ArNO and Cu<sub>n</sub>/O<sub>2</sub> analogues (Table 6). The side-on  
433 arylnitrosyl  $3^H$  species (entry 1) gets reduced at a potential  
434 similar to that of Warren's side-on arylnitrosylnickel(II)  
435 complex.<sup>52</sup> When ArNO binds in a 1,2-fashion (end-on)  
436 between two Ni(II) centers, the potential for ArNO<sup>2-/•-</sup>  
437 conversion is decreased by ca. 650 mV (entry 3).<sup>44</sup> Comparing  
438 ArNO with O<sub>2</sub> complexes would be interesting, but so far there  
439 is no reported redox data for monocopper superoxo species  
440 that would be similar in structure to  $3^H$ . The exception is the  
441 recent work by Reinaud et al., which showed by spectroelec-  
442 trochemistry that an in situ generated calix[6]amino-tren end-  
443 on superoxo complex could not be reduced above  $-0.90$  V  
444 versus Fc at  $-60$  °C (113 K) in acetone.<sup>73</sup> On the other hand,  
445 a few dicopper peroxo and superoxo species have been well  
446 characterized by electrochemistry with the help of low-  
447 temperature approaches (entries 4–7). Here, the irreversible  
448 1e reduction of  $3^R$  is comparable to the mono-electronic and  
449 reversible electron-exchange reactions detected for the end-on  
450 superoxo/peroxo pyrazolate- and xylO-based complexes  
451 (entries 4 and 5).<sup>74,75</sup> Interestingly, the reduction potential  
452 of  $3^{NO_2}$  (entry 8) is close to that of Kodera's side-on  
453 peroxodicopper(II) species (entry 7), although the latter is a  
454 2e process.<sup>76</sup> Overall, using such comparisons to make  
455 educated assignments of the electrochemical processes remains  
456 tentative given the large variety of ligands, charge, nuclearity,  
457 and bonding topology of the reported complexes. While data  
458 for  $\mu$ -hydroxodicopper complexes that are reminiscent of Cu<sub>n</sub>/  
459 O<sub>2</sub> species is readily available,<sup>77–82</sup> comparisons with the  $3^R$   
460 complexes would be even more tentative.

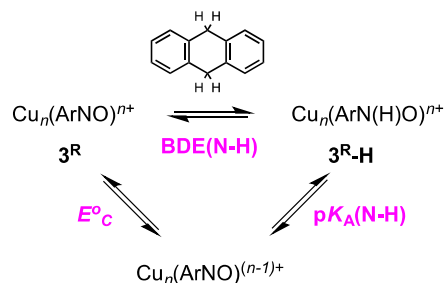
461 **HAT Reactivity.** We evaluated the reactivity of  $3^{Cl}$ ,  $3^{Br}$ , and  
462  $3^{NO_2}$  for HAT reactivity (Scheme 6). In previous work, Warren  
463 et al. reported a Ni<sup>II</sup>-( $\eta^2$ -ArNO<sup>•-</sup>) that converts into the  
464 related Ni<sup>II</sup>-( $\eta^2$ -ArN(H)O) complex (protonated hydroxyl-  
465 amine) upon reaction with 9,10-dihydroanthracene (DHA).<sup>52</sup>  
466 Conversely, Meyer et al. reported a dinuclear Ni<sup>II</sup><sub>2</sub>-( $\mu$ - $\eta^1$ : $\eta^1$ -

Table 6. Electrochemical Data of  $3^R$  and Related Ni<sub>n</sub>/ArNO and Cu<sub>n</sub>/O<sub>2</sub> Complexes

Entry	Reaction <sup>a</sup>	$E^b$	Ref.
1		$-0.92^c$	This work
2		$-0.89^d$	52
3		$-1.53^e$	44
4		$-0.59^e$	74
5		$-0.36^e$	75
6		$-0.01^{d,f}$	82
7		$-0.75^c$	76
8		$-0.72^c$	This work

<sup>a</sup>The reaction is written in a way it was carried out either as an oxidation or as a reduction. Abbreviations: n/c, compound not characterized; <sup>c</sup>P, cis-end-on peroxo; <sup>s</sup>C, cis-end-on peroxo; <sup>s</sup>P, side-on peroxo; O, bis( $\mu$ -oxo). <sup>b</sup>Potential versus Fc<sup>+/0</sup>. <sup>c</sup>Irreversible cathodic peak. <sup>d</sup>Reversible reduction. <sup>e</sup>Reversible oxidation. <sup>f</sup>Converted from the value versus saturated calomel electrode (SCE) using  $E_{1/2}(Fc^{+/0}) = 560$  mV versus SCE in these conditions.

### Scheme 6. Thermodynamic Analysis of HAT Reactivity



$$BDFE(DHA-H) = 1.47pK_A + 23.06E^o_C + C \quad (\text{Eqn. 1})$$

ArN(H)O) species that released its H atom to a phenoxyl 467 radical to form the related Ni<sup>II</sup><sub>2</sub>-( $\mu$ - $\eta^1$ : $\eta^1$ -ArNO<sup>•-</sup>) species and 468 evaluated a bond dissociation energy BDE(N–H) of around 469



62–65 kcal mol<sup>-1</sup>).<sup>44</sup> Following these examples, we reacted to  
471 3<sup>Cl</sup>, 3<sup>Br</sup>, and 3<sup>NO<sub>2</sub></sup> with DHA (bond dissociation free energy  
472 BDFE = 76.0 mol<sup>-1</sup>)<sup>83</sup> under UV–vis monitoring. A significant  
473 decrease of the 3<sup>R</sup> spectrum was observed upon the addition of  
474 40 mol equiv of DHA in THF at 45 °C, which was corrected  
475 for self-decomposition of the 3<sup>R</sup> complexes at this temperature.  
476 By analogy with the above examples, we presume that the  
477 reaction yielded complexes of ArN(H)O, labeled 3<sup>R</sup>-H  
478 hereafter (Scheme 6), but their instability prevented further  
479 analysis of the reaction and its mechanism.  
480 The electron-withdrawing NO<sub>2</sub> group induces a faster  
481 oxidation of DHA, consistent with 3<sup>NO<sub>2</sub></sup> being a stronger  
482 oxidant (higher  $E_{1/2}^C$ ) than 3<sup>Br</sup> and 3<sup>Cl</sup>. The initial rates of  
483 reaction depend on the R substituent: 0.029, 0.021, and 0.051  
484 ± 0.005 mM min<sup>-1</sup> for 3<sup>Cl</sup>, 3<sup>Br</sup>, and 3<sup>NO<sub>2</sub></sup>, respectively. Using  
485 eq 1 (Scheme 6)<sup>83</sup> with a temperature correction, the value of  
486  $E_{1/2}^C$  for 3<sup>R</sup> taken as  $E_{pc}^C$ , and using C = 66 kcal mol<sup>-1</sup> in THF,<sup>84</sup>  
487 the pK<sub>A</sub> value of the N–H bond in 3<sup>R</sup>-H is evaluated around  
488 18 and 19.5 for the NO<sub>2</sub> and Br adducts, respectively, in order  
489 to perform HAT from DHA. Similarly, 2<sup>NO<sub>2</sub></sup> reacts, but slowly,  
490 with 1,2-diphenylhydrazine (BDFE = 67.1 kcal mol<sup>-1</sup>) at 25  
491 °C. This brings the pK<sub>A</sub> value to around 13, but this reaction is  
492 complicated by the byproduct azobenzene, which can interact  
493 with Cu(I) and dissociate 2<sup>NO<sub>2</sub></sup>. Further studies with different  
494 substrates are necessary to decipher how nitrosoarene  
495 complexes perform this reaction, i.e., in a concerted or  
496 sequential manner.<sup>85,86</sup>

## 497 ■ CONCLUSIONS

498 In summary, placing a synthetic handle at the para position of  
499 nitrosoarenes enables control over the degree of electron  
500 transfer from Cu(I) complexes, from 0e with electron-donating  
501 substituents to 1e with electron-neutral substituents and 2e  
502 with electron-poor substituents. As the Cu/ArNO adducts are  
503 undergoing self-assembly, the geometric preferences of the Cu  
504 center will prevail.<sup>37</sup> Thus, Cu(I) will be found in trigonal  
505 geometries, with κN-ArNO coordination, whereas a square-  
506 pyramidal Cu(II) will force η<sup>2</sup>-ArNO<sup>•-/-2-</sup> coordination. One  
507 of the novel features of this work is the use of <sup>15</sup>N NMR as a  
508 direct, local probe for the redox level of the ArNO moiety.  
509 Thus, the absence of a <sup>15</sup>N NMR signal coincides with the  
510 radical state. A side effect of the self-assembly is, however, the  
511 relative instability of the adducts upon external electron-  
512 transfer events. Notwithstanding, this series of complexes  
513 provides structural snapshots of the isovalent Cu/O<sub>2</sub>  
514 chemistry, without the complication of thermal sensitivity of  
515 Cu/O<sub>2</sub> species. It also enables redox studies to be performed,  
516 although much remains to be done before a proper ArNO/O<sub>2</sub>  
517 redox benchmark can be established. This series also highlights  
518 the variety of intermediates that could occur during Cu-  
519 catalyzed ArNO transformations and suggests that, perhaps,  
520 bond-forming events from ArNO precursors may proceed via  
521 radical states.

## 522 ■ EXPERIMENTAL SECTION

523 **Materials.** Chemicals were obtained from Sigma-Aldrich and Alfa  
524 Aesar, except acetanilide-<sup>15</sup>N, which was purchased from Cambridge  
525 Isotope Laboratories. Air-sensitive samples were handled under an  
526 inert atmosphere (N<sub>2</sub>) in a dry nitrogen glovebox (O<sub>2</sub> < 0.1 ppm;  
527 H<sub>2</sub>O < 0.1 ppm) or using standard Schlenk techniques. Solvents were  
528 dried by standard procedures, degassed, and stored over 4 Å  
529 molecular sieves in the glovebox. N,N,N',N'-Tetramethyl-1,3-  
530 propanediamine (TMPD) was distilled over CaH<sub>2</sub> under nitrogen

and stored in the glovebox. The copper salt [(MeCN)<sub>4</sub>Cu](TfO) was  
531 prepared by adapting the Kubas procedure using TfOH.<sup>87</sup> 4-  
532 Dimethylaminonitrosobenzene (2<sup>NMe<sub>2</sub></sup>),<sup>88,89</sup> 4-chloronitrosobenzene  
533 (2<sup>Cl</sup>),<sup>90</sup> 4-bromonitrosobenzene (2<sup>Br</sup>),<sup>90</sup> and 4-nitrosobenzene  
534 (2<sup>NO<sub>2</sub></sup>)<sup>91</sup> were prepared via literature procedures. Isotopically labeled  
535 <sup>15</sup>N-4-nitrosobenzene and [(TMPDCu)<sub>2</sub>(μ-TfO)(μ-η<sup>2</sup>:η<sup>2</sup>-p-  
536 NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>NO)](TfO) were prepared following the procedure  
537 reported earlier.<sup>25</sup> 4-Bromoaniline-<sup>15</sup>N was prepared from <sup>15</sup>N-  
538 acetamide as reported in the Supporting Information. <sup>15</sup>N derivatives  
539 of 2<sup>H</sup>, 2<sup>Cl</sup>, and 2<sup>Br</sup> were prepared similarly to the <sup>14</sup>N samples (see the  
540 Supporting Information).<sup>90</sup>

**Characterization Methods.** NMR spectra were recorded on a  
542 Varian Innova-500 MHz instrument. All spectra were recorded in  
543 CDCl<sub>3</sub> unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C NMR spectra were  
544 referenced to internal tetramethylsilane. For 3<sup>R</sup> species, the signal for  
545 the TfO<sup>-</sup> anion is not reported; it is observed at 119.5 ppm in  
546 concentrated samples. <sup>15</sup>N NMR spectra were referenced to external  
547 formamide in dimethyl sulfoxide. IR spectra were recorded on a  
548 Nicolet iS5 (Thermo Scientific) attenuated-total-reflectance instru-  
549 ment. UV–vis spectra were recorded on an Agilent 8453  
550 spectrophotometer or a B&W Tek i-Trometer. Elemental analysis  
551 was performed by the Laboratoire d'Analyse Élémentaire de  
552 l'Université de Montréal. The presence of F atoms in the samples  
553 interfered with the normal integration peak for H atoms. The value  
554 for H is not necessarily trustworthy.

**X-ray Crystallography.** Crystallographic analysis was performed  
556 on a Bruker APEX-DUO diffractometer. The frames were integrated  
557 with the Bruker SAINT software package using a narrow-frame  
558 algorithm. Data were corrected for absorption effects using the  
559 multiscan method (SADABS or TWINABS). The structures were  
560 solved by direct methods and refined using the APEX3 software  
561 package. All non-H atoms were refined with anisotropic thermal  
562 parameters. H atoms were generated in idealized positions, riding on  
563 the carrier atoms with isotropic thermal parameters.

**Electrochemistry.** Room temperature electrochemical studies of  
565 the nitrosoarene ligands and their copper complexes were performed  
566 in a glovebox (Jacomex; O<sub>2</sub> < 1 ppm and H<sub>2</sub>O < 1 ppm) with a home-  
567 designed three-electrode cell (WE, glassy carbon or platinum; RE,  
568 platinum wire in a Fc<sup>+</sup>/Fc solution; CE, platinum or graphite rod).  
569 Ferrocene was added at the end of the experiments to determine the  
570 redox potential values. The potential of the cell was controlled by an  
571 AUTOLAB PGSTAT 100 (Metrohm) potentiostat monitored by the  
572 NOVA 1.11 software. Dichloromethane (Acros) was distilled over  
573 CaH<sub>2</sub> under an inert atmosphere and stored in a glovebox. The  
574 supporting salt NBu<sub>4</sub>PF<sub>6</sub> was synthesized from NBu<sub>4</sub>OH (Acros) and  
575 HPF<sub>6</sub> (Aldrich). It was then purified, dried under vacuum for 48 h at  
576 100 °C, and then kept under argon in the glovebox. NBu<sub>4</sub>Otf  
577 (Aldrich, 99%) was stored as received in the glovebox. Electrolytic  
578 solutions were prepared in the glovebox and dried for a few days  
579 under molecular sieves (3 Å) to remove traces of water before use.

**Computational Details.** All theoretical calculations were  
581 performed with the ORCA program package.<sup>92</sup> Full geometry  
582 optimizations were carried out for all complexes using the generalized  
583 gradient approximation functional BP86<sup>93–95</sup> in combination with the  
584 TZV/P<sup>96</sup> basis set for all atoms and by taking advantage of the  
585 resolution of the identity (RI) approximation in the Split-RI-J  
586 variant<sup>97</sup> with the appropriate Coulomb fitting sets.<sup>98</sup> Increased  
587 integration grids (Grid4 in the ORCA convention) and tight self-  
588 consistent-field convergence criteria were used. IR spectra were  
589 obtained from numerical frequency calculations performed on DFT-  
590 optimized structures. Isotope shift effects (<sup>14</sup>N/<sup>15</sup>N) were taken into  
591 account using the *orca\_vib* utility program, and vibrational normal  
592 modes were visualized with Chemcraft<sup>99</sup> software. Solvent effects were  
593 accounted for according to the experimental conditions. For that  
594 purpose, we used the CH<sub>2</sub>Cl<sub>2</sub> (ε = 9.08) solvent within the framework  
595 of the conductor-like screening (COSMO) dielectric continuum  
596 approach.<sup>100</sup> Single-point optical properties were predicted from  
597 additional single-point calculations using the same functional/basis set  
598 as that employed previously. Electronic transition energies and dipole  
599 moments for all models were calculated using TD-DFT<sup>101–103</sup> within 600

601 the Tamm–Dancoff approximation.<sup>104,105</sup> To increase the computa-  
602 tional efficiency, the RI approximation<sup>106</sup> was used to calculate the  
603 Coulomb term. At least 40 excited states were calculated in each case,  
604 and difference transition density plots were generated for each  
605 transition. For each transition, difference density plots were generated  
606 using the ORCA plot utility program and visualized with the  
607 Chemcraft program. The same procedure was also employed to  
608 generate and visualize spin-density plots as well as molecular orbitals.

609 **Synthetic Procedures.** *General Procedure for the Synthesis of*  
610 **3<sup>R</sup> Complexes (R = NMe<sub>2</sub>, H, Cl, Br).**<sup>25</sup> To a stirring solution of  
611 TMPD (0.28 mmol, 1.1 equiv) and the corresponding nitrosobenzene  
612 **2<sup>R</sup>** (0.27 mmol, 1.05 equiv) in 5 mL of THF was added dropwise at  
613 25 °C a solution of [(MeCN)<sub>4</sub>Cu](TfO) (0.26 mmol, 1 equiv) in 2  
614 mL of THF. The solution was stirred for 15 min and then cooled to  
615 –30 °C. Dropwise addition of the solution to 15 mL of swirling  
616 pentane previously cooled to –30 °C resulted in the precipitation of a  
617 solid. The solid was isolated, washed with diethyl ether and pentane,  
618 and dried in vacuo (yields typically 70–85%). Crystals suitable for X-  
619 ray structure determination were grown through the slow layered  
620 diffusion of pentane into a concentrated solution of the complex in  
621 THF at –30 °C.

622 [(TMPDCu)(TfO)(κN-p-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>NO)](TfO) (**3<sup>NMe<sub>2</sub></sup>**). Yield: dark  
623 purple solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> 1.76 (m, 2H), 2.51  
624 (s, 12H), 2.84 (m, 4H), 3.22 (s, 6H), 6.81 (br, 2H), 9.09 (very br,  
625 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> 22.89, 40.80, 48.69, 61.75,  
626 112.2, 122.05, 156.26, 158.23. <sup>15</sup>N NMR (50.7 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub>  
627 668.58 (NO moiety). Anal. Calcd for C<sub>16</sub>H<sub>28</sub>CuF<sub>3</sub>N<sub>4</sub>O<sub>4</sub>S: C, 38.98;  
628 H, 5.72; N, 11.36; S, 6.50. Found: C, 37.86; H, 5.82; N, 11.13; S,  
629 6.61.

630 [(TMPDCu)<sub>2</sub>(μ-TfO)(μ-η<sup>2</sup>:η<sup>1</sup>-PhNO)](TfO) (**3<sup>H'</sup>**). Yield: brown solid.  
631 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> 1.72 (br, 4H), 2.55 (br, 24H),  
632 2.69 (br, 8H), 7.49 (t, 2H), 7.67 (t, 1H), 8.09 (d, 2H). <sup>13</sup>C NMR  
633 (125 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> 22.36, 48.59, 60.59, 120.97 (d upon <sup>15</sup>N  
634 labeling, J(<sup>13</sup>C–<sup>15</sup>N) = 3 Hz), 130.94 (d upon <sup>15</sup>N labeling,  
635 J(<sup>13</sup>C–<sup>15</sup>N) = 2 Hz), 131.78, 160.93. Anal. Calcd for  
636 C<sub>22</sub>H<sub>41</sub>Cu<sub>2</sub>F<sub>6</sub>N<sub>5</sub>O<sub>7</sub>S<sub>2</sub>: C, 33.33; H, 5.21; N, 8.83; S, 8.09. Found:  
637 C, 31.28; H, 5.35; N, 8.37; S, 8.19 (precision is lacking because this  
638 compound contains a minor quantity of **3<sup>H</sup>** in the solid state).

639 [(TMPDCu)(TfO)(η<sup>2</sup>-PhNO)](TfO) (**3<sup>H</sup>**). Yield: prepared in situ  
640 (green solution). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> 1.69 (br, 2H),  
641 2.47 (12H), 2.63 (4H), 7.43 (t, 2H), 7.63 (t, 1H), 7.97 (d, 2H). <sup>13</sup>C  
642 NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> 20.37, 46.59, 59.24, 119.34 (d upon  
643 <sup>15</sup>N labeling, J(<sup>13</sup>C–<sup>15</sup>N) = 5 Hz), 127.97 (d upon <sup>15</sup>N labeling,  
644 J(<sup>13</sup>C–<sup>15</sup>N) = 2 Hz), 130.78, 160.67 (d upon <sup>15</sup>N labeling,  
645 J(<sup>13</sup>C–<sup>15</sup>N) = 6 Hz). <sup>15</sup>N NMR (50.7 MHz, CDCl<sub>3</sub>): not observed.

646 [(TMPDCu)(TfO)(η<sup>2</sup>-p-ClC<sub>6</sub>H<sub>4</sub>NO)](TfO) (**3<sup>Cl</sup>**). Yield: green solid. <sup>1</sup>H  
647 NMR (500 MHz, acetone-d<sub>6</sub>): δ<sub>ppm</sub> 2.42 (br, 2H), 3.06 (s, 12H), 3.45  
648 (br, 4H), 7.77 (d, 2H), 7.97 (d, 2H). <sup>13</sup>C NMR (125 MHz, acetone-  
649 d<sub>6</sub>): δ<sub>ppm</sub> 20.17, 43.19, 55.50, 122.16, 126.10, 130.01, 166.47. Anal.  
650 Calcd for C<sub>14</sub>H<sub>22</sub>ClCuF<sub>3</sub>N<sub>3</sub>O<sub>4</sub>S: C, 34.71; H, 4.58; N, 8.67; S, 6.62.  
651 Found: C, 34.27; H, 4.49; N, 8.16; S, 6.38.

652 [(TMPDCu)(TfO)(η<sup>2</sup>-p-Br-C<sub>6</sub>H<sub>4</sub>NO)](TfO) (**3<sup>Br</sup>**). Yield: green solid.  
653 <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> 1.74 (br, 2H), 2.65 (br, 12H),  
654 2.78 (br, 4H), 7.54 (d, 2H), 7.91 (d, 1H). <sup>13</sup>C NMR (125 MHz,  
655 CDCl<sub>3</sub>): δ<sub>ppm</sub> 22.28, 48.52, 60.29, 122.81 (d upon <sup>15</sup>N labeling,  
656 J(<sup>13</sup>C–<sup>15</sup>N) = 5 Hz), 126.01, 133.55 (d upon <sup>15</sup>N labeling,  
657 J(<sup>13</sup>C–<sup>15</sup>N) = 2.5 Hz), 160.59 (d upon <sup>15</sup>N labeling, J(<sup>13</sup>C–<sup>15</sup>N) =  
658 5 Hz). <sup>15</sup>N NMR (50.7 MHz, CDCl<sub>3</sub>): not observed. Anal. Calcd for  
659 C<sub>14</sub>H<sub>22</sub>BrCuF<sub>3</sub>N<sub>3</sub>O<sub>4</sub>S: C, 31.80; H, 4.19; N, 7.95; S, 6.06. Found: C,  
660 31.29; H, 4.49; N, 7.81; S, 6.37.

661 X-ray data for **3<sup>NMe<sub>2</sub></sup>**, **3<sup>H</sup>**, **3<sup>H'</sup>**, and **3<sup>Cl</sup>** are available as CCDC  
662 1959040–1959043, respectively. Note that **3<sup>NO<sub>2</sub></sup>** is CCDC 1029423.

## 663 ■ ASSOCIATED CONTENT

### 664 ■ Supporting Information

665 The Supporting Information is available free of charge at  
666 <https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03175>.

Experimental supplements, including a crystallography 667  
table, a Job plot, <sup>15</sup>N labeling, IR data, electrochemistry 668  
supplements, DFT data, and NMR spectra (PDF) 669

## 670 Accession Codes

671 CCDC 1959040–1959043 contain the supplementary crys-  
672 tallographic data for this paper. These data can be obtained  
673 free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by  
674 emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The  
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### 706 Author Contributions

707 The manuscript was written through contributions of all  
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