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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,*
4 and X. Ottenwaelder*



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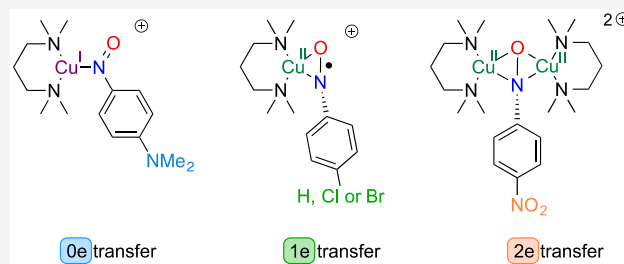


Article Recommendations



Supporting Information

5 **ABSTRACT:** A series of copper/nitrosoarene complexes were
6 created that mimic several steps in biomimetic O₂ 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: κN for ArNO, mononuclear $\eta^2\text{-NO}$ and dinuclear $\mu\text{-}\eta^2\text{:}\eta^1$ for ArNO^{•-}, and dinuclear $\mu\text{-}\eta^2\text{:}\eta^2$ for ArNO²⁻. ¹⁵N
17 isotopic labeling confirms the reduction state by measuring the NO stretching frequency (1392 cm⁻¹ for κN -ArNO, 1226 cm⁻¹ for
18 η^2 -ArNO^{•-}, 1133 cm⁻¹ for dinuclear $\mu\text{-}\eta^2\text{:}\eta^1$ -ArNO^{•-}, and 875 cm⁻¹ for dinuclear $\mu\text{-}\eta^2\text{:}\eta^2$ for ArNO²⁻). The ¹⁵N NMR signal
19 disappears for the ArNO^{•-} 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–O₂ 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^{1–7} and catalytic C–N bond formation processes.^{8–12}
29 Chemists now have a good understanding of the geometric
30 structure of transition metal/nitrosoarene complexes.^{13,14} In
31 addition, ArNO species are redox-noninnocent ligands,^{15–17}
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 O₂, the reduction
35 of ArNO by a transition metal is akin to the reduction of O₂ to
36 the superoxide ion (O₂^{•-}, 1e reduction) or the peroxide ion
37 (O₂²⁻, 2e reduction). Therefore, metal/ArNO adducts are
38 often regarded as surrogates for metal/O₂ adducts. In
39 particular, and with relevance to the present paper, the
40 activation of O₂ by Cu(I) centers is paramount in the
41 biological world. This process fuels enzymes such as
42 dopamine- β -hydroxylase, tyrosinase, and particulate methane
43 monooxygenase, to name but a few.^{18,19} This has inspired
44 numerous biomimetic studies in which an electron-rich Cu(I)
45 species is reacted with O₂.^{20–22} Without protection of the
46 protein backbone, however, the ensuing Cu/O₂ complexes are

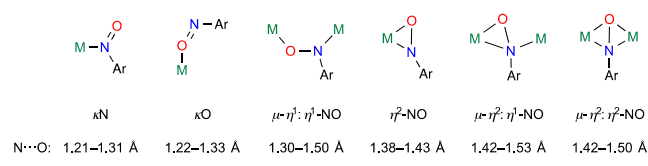
usually too oxidative to be stable above –60 °C. By contrast, 47
Cu/ArNO adducts have been shown to have geometric and 48
electronic structures very similar to those in Cu/O₂ adducts 49
but were advantageously characterized at ambient temper- 50
ature.^{17,23–25} 51

Owing to the asymmetric structure of ArNO in comparison 52
with that of O₂, the structural variety of metal/nitrosoarene 53
complexes exceeds that of metal/O₂ compounds. Some of the 54
main bonding modes of ArNO to metal ions are shown in 55
Scheme 1,^{13,14} with the most common one being through the 56 s1
N atom (κN). 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 Lengths¹³



63 the degree of reduction of the ArNO moiety, as was already
64 shown with metal/O₂ adducts.²⁶ 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 κN 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,^{13,14,27–29} unless back-bonding from the metal becomes
74 significant.¹⁶ A radical character of the κN -ArNO moiety, and
75 thus formally a 1.5 bond order, has been confirmed or inferred
76 in a few species (Scheme 2a).^{16,30,31}

77 (ii) Most mononuclear κO complexes with non-d¹⁰
78 transition metals are structurally disordered,^{13,14,32–36} 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 [(Me₆tren)Cu(κO -PhNO)]X
82 (X = TfO⁻, SbF₆⁻; Scheme 2b) show significant NO bond
83 elongation. The radical character of the PhNO moiety (to an

arylnitrosyl radical anion) was confirmed by magnetic 84
measurements and vibrational and computational studies.^{17,37} 85

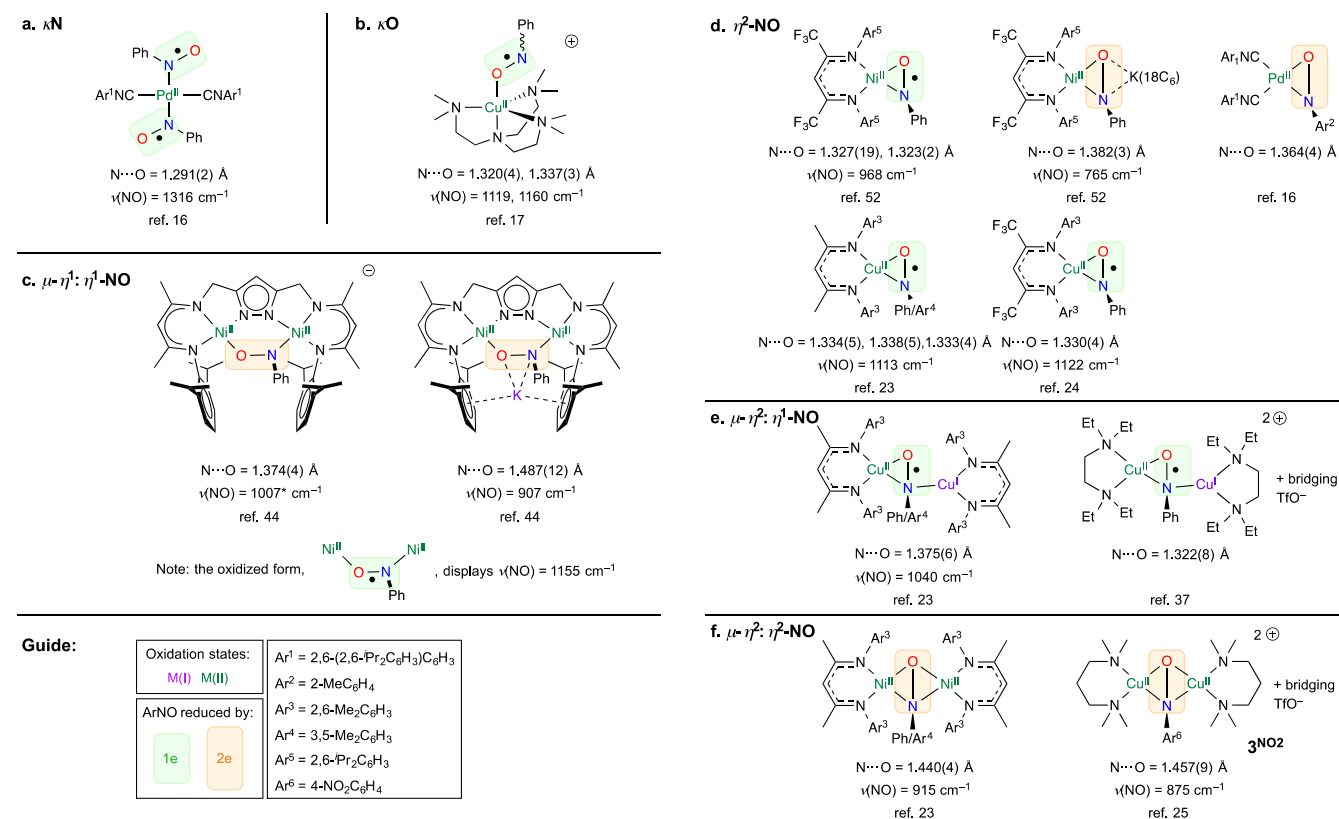
(iii) Dinuclear $\mu\text{-}\eta^1\text{:}\eta^1$ (end-on) complexes present varying 86
degrees of ArNO reduction: by 0e (NO = 1.257–1.32 87
Å),^{28,29,38–41} 1e (1.33–1.35 Å),⁴² and 2e (1.37–1.49 Å; 88
Scheme 2c).^{43,44}

(iv) In $\eta^2\text{-NO}$ complexes, the NO bond length (1.323– 89
1.432 Å)^{16,23,31,45–52} is significantly longer than that in free 91
nitrosoarenes. 1e reduction of the ArNO moiety has been 92
confirmed in Cu and Ni complexes (Scheme 2d).^{23,52} Further 93
reduction of the Ni complex led to a doubly reduced PhNO²⁻ 94
moiety.⁵² 2e reduction of the ArNO moiety was also confirmed 95
in a square-planar Pd(II) species upon reaction of a Pd⁰ species 96
with TolNO.¹⁶

(v) Alongside several ArNO²⁻ examples (N–O = 1.40–1.53 98
Å),^{31,53–58} dinuclear $\mu\text{-}\eta^2\text{:}\eta^1$ complexes have been found in the 99
solid-state structures of Cu complexes with shorter NO bond 100
lengths (1.322–1.375 Å).^{23,37} Typically, the 1e-reduced 101
ArNO^{•-} moiety binds η^2 to a Cu(II) center and η^1 to a 102
Cu(I) center (Scheme 2e). These species are thought to be in 103
equilibrium with the mononuclear form [Cu^{II}(η^2 -ArNO^{•-})] in 104
solution.^{23,37}

(vi) Dinuclear $\mu\text{-}\eta^2\text{:}\eta^2$ complexes are quite rare, and only a 106
few examples with Rh,⁵⁷ Zr,⁵⁹ Hf,⁵⁹ Ni,²³ and Cu²⁵ are 107
reported in the literature. With an NO bond length in the 108
range of single bonds (1.422–1.500 Å), these complexes 109
possess a doubly reduced ArNO²⁻ moiety. In the case of the 110
Cu complex (Scheme 2f), this 2e reduction was made possible 111
by using a very electron-poor nitrosoarene bearing a *p*-NO₂ 112
substituent. More on this complex will be discussed below. 113

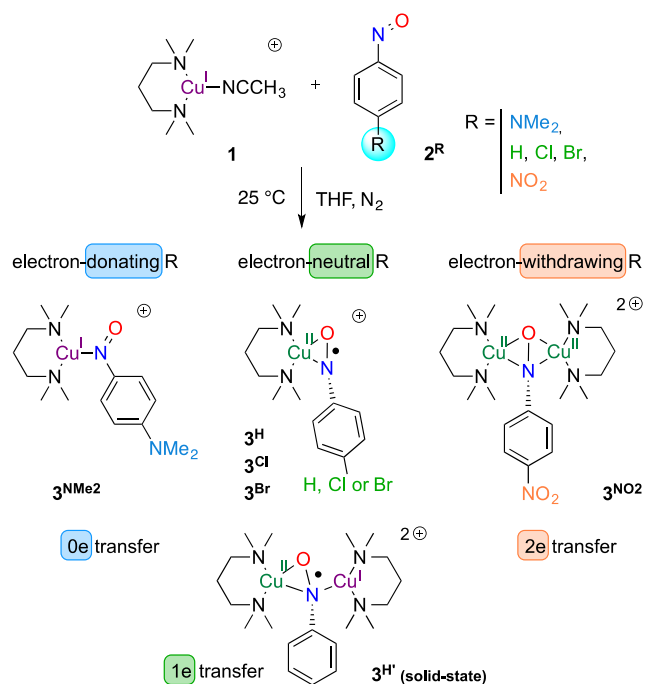
Scheme 2. Confirmed Examples of Group 10 and 11 Complexes in Which ArNO Gets Reduced by 1e or 2e upon Reaction^a



^aAsterisks 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⁻¹
 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⁻¹. 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⁻¹ for free PhNO),
 122 although these values can be modified significantly when back-
 123 bonding is present.¹⁶ 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.⁶⁰
 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^R (R = NMe₂, H, Cl, Br, NO₂) formed upon
 131 intermolecular reaction of para-substituted nitrosobenzenes 2^R
 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/O₂ chemistry is known.^{61–63}

Scheme 3. Formation of the 3^R Adducts^a



^aWith a TfO⁻ counterion. 3^{NO₂} was already reported.²⁵

135 ■ RESULTS AND DISCUSSION

136 **Synthesis and Crystallography.** The slow addition of a
 137 [(MeCN)₄Cu](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 = NO₂), 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).

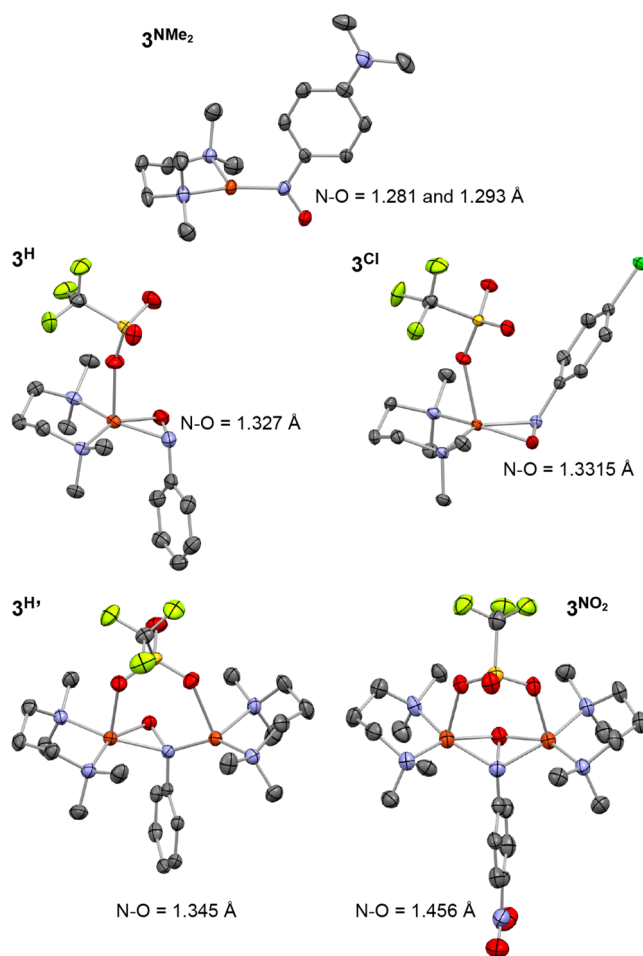


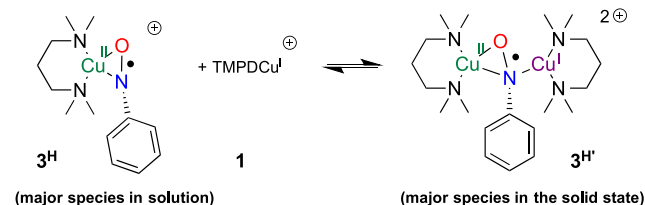
Figure 1. ORTEP at 50% probability of 3^{NMe₂} (one of two independent molecules), 3^H, 3^{Cl}, and 3^{NO₂}, with relevant N–O bond lengths. Uncoordinated TfO⁻ anions (3^{NMe₂} and 3^{NO₂}) and H atoms were omitted for clarity.

The structure of 3^{NMe₂} is that of a copper(I) arylnitroso 147 complex, i.e., mere κN coordination of 1^{NMe₂} onto the [TMPD-
 Cu^I]⁺ 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^{NMe₂} 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.^{16,37} 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^{II}(η²-PhNO^{•-})- 160
 (TfO)] species (3^H). This complex displays an η²-NO 161
 coordination with an elongated N–O bond of 1.327 Å, 162
 consistent with a 1.5 bond order.^{23,52} Cu sits in a square- 163
 pyramidal environment with a TfO⁻ anion as a weak axial 164
 ligand (Cu⋯O = 2.345 Å). The brown major component, 3^H, 165
 of the formula [TMPDCu^{II}(μ-η²:η¹-PhNO^{•-})(μ-TfO)- 166
 Cu^ITMPD](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^a



^aTfO⁻ anions are not shown.

175 association were already described in the literature.^{23,37}
 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^{II}(η^2 - 2^{Cl} •⁻)(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⁻ 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.²⁵ It is a
 187 dinuclear species of the formula [TMPDCu^{II}(μ - η^2 : η^2 -
 188 PhNO²⁻)(μ -TfO)Cu^{II}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⁻ 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 ¹⁴N or ¹⁵N. Synthesis of
 200 the ¹⁵N-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⁻¹ for 3^{NMe_2} to 1226 cm⁻¹ for 3^{Br} to 875 cm⁻¹ for 3^{NO_2} .²⁵
 221 This trend, supported by DFT calculations, is fully consistent

Table 1. NO Stretching Frequencies^a

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

^aMeasured at 25 °C on species labeled with ¹⁴N and ¹⁵N on the NO moiety. Full data are given in the Supporting Information. ^bSyn ArN(O)N(O)Ar dimer. ^cContains a small amount of mononuclear species 3^H . ^dAnti 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⁻¹, consistent with the electron density being
 225 delocalized onto the additional Cu(I) center.
 226

NMR Properties. In CDCl₃, CD₂Cl₂, or acetone-*d*₆
 227 solutions, all 3^R species display diamagnetic ¹H and ¹³C
 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 η^2 -
 230 ArNO complexes.^{23,24,37} By analogy with structurally similar
 231 η^2 -superoxocopper(II) species, this ground-state singlet is
 232 expected to be highly delocalized.⁶⁴ This situation also
 233 contrasts with the end-on topology, where end-on
 234 superoxocopper(II) complexes have a *S* = 1 ground
 235 state,^{65–68} as do Cu^{II}(κ O-ArNO•⁻) complexes when Cu–
 236 O–N–C_{Ar} is coplanar.¹⁷
 237

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

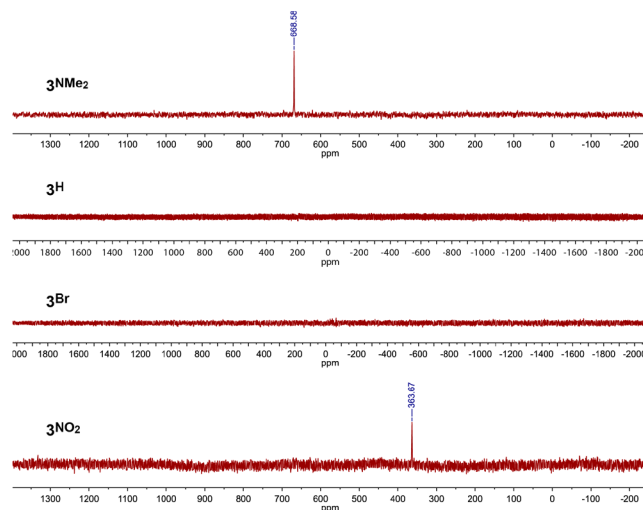


Figure 2. ¹⁵N NMR data (50.7 MHz) of the 3^R species (R = NMe₂, H, Br, NO₂), ¹⁵N-enriched at the NO position, in CDCl₃ at 25 °C. Species 3^H was made in situ by mixing equimolar amounts of [Cu(MeCN)₄](TfO), and 2^H .

and Table 2). For comparison, the ¹⁵N NMR spectra of the
 240 12 ¹⁵N-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}N NMR Data^a

species	$\delta(^{15}\text{N})/\text{ppm}$	species	$\delta(^{15}\text{N})/\text{ppm}$
2^{NMe_2}	787.58	3^{NMe_2}	668.58
2^{H}	885.83	3^{H}	not observed
2^{Br}	878.67	3^{Br}	not observed
2^{NO_2}	913.23	3^{NO_2}	363.67

^aMeasured in CDCl_3 at 25 °C on a 500 MHz instrument; $\nu(^{15}\text{N}) = 50.7$ MHz.

(ArNO^{2-}) and therefore quite electron-rich. Interestingly, no ^{15}N signal was observed for 3^{H} and 3^{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}N NMR resonance outside the acquisition window (Fermi contact at ^{15}N).⁶⁹ 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).

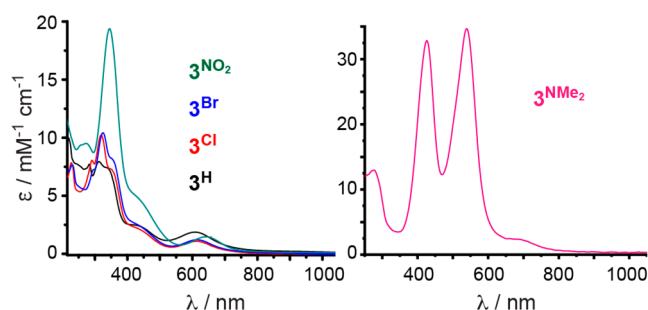


Figure 3. UV–vis spectra of 3^{R} species in CH_2Cl_2 at 25 °C.

Table 3. UV–Vis Data of 3^{R} Complexes^a

species	λ_{max} (ε) ^b	λ_{max} (ε) ^b	λ_{max} (ε) ^b
3^{NMe_2}	426 (32.8)	538 (34.7)	690 (2.3)
3^{H}	313 (8.0), 338 (7.4)	440 (sh)	609 (1.9)
3^{Cl}	319 (10.2), 350 (7.3)	440 (sh)	614 (1.1)
3^{Br}	325 (10.4), 350 (8.2)	440 (sh)	614 (1.2)
3^{NO_2}	345 (19.4)	440 (sh)	644 (1.5)

^aMeasured in CH_2Cl_2 at 25 °C. ^b $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mM}^{-1} \text{cm}^{-1}$).

Complexes 3^{H} , 3^{Cl} , and 3^{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^{NO_2} exhibits the same spectral shape, but the 345 nm band is twice as intense.

The spectrum for complex 3^{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.

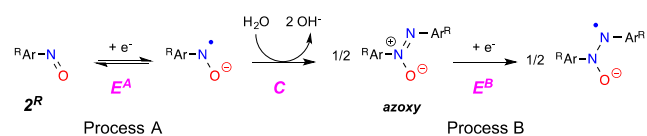
DFT Calculations. DFT calculations have been undertaken on the 3^{R} complexes to gain insight into the nature of the species observed experimentally and to correlate their electronic structures to the experimental data. The structures of the 3^{R} species were subjected to geometry optimization, and

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^{NMe_2} , 1.287–1.288 Å for 3^{H} , 3^{Cl} , and 3^{Br} , 1.313 Å for $3^{\text{H}'}$, and 1.405 Å for 3^{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 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^{NMe_2} , 3^{H} , 3^{Cl} , 3^{Br} , $3^{\text{H}'}$, and 3^{NO_2} , respectively.

Time-dependent DFT (TD-DFT) calculations were performed on the 3^{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^{H} , 3^{Cl} , 3^{Br} , and 3^{NO_2} are similar and dominated by two main absorption bands of different intensities, while that of 3^{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^{NO_2} were already analyzed.²⁵ 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.²² For 3^{H} , 3^{Cl} , and 3^{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^{R} complexes. Vibrational analysis also confirmed the experimental observations (vide supra). Consequently, 3^{NMe_2} can be described as a Cu(I) complex, while 3^{H} , 3^{Cl} , and 3^{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^{NO_2} was previously shown to be a $\text{Cu}^{\text{II}}\text{-Cu}^{\text{II}}$ complex with a ArNO^{2-} moiety (2e-reduced ArNO).

Electrochemical Studies. Because this work aims at tuning the redox properties by simple substitution, we studied the electrochemical behavior of both precursors 2^{R} and complexes 3^{R} for the whole series of R substituents (NMe_2 , H, Cl, Br, and NO_2). The goal was to correlate the electrochemical properties with the reactivity (0e, 1e, or 2e transfer) observed upon reaction with the [(TMPD) Cu^{I}]⁺ complex **1** and the H-atom-transfer (HAT) reactivity of the 3^{R} complexes (see below). The data were also compared to existing records for analogous ArNO and O_2 complexes. Cyclic voltammetry (CV) studies were performed at a glassy-carbon working electrode in dry CH_2Cl_2 with 0.1 M NBu_4OTf as the supporting electrolyte. In what follows, all potentials are referenced to the $\text{Fc}^{+/0}$ couple.

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

Scheme 5. Reduction Steps of 2^R Species

340 = -1.40 V (process A) and $E_{1/2}^B = -1.86$ V versus $Fc^{+/0}$
 341 (process B) (Figure S21 and Table 4). An irreversible

Table 4. Electrochemical Data of the 2^R Nitrosoarenes^a

species	$E_{1/2}^A(2^R)$	$E_{1/2}^B(2^R)$	σ_{para}^b
2^{NMe_2}	-1.69 (120) ^c	<i>d</i>	-0.83
2^H	-1.40 (90)	-1.86 (100)	0
2^{Cl}	-1.32 (110)	-1.79 (90)	0.227
2^{Br}	-1.30 (90)	-1.75 (90)	0.232
2^{NO_2}	-0.93 (90)	-1.33 (100) ^e	0.78

^aIn CH_2Cl_2 containing 0.1 M NBu_4OTf at 25 °C (glassy-carbon working electrode); scan rate $\nu = 0.1$ V s^{-1} , E/V versus $Fc^{+/0}$ ($\Delta E_p/mV$). ^b σ_{para} Hammett parameters. ^cDetermined at $\nu = 0.5$ V s^{-1} . ^dNot determined. ^eAn 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,^{70,71} process A corresponds to the monoelectronic
 350 reduction of 2^H (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, $i_{pc}^B/i_{pc}^A \approx 0.5$ (assuming similar diffusion coefficients).
 355 In addition, the value of $E_{1/2}^B$ is in good agreement with the
 356 standard potential values for the azoxy species in organic
 357 solvents.^{70–72}

358 The processes described in Scheme 5 occur for 2^R with
 359 different para substituents ($R = NMe_2, H, Cl, Br, NO_2$) but at
 360 different redox potentials (Figure S21 and Table 4). Under the
 361 same experimental conditions, 2^H , 2^{Cl} , and 2^{Br} display almost
 362 the same redox pattern, i.e., one quasi-reversible redox system
 363 at ca. $E_{1/2}^A = -1.3$ V and a second one at ca. $E_{1/2}^B = -1.8$ V. For
 364 2^{NMe_2} , $E_{1/2}^A$ is shifted negatively by ca. 300 mV with respect to
 365 $E_{1/2}^A(2^H)$, and the $(2^{NMe_2})^{\bullet-}$ radical anion is relatively unstable
 366 because process A occurs irreversibly for $\nu < 0.2$ V s^{-1} (Figure
 367 S21a). For 2^{NO_2} , $E_{1/2}^A$ and $E_{1/2}^B$ are shifted positively by ca. 500
 368 mV (Figure S21b).

369 Thus, a span of +760 mV is observed for $E_{1/2}^A$ upon NMe_2 /
 370 NO_2 substitution, consistent with the electron-donating/
 371 withdrawing properties of the substituents. Fittingly, plots of
 372 $E_{1/2}^A$ versus the σ_{para} 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^R . CV studies of the
 376 3^R complexes ($R = NMe_2, H, Br, NO_2$) were performed under
 377 the same experimental conditions as those for 2^R ligands
 378 (Figure 4 and Table 5). Adding 2^R to a solution of **1** under CV
 379 monitoring led to the same conclusions as those below (Figure
 380 S25). All 3^R complexes display a first irreversible reduction

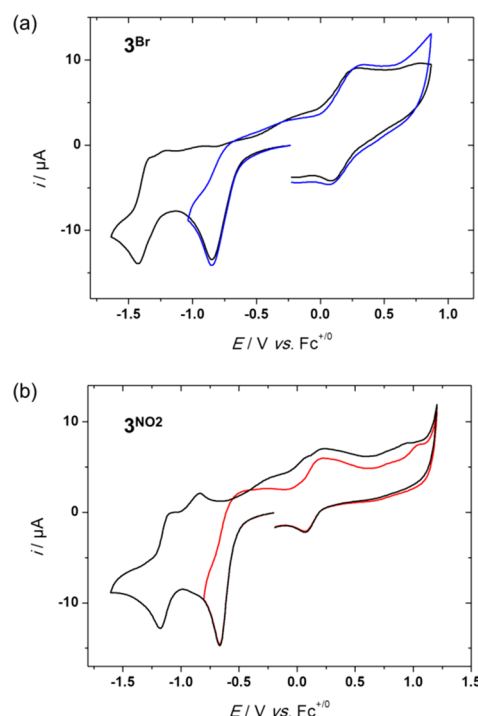


Figure 4. CV cycles at a glassy-carbon working electrode (E/V vs $Fc^{+/0}$; $\nu = 0.1$ V s^{-1}) of 3^R (1.0 mM) in dry CH_2Cl_2 and 0.1 M NBu_4OTf : (a) $R = Br$; (b) $R = NO_2$.

Table 5. Electrochemical Data of 3^R Complexes^a

	$E_{pc}^C(3^R)$	$E_{1/2}^D(3^R)$	$E_{1/2}^E(3^R)$	σ_{para}^b
3^{NMe_2}	-1.05	-1.75	-0.36 (140)	-0.83
3^H	-0.92	-1.45^c	0.28	0.00
3^{Br}	-0.82	-1.22 (180)	0.08 (130)	0.23
3^{NO_2}	-0.72	-1.17 (145)	0.11 (120)	0.78

^aIn CH_2Cl_2 containing 0.1 M NBu_4OTf at 25 °C; scan rate $\nu = 0.1$ V s^{-1} . E/V versus $Fc^{+/0}$ ($\Delta E_p/mV$). ^b σ_{para} Hammett parameters. ^cIrreversible cathodic peak.

381 peak E_{pc}^C (process C) extending from -1.05 V for 3^{NMe_2} to
 382 -0.72 V for 3^{NO_2} (Figure 4 and Table 5). As was the case with
 383 process A for the 2^R ligands, the redox potential is mainly
 384 controlled by electronic effects, which is confirmed by the
 385 linear variation of E_{pc}^C versus σ_{para} Hammett parameters (Figure
 386 S29). Whatever the nature of R, the first system remains
 387 irreversible at moderate scan rates ($\nu < 10$ V s^{-1} ; 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 $R = NO_2$, by the linear behavior of E_{pc}^C
 391 versus $\log \nu$ (33 mV decade⁻¹; Figure S27b) and the constancy
 392 of the normalized current intensity ($i_{pc}^C \nu^{-1/2}$) 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^D (-1.75 V $< E^D < -1.21$ 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_{pc}^C and i_{pc}^D (Figure S27c,d
 399 for 3^{NO_2}), 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^D
 402 originates from the first electrochemical reduction of the 3^R
 403 complex. As shown in Table 5, the potential value at E^D is 403

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.²³

430 The reduction data obtained for the 3^R complexes can be
 431 compared with the few redox processes reported for Ni_n/
 432 ArNO and Cu_n/O₂ 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.⁵² When ArNO binds in a 1,2-fashion (end-on)
 436 between two Ni(II) centers, the potential for ArNO^{2-/•-}
 437 conversion is decreased by ca. 650 mV (entry 3).⁴⁴ Comparing
 438 ArNO with O₂ 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.⁷³ 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).^{74,75} 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.⁷⁶ 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 μ -hydroxodicopper complexes that are reminiscent of Cu_n/
 459 O₂ species is readily available,^{77–82} comparisons with the 3^R
 460 complexes would be even more tentative.

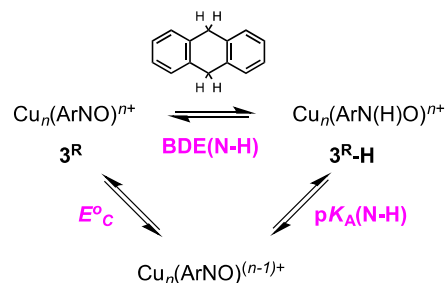
461 **HAT Reactivity.** We evaluated the reactivity of 3^{Cl} , 3^{Br} , and
 462 3^{NO_2} for HAT reactivity (Scheme 6). In previous work, Warren
 463 et al. reported a Ni^{II}-(η^2 -ArNO^{•-}) that converts into the
 464 related Ni^{II}-(η^2 -ArN(H)O) complex (protonated hydroxyl-
 465 amine) upon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

Table 6. Electrochemical Data of 3^R and Related Ni_n/ArNO and Cu_n/O₂ Complexes

Entry	Reaction ^a	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

^aThe reaction is written in a way it was carried out either as an oxidation or as a reduction. Abbreviations: n/c, compound not characterized; ^cP, cis-end-on peroxo; ^sP, side-on peroxo; O, bis(μ -oxo). ^bPotential versus Fc^{+/0}. ^cIrreversible cathodic peak. ^dReversible reduction. ^eReversible oxidation. ^fConverted 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



ArN(H)O) species that released its H atom to a phenoxyl radical to form the related Ni^{II}₂-(μ - η^1 : η^1 -ArNO^{•-}) species and 468 evaluated a bond dissociation energy BDE(N–H) of around 469

62–65 kcal mol⁻¹).⁴⁴ Following these examples, we reacted to
471 3^{Cl}, 3^{Br}, and 3^{NO₂} with DHA (bond dissociation free energy
472 BDFE = 76.0 mol⁻¹)⁸³ under UV–vis monitoring. A significant
473 decrease of the 3^R 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^R 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^R-H
478 hereafter (Scheme 6), but their instability prevented further
479 analysis of the reaction and its mechanism.
480 The electron-withdrawing NO₂ group induces a faster
481 oxidation of DHA, consistent with 3^{NO₂} being a stronger
482 oxidant (higher $E_{1/2}^C$) than 3^{Br} and 3^{Cl}. The initial rates of
483 reaction depend on the R substituent: 0.029, 0.021, and 0.051
484 ± 0.005 mM min⁻¹ for 3^{Cl}, 3^{Br}, and 3^{NO₂}, respectively. Using
485 eq 1 (Scheme 6)⁸³ with a temperature correction, the value of
486 $E_{1/2}^C$ for 3^R taken as E_{pc}^C , and using C = 66 kcal mol⁻¹ in THF,⁸⁴
487 the pK_A value of the N–H bond in 3^R-H is evaluated around
488 18 and 19.5 for the NO₂ and Br adducts, respectively, in order
489 to perform HAT from DHA. Similarly, 2^{NO₂} reacts, but slowly,
490 with 1,2-diphenylhydrazine (BDFE = 67.1 kcal mol⁻¹) at 25
491 °C. This brings the pK_A value to around 13, but this reaction is
492 complicated by the byproduct azobenzene, which can interact
493 with Cu(I) and dissociate 2^{NO₂}. 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.^{85,86}

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.³⁷ Thus, Cu(I) will be found in trigonal
505 geometries, with κN-ArNO coordination, whereas a square-
506 pyramidal Cu(II) will force η²-ArNO^{•-/-2-} coordination. One
507 of the novel features of this work is the use of ¹⁵N NMR as a
508 direct, local probe for the redox level of the ArNO moiety.
509 Thus, the absence of a ¹⁵N 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/O₂
514 chemistry, without the complication of thermal sensitivity of
515 Cu/O₂ species. It also enables redox studies to be performed,
516 although much remains to be done before a proper ArNO/O₂
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-¹⁵N, which was purchased from Cambridge
525 Isotope Laboratories. Air-sensitive samples were handled under an
526 inert atmosphere (N₂) in a dry nitrogen glovebox (O₂ < 0.1 ppm;
527 H₂O < 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 CaH₂ under nitrogen

and stored in the glovebox. The copper salt [(MeCN)₄Cu](TfO) was 531
prepared by adapting the Kubas procedure using TfOH.⁸⁷ 4- 532
Dimethylaminonitrosobenzene (2^{NMe₂}),^{88,89} 4-chloronitrosobenzene 533
(2^{Cl}),⁹⁰ 4-bromonitrosobenzene (2^{Br}),⁹⁰ and 4-nitrosobenzene 534
(2^{NO₂})⁹¹ were prepared via literature procedures. Isotopically labeled 535
¹⁵N-4-nitrosobenzene and [(TMPDCu)₂(μ-TfO)(μ-η²:η²-p- 536
NO₂-C₆H₄NO)](TfO) were prepared following the procedure 537
reported earlier.²⁵ 4-Bromoaniline-¹⁵N was prepared from ¹⁵N- 538
acetamide as reported in the Supporting Information. ¹⁵N derivatives 539
of 2^H, 2^{Cl}, and 2^{Br} were prepared similarly to the ¹⁴N samples (see the 540
Supporting Information).⁹⁰ 541

Characterization Methods. NMR spectra were recorded on a 542
Varian Innova-500 MHz instrument. All spectra were recorded in 543
CDCl₃ unless otherwise noted. ¹H and ¹³C NMR spectra were 544
referenced to internal tetramethylsilane. For 3^R species, the signal for 545
the TfO⁻ anion is not reported; it is observed at 119.5 ppm in 546
concentrated samples. ¹⁵N 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. 555

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. 564

Electrochemistry. Room temperature electrochemical studies of the 565
nitrosoarene ligands and their copper complexes were performed 566
in a glovebox (Jacomex; O₂ < 1 ppm and H₂O < 1 ppm) with a home- 567
designed three-electrode cell (WE, glassy carbon or platinum; RE, 568
platinum wire in a Fc⁺/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
CaH₂ under an inert atmosphere and stored in a glovebox. The 574
supporting salt NBu₄PF₆ was synthesized from NBu₄OH (Acros) and 575
HPF₆ (Aldrich). It was then purified, dried under vacuum for 48 h at 576
100 °C, and then kept under argon in the glovebox. NBu₄Otf 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. 580

Computational Details. All theoretical calculations were 581
performed with the ORCA program package.⁹² Full geometry 582
optimizations were carried out for all complexes using the generalized 583
gradient approximation functional BP86^{93–95} in combination with the 584
TZV/P⁹⁶ basis set for all atoms and by taking advantage of the 585
resolution of the identity (RI) approximation in the Split-RI-J 586
variant⁹⁷ with the appropriate Coulomb fitting sets.⁹⁸ 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 (¹⁴N/¹⁵N) were taken into 591
account using the *orca_vib* utility program, and vibrational normal 592
modes were visualized with Chemcraft⁹⁹ software. Solvent effects were 593
accounted for according to the experimental conditions. For that 594
purpose, we used the CH₂Cl₂ (ε = 9.08) solvent within the framework 595
of the conductor-like screening (COSMO) dielectric continuum 596
approach.¹⁰⁰ 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^{101–103} within 600

601 the Tamm–Dancoff approximation.^{104,105} To increase the computa-
602 tional efficiency, the RI approximation¹⁰⁶ 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^R Complexes (R = NMe₂, H, Cl, Br).**²⁵ To a stirring solution of
611 TMPD (0.28 mmol, 1.1 equiv) and the corresponding nitrosobenzene
612 **2^R** (0.27 mmol, 1.05 equiv) in 5 mL of THF was added dropwise at
613 25 °C a solution of [(MeCN)₄Cu](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-NMe₂-C₆H₄NO)](TfO) (**3^{NMe₂}**). Yield: dark
623 purple solid. ¹H NMR (500 MHz, CDCl₃): δ_{ppm} 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). ¹³C NMR (125 MHz, CDCl₃): δ_{ppm} 22.89, 40.80, 48.69, 61.75,
626 112.2, 122.05, 156.26, 158.23. ¹⁵N NMR (50.7 MHz, CDCl₃): δ_{ppm}
627 668.58 (NO moiety). Anal. Calcd for C₁₆H₂₈CuF₃N₄O₄S: 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)₂(μ-TfO)(μ-η²:η¹-PhNO)](TfO) (**3^{H'}**). Yield: brown solid.
631 ¹H NMR (500 MHz, CDCl₃): δ_{ppm} 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). ¹³C NMR
633 (125 MHz, CDCl₃): δ_{ppm} 22.36, 48.59, 60.59, 120.97 (d upon ¹⁵N
634 labeling, J(¹³C–¹⁵N) = 3 Hz), 130.94 (d upon ¹⁵N labeling,
635 J(¹³C–¹⁵N) = 2 Hz), 131.78, 160.93. Anal. Calcd for
636 C₂₂H₄₁Cu₂F₆N₅O₇S₂: 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^H** in the solid state).

639 [(TMPDCu)(TfO)(η²-PhNO)](TfO) (**3^H**). Yield: prepared in situ
640 (green solution). ¹H NMR (500 MHz, CDCl₃): δ_{ppm} 1.69 (br, 2H),
641 2.47 (12H), 2.63 (4H), 7.43 (t, 2H), 7.63 (t, 1H), 7.97 (d, 2H). ¹³C
642 NMR (125 MHz, CDCl₃): δ_{ppm} 20.37, 46.59, 59.24, 119.34 (d upon
643 ¹⁵N labeling, J(¹³C–¹⁵N) = 5 Hz), 127.97 (d upon ¹⁵N labeling,
644 J(¹³C–¹⁵N) = 2 Hz), 130.78, 160.67 (d upon ¹⁵N labeling,
645 J(¹³C–¹⁵N) = 6 Hz). ¹⁵N NMR (50.7 MHz, CDCl₃): not observed.

646 [(TMPDCu)(TfO)(η²-p-ClC₆H₄NO)](TfO) (**3^{Cl}**). Yield: green solid. ¹H
647 NMR (500 MHz, acetone-*d*₆): δ_{ppm} 2.42 (br, 2H), 3.06 (s, 12H), 3.45
648 (br, 4H), 7.77 (d, 2H), 7.97 (d, 2H). ¹³C NMR (125 MHz, acetone-
649 *d*₆): δ_{ppm} 20.17, 43.19, 55.50, 122.16, 126.10, 130.01, 166.47. Anal.
650 Calcd for C₁₄H₂₂ClCuF₃N₃O₄S: 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)(η²-p-Br-C₆H₄NO)](TfO) (**3^{Br}**). Yield: green solid.
653 ¹H NMR (500 MHz, CDCl₃): δ_{ppm} 1.74 (br, 2H), 2.65 (br, 12H),
654 2.78 (br, 4H), 7.54 (d, 2H), 7.91 (d, 1H). ¹³C NMR (125 MHz,
655 CDCl₃): δ_{ppm} 22.28, 48.52, 60.29, 122.81 (d upon ¹⁵N labeling,
656 J(¹³C–¹⁵N) = 5 Hz), 126.01, 133.55 (d upon ¹⁵N labeling,
657 J(¹³C–¹⁵N) = 2.5 Hz), 160.59 (d upon ¹⁵N labeling, J(¹³C–¹⁵N) =
658 5 Hz). ¹⁵N NMR (50.7 MHz, CDCl₃): not observed. Anal. Calcd for
659 C₁₄H₂₂BrCuF₃N₃O₄S: 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^{NMe₂}**, **3^H**, **3^{H'}**, and **3^{Cl}** are available as CCDC
662 1959040–1959043, respectively. Note that **3^{NO₂}** 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, ¹⁵N 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, or by
674 emailing data_request@ccdc.cam.ac.uk, or by contacting The
675 Cambridge Crystallographic Data Centre, 12 Union Road,
676 Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

677 ■ AUTHOR INFORMATION

678 Corresponding Authors

679 Nicolas Le Poul – *Laboratoire de Chimie, Électrochimie*
680 *Moléculaires et Chimie Analytique, UMR, CNRS 6521,*
681 *Université de Bretagne Occidentale, Brest 29238, France;*
682 orcid.org/0000-0002-5915-3760; Email: nicolas.lepoul@univ-brest.fr 683

684 X. Ottenwaelder – *Department of Chemistry and Biochemistry,*
685 *Concordia University, Montreal, Quebec H3G 1M8, Canada;*
686 orcid.org/0000-0003-4775-0303; Email: dr.x@concordia.ca 687

688 Authors

689 Mohammad S. Askari – *Department of Chemistry and*
690 *Biochemistry, Concordia University, Montreal, Quebec H3G*
691 *1M8, Canada;* orcid.org/0000-0002-1746-5141

692 Farshid Effaty – *Department of Chemistry and Biochemistry,*
693 *Concordia University, Montreal, Quebec H3G 1M8, Canada;*
694 orcid.org/0000-0002-2389-4903

695 Federica Gennarini – *Department of Chemistry and*
696 *Biochemistry, Concordia University, Montreal, Quebec H3G*
697 *1M8, Canada; Laboratoire de Chimie, Électrochimie*
698 *Moléculaires et Chimie Analytique, UMR, CNRS 6521,*
699 *Université de Bretagne Occidentale, Brest 29238, France;*
700 orcid.org/0000-0001-5679-512X

701 Maylis Orrio – *Aix Marseille Université, CNRS, Centrale*
702 *Marseille, iSm2, Marseille 13007, France;* orcid.org/0000-0002-9317-8005 703

704 Complete contact information is available at:
705 <https://pubs.acs.org/10.1021/acs.inorgchem.9b03175>

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