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Photolytic *C*-Diazeniumdiolate Disassembly in the β-Diketiminate Complexes [^{Me}LM($O_2N_2CPh_3$)] (M = Fe, Co, Cu)

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Supporting Information Placeholder

ABSTRACT: Reaction of [K(18-crown-6)][$O_2N_2CPh_3$] with [^{Me}LCo(μ-Br)$_2$Li(OEt$_2$)] (^{Me}L = {(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)}$_2$CH) generates the trityl diazeniumdiolate complex, [^{Me}LCo($O_2N_2CPh_3$)] (**1**), in moderate yield. Similar metathesis reactions result in formation of the Fe and Cu analogues, [^{Me}LM($O_2N_2CPh_3$)] (Fe, **2**; Cu, **3**), which can also be isolated in moderate yields. Complexes **1**–**3** were characterized by UV-vis spectroscopy and their solid-state structures were determined by X-ray crystallography. These complexes were further characterized via ^{1}H NMR spectroscopy (in the case of **1** and **2**) or EPR spectroscopy (in the case of **3**). Irradiation of complexes **1** and **2** with 371 nm light generates the known dinitrosyl complexes, [^{Me}LM(NO)$_2$] (M = Co, **4**; Fe, **5**), along with Ph_3CH and 9-phenylfluorene. We propose that **4** and **5** are formed via the putative hyponitrite intermediates, [^{Me}LM(κ^2-*O*,*O*-ONNO)], which are formed by photo-induced homolysis of the C–N bond of the [$O_2N_2CPh_3$] ligand. In contrast, irradiation of complex **3** with 371 nm light, in the presence of 1 equiv of PPh_3, led to the formation of the Cu(I) complexes, [^{Me}LCu(PPh$_3$)], [(ArNC^{Me}C(*N*O)C^{Me}*N*Ar)Cu(PPh$_3$)] (**6**), and [(ArNC^{Me}C(*N*O)C^{Me}*N*Ar)Cu]$_2$ (**7**), of which the latter two are products of γ-nitrosation of the β-diketiminiate ligand. Also formed in this transformation are Ph$_3$CN(*H*)OCPh$_3$, Ph$_3$PO, and N_2O, along with trace amounts of NO.

INTRODUCTION

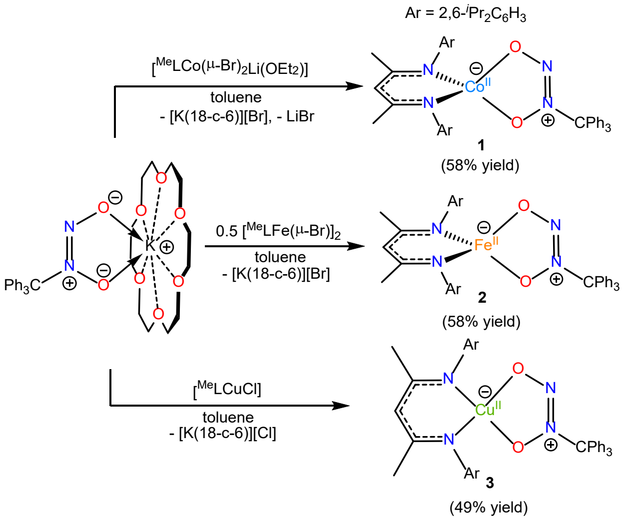
Diazeniumdiolates (DAZDs) have received significant interest for their ability to release nitric oxide (NO) in a controlled fashion.[1–4] Of the two classes of DAZDs, *N*-diazeniumdiolates have been investigated to the greatest extent;[5–8] *C*-diazeniumdiolates are comparatively understudied, presumably because early studies indicated their preference for N_2O release instead of NO release.[9,10] Several other products have also been observed upon *C*-DAZD disassembly, further complicating their use as NO delivery agents. For example, photolysis or thermolysis of [NH$_4$][O_2N_2Ph] results in formation of azoxybenzene in addition to the desired product, NO,[11] whereas oxidation of [NH$_4$][O_2N_2Ph] results in formation of NO and nitrosobenzene.[12,13] Similarly, hydrolysis of *N*-(4-methoxybenzyl)guanidinium diazeniumdiolate at pH 3.1 releases NO, but also N_2O, *N*-(4-methoxybenzyl)urea, *N*'-(4-methoxybenzyl)-*N*-hydroxyguanidine, *N*-(4-methoxybenzyl)aminocyanamide, and *N*'-(4-methoxybenzyl)-*N*-nitrosoimine.[14,15] Lastly, the diazeniumdiolate-containing siderophore gramibactin generates both NO and the corresponding oxime when photolyzed.[16] The wide range of disassembly pathways and associated reaction products not only renders these reactions inefficient with respect to NO release, but the unknown reaction stoichiometries could make these complexes difficult to advance to the clinic.[5,17–19] Nonetheless, it is clear that NO release from *C*-diazeniumdiolates is possible,[20–23] although the yields of NO release are often low.[14,24]

We recently reported the synthesis of a series of triphenylmethyl (trityl) diazeniumdiolate metal complexes, namely, [K(18-crown-6)][M($O_2N_2CPh_3$)$_3$] (M = Fe, Co, Zn).[23,25] As was observed in other *C*-diazeniumdiolate systems, photolysis of these complexes led to formation of several reaction products, including NO, N_2O, Ph$_3$CN(*H*)OCPh$_3$, Ph$_3$CH, and 9-phenylfluorene. Importantly, the observation of N_2O and Ph$_3$CN(*H*)OCPh$_3$ pointed to incomplete diazeniumdiolate fragmentation, which necessarily limits the yield of NO. Additionally, the fate of the metal ion in these transformations could not be determined. It is also notable that NO release in this system was only observed upon photolysis; thermolysis or oxidation did not result in any detectable NO formation. To remedy the abovementioned drawbacks, we surmised that introduction of a co-ligand could disfavor unwanted reaction pathways and improve the yield of NO. To test this hypothesis, we examined if the well-known β-diketiminate ligand,[26] ^{Me}L (^{Me}L = {(2,6-^{i}Pr$_2$C$_6$H$_3$)NC(Me)}$_2$CH), could help confer control over the photolytic chemistry and simplify the product distribution. Herein we report the synthesis, characterization, and photochemistry of a series of β-diketiminate-supported *C*-diazeniumdiolate complexes, namely, [^{Me}LM($O_2N_2CPh_3$)] (M = Fe, Co, Cu).

RESULTS AND DISCUSSION

Synthesis of [^{Me}LM($O_2N_2CPh_3$)] (M = Fe, Co, Cu). Addition of a colorless slurry of [K(18-crown-6)][$O_2N_2CPh_3$][25] to a dark brown solution of [^{Me}LCo(μ-Br)$_2$Li(OEt$_2$)] in toluene resulted in formation of a red-orange mixture, from which [^{Me}LCo($O_2N_2CPh_3$)] (**1**) was isolated in 58% yield (Scheme 1). The Fe and Cu analogues, [^{Me}LFe($O_2N_2CPh_3$)] (**2**) and [^{Me}LCu($O_2N_2CPh_3$)] (**3**), were prepared using similar metathetical protocols (Scheme 1) and were isolated in 58% and 49%

yields, respectively. Complexes **1**–**3** are insoluble in aliphatic solvents but are soluble in Et_2O, benzene, toluene, THF, and CH_2Cl_2. All complexes are stable as solids for multiple weeks when stored at –24 °C under an inert gas atmosphere.



Scheme 1. Synthesis of diazeniumdiolate complexes **1**–**3**.

The ^1H NMR spectrum of complex **1** in C_6D_6 features resonances at -33.15 and -42.78 ppm, which are assignable to the γ-CH environment of the β-diketiminate ligand and the *p*-CH environment of the trityl group, respectively. For complex **2**, the γ-CH and trityl *p*-CH resonances are located at -4.79 and 10.40 ppm, respectively, in its ^1H NMR spectrum. Both complexes **1** and **2** only feature two ^iPr methyl environments in their ^1H NMR spectra, suggestive of C_{2v} symmetry, and indicating that their trityl diazeniumdiolate ligands are fluxional in solution. The X-band solution-phase EPR spectrum of **3** in toluene, recorded at room temperature, shows a multiplet with $g_{iso} = 2.0981$, indicative of both $^{63/65}Cu$ and ^{14}N hyperfine coupling (Figure S27). Similar spectra have been previously reported for other square planar, β-diketiminate-supported Cu(II) complexes.[27,28] The UV-vis spectra of complexes **1**–**3** in C_7H_8 all displayed strong absorptions in the 310–370 nm region, consistent with LMCT excitations (Figures S29-S31), as well as weaker absorption bands in the 400-600 nm region that are assignable to *d*-*d* transitions.

Complexes **1** and **2** both crystallized in the triclinic space group *P*-1 as the Et_2O solvates, **1**·Et_2O and **2**·Et_2O, whereas complex **3** crystallized in the orthorhombic space group *Pca*2$_1$ with two independent molecules in the asymmetric unit. The metrical parameters of the two independent molecules are very similar and only those of one will be discussed in detail. Complexes **1**·Et_2O and **2**·Et_2O are isomorphous, and their solid-state structures show the trityl diazeniumdiolate ligand is bound in a *O*,*O*-κ^2 fashion, generating distorted tetrahedral geometries (**1**: $\tau_4 = 0.81$; **2**: $\tau_4 = 0.79$)[29] around each metal center (Figures 1 and S18). In contrast, the solid-state structure of **3** reveals a distorted square planar geometry about the Cu center ($\tau_4 = 0.20$),[29] consistent with its d^9 electronic configuration. It also displays a *O*,*O*-κ^2 coordination of the diazeniumdiolate ligand, similar to other four-coordinate Cu diazeniumdiolates.[27,28,30] Complex **1** has Co–O1 and Co–O2 bond distances of 1.960(2) and 1.968(1) Å, respectively (Table 1), which are understandably shorter than those found in the octahedral Co diazeniumdiolate [K(18-crown-6)][$Co(O_2N_2CPh_3)_3$],[23] owing to the lower coordination number of **1**. Similarly, the Fe–O1 and Fe–O2 bond distances in complex **2** are shorter than those found in [K(18-crown-6)][$Fe(O_2N_2CPh_3)_3$].[23] Complex **3** features Cu–O1 and Cu–O2 bond distances of 1.972(9) and 1.94(1) Å, respectively. These distances compare relatively well with those found in the closely related square planar Cu diazeniumdiolates, [$^{Me*}LCu(O_2N_2Ar)$], ($^{Me*}L = \{(2,6\text{-}Me_2C_6H_3)NC(Me)\}_2CH$; Ar = 3,5-$Me_2C_6H_3$),[27] and [$^{CF3*}LCu(O_2N_2Ph)$] ($^{CF3*}L = \{(2,6\text{-}Me_2C_6H_3)NC(CF_3)\}_2CH$).[28] Finally, the metrical parameters of the diazeniumdiolate fragments within the three complexes are essentially identical (Table 1).

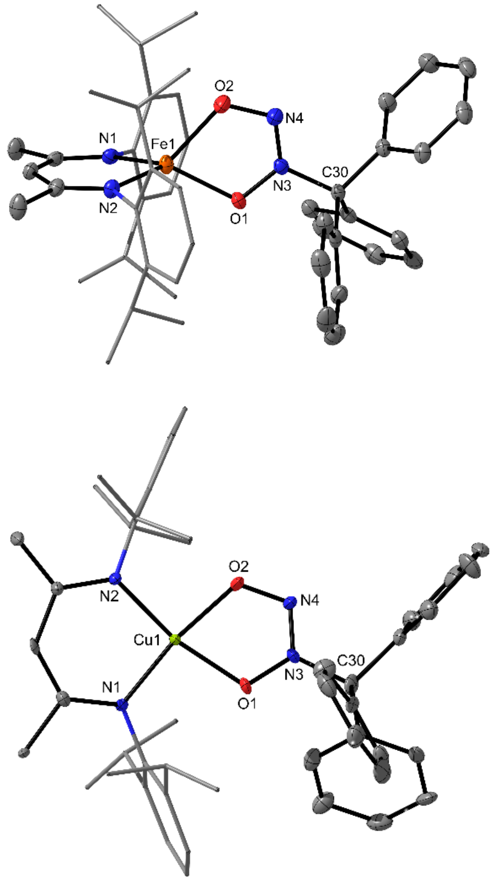


Figure 2. Solid-state structures of **2**·Et_2O (top) and **3** (bottom). Thermal ellipsoids drawn at 50% probability. Solvate molecules and hydrogen atoms omitted for clarity. Wireframe used for 2,6-$^iPr_2C_6H_3$ substituents.

Table 3. Selected bond metrics and τ_4 values for **1**·Et_2O, **2**·Et_2O, and **3**.

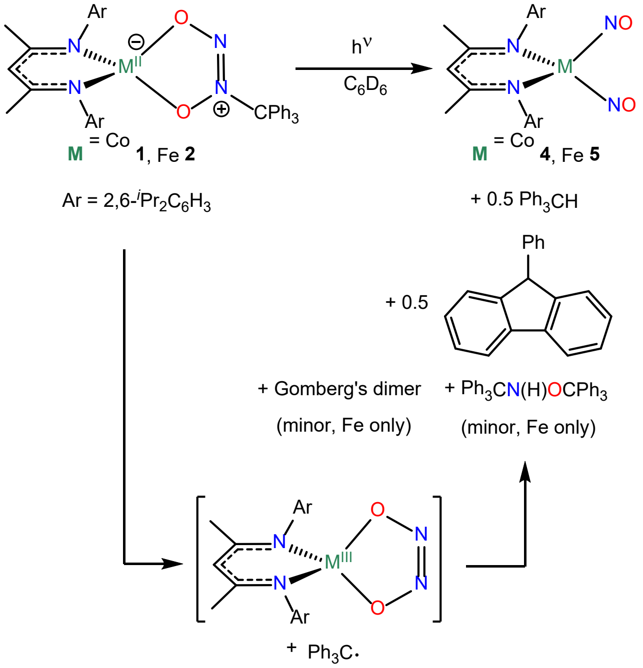
Bond/angle	**1**·Et_2O	**2**·Et_2O	3
M–O1 (Å)	1.960(2)	1.988(2)	1.972(9)
M–O2 (Å)	1.968(1)	2.006(2)	1.94(1)
M–N1 (Å)	1.945(2)	1.982(2)	1.93(1)
M–N2 (Å)	1.939(2)	1.974(2)	1.95(2)
N3–O1 (Å)	1.326(2)	1.322(3)	1.34(1)
N4–O2 (Å)	1.311(3)	1.310(3)	1.28(2)
N3–N4 (Å)	1.280(2)	1.286(2)	1.27(2)
N3–C30 (Å)	1.502(3)	1.504(4)	1.50(2)
N1–M–N2 (°)	97.56(6)	94.88(8)	96.3(5)
O1–M–O2 (°)	79.93(5)	77.20(7)	78.3(4)

τ_4	0.81	0.79	0.20

Photochemistry of [^{Me}LM($O_2N_2CPh_3$)] (M = Fe, Co, Cu). Irradiation of an orange C_6D_6 solution of **1** for 116 h with λ_{irr} = 371 nm (LED lightstrip) resulted in formation of a dark brown solution. This wavelength was chosen to facilitate comparison with our earlier results. A ^{1}H NMR spectrum of the final reaction mixture revealed the full consumption of **1**, concomitant with the clean formation of Ph_3CH, 9-phenylfluorene, and the known diamagnetic di(nitrosyl) complex, [^{Me}LCo(NO)$_2$] (**4**) (Scheme 2). Ph_3CH and 9-phenylfluorene were formed in 50% and 43% yields (calculated on the basis of trityl equivalents; Table 2), respectively, while **4** was formed in 91% yield (calculated on the basis of ^{Me}L equivalents), according to integration against an internal standard (C_6Me_6). Unlike the photolyses of [K(18-crown-6)][M($O_2N_2CPh_3$)$_3$],[23,25] no other trityl-containing products were observed in the reaction mixture. Additionally, no other β-diketiminate-containing products were present in the reaction mixture. The presence of these three products was confirmed by comparison to their reported ^{1}H NMR spectra.[25,31,32] The presence of **4** was further confirmed by the observation of diagnostic ν_{NO} bands at 1801 and 1703 cm^{-1} in the solution-phase IR spectrum of a photolyzed sample of **1** (Figure S24). These values are identical to those previously reported for this complex.[31]

To explain the observed product distribution, we hypothesize that photolysis of **1** results in an initial C–N bond homolysis to generate the Co(III) *O*,*O*-κ^2 hyponitrite complex, [^{Me}LCo(ONNO)], and $\cdot CPh_3$ (Scheme 2). The hyponitrite intermediate subsequently rearranges to form **4** via N=N bond cleavage, while $\cdot CPh_3$ undergoes disproportionation to form Ph_3CH and 9-phenylfluorene, a transformation that is known to occur upon irradiation with visible light.[33] Significantly, the near quantitative formation of Ph_3CH, 9-phenylfluorene, and **4** demonstrates the first example of complete *C*-diazeniumdiolate disassembly. In addition, this reaction confirms that the presence of a co-ligand can indeed simplify *C*-diazeniumdiolate fragmentation, as initially surmised. That said, NO release from **1** is obviously compromised as the Co center sequesters any NO generated to form **4**.

Irradiation of an amber C_6D_6 solution of **2** for 9 h with λ_{irr} = 371 nm (LED lightstrip) resulted in formation of a dark brown solution. Analysis of the final mixture by ^{1}H NMR spectroscopy revealed formation of Ph_3CH and 9-phenylfluorene as the major trityl-containing products. These two species were present in 34%, and 29% yields (calculated on the basis of trityl equivalents; Table 2), respectively, according to integration against an internal standard ($O(SiMe_3)_2$). Also present in the reaction mixture, in much smaller amounts, were Gomberg's dimer, $Ph_3CN(H)OCPh_3$, ^{Me}LH, and the diimine tautomer of ^{Me}LH.[34] The presence of these products in the reaction mixture was confirmed by comparison to their reported ^{1}H and ^{13}C NMR spectra (Figure S6 and S7).[25,34–36] Intriguingly, an IR spectrum of the photolyzed reaction mixture revealed the presence of two intense ν_{NO} bands at 1761 and 1709 cm^{-1}, which are assignable to the known β-diketiminate-supported DNIC, [^{Me}LFe(NO)$_2$] (**5**).[37] To corroborate DNIC formation, the solution-phase X-band EPR spectrum of a photolyzed sample of **2** in toluene was recorded at room temperature, which exhibited an intense isotropic signal at $g = 2.0315$. This compares well with the reported *g*-value for **5**, recorded in 2-methyltetrahydrofuran at room temperature ($g_{iso} = 2.06$), as well as the *g*-values for other DNICs.[38–42] Importantly, the observed product distribution, and thus reaction mechanism, is analogous to that seen in the photolysis of **1**. Although, the presence of small amounts of Gomberg's dimer, $Ph_3CN(H)OCPh_3$, and ^{Me}LH demonstrates that the transformation is not quite as clean as the Co example.



Scheme 2. Photolysis of complexes **1** and **2**.

Table 2. Observed product yields formed upon photolysis of **1** and **2**.

Complex	[^{Me}LM(NO)$_2$] (%)	Ph_3CH (%)	9-phenylfluorene	$Ph_3CN(H)OCPh_3$ (%)	Gomberg's dimer
1 (Co)	91^a	50^b	43^b	0^b	0^b
2 (Fe)	n.d.	34	29	12	7

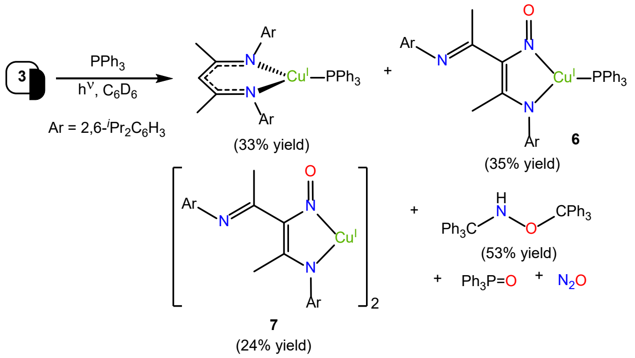
a. calculated on the basis of ^{Me}L equivalents

b. calculated on the basis of trityl equivalents

The reactions reported in Scheme 2 represent extremely rare examples of formal hyponitrite cleavage to nitric oxide, and the first example at a single metal site. In fact, the only other example of this reaction, to our knowledge, is the formation of [(OEP)FeNO] from the bimetallic *trans*-hyponitrite complex [(OEP)Fe]$_2$(μ-O_2N_2) (OEP =octaethylporphyrin), which occurs upon heating.[43] This reaction represents the microscopic reverse of hyponitrite formation in Nitric Oxide Reductase, a key denitrifying step in the global nitrogen cycle.[44–47] In contrast, the vast majority of transition metal hyponitrite complexes decompose via nitrous oxide release and "M=O" formation.[48–52]

We next monitored the photolysis of complex **3**, under the premise that NO release into the reaction medium upon diazeniumdiolate disassembly was more probable, given that Cu is much less likely to yield a stable nitrosyl complex.[53–57] To simplify the product distribution, PPh_3 was included in the reaction mixture to trap the [^{Me}LCu^I] fragment that would be formed upon diazeniumdiolate disassembly. Thus, irradiation of a red-brown C_6D_6 solution of **3**, in the presence of 1 equiv of

PPh_3, for 17 h with λ_{irr} = 371 nm (LED lightstrip) resulted in formation of a brown solution. Analysis of the reaction mixture by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy revealed the presence of the previously reported Cu(I) complex, $[^{Me}LCu(PPh_3)]$,[58] as evidenced by its diagnostic γ-CH resonances at 5.13 and 95.20 ppm in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively (Scheme 3). This product was formed in 33% yield (calculated on the basis of ^{Me}L equivalents), as determined by integration against an internal standard ($O(SiMe_3)_2$). Also present in the ^1H NMR spectrum of the final mixture are resonances assignable to the Cu(I) phosphine complex, $[(ArNC^{Me}C(\mathit{N}O)C^{Me}\mathit{N}Ar)Cu(PPh_3)]$ (**6**). This species is formed in 35% yield (calculated on the basis of ^{Me}L equivalents), as judged by the ^1H NMR spectrum, and it features ^1H resonances consistent with a C_S-symmetric ^{Me}L ligand and with no γ-H resonance. This spectral signature is indicative of β-diketiminate nitrosation. An additional β-diketiminate-containing species is also present in the reaction mixture. This species is formed in 24% yield (calculated on the basis of ^{Me}L equivalents), and it also features a C_S-symmetric ^{Me}L ligand with no γ-H resonance consistent with γ-nitrosation. We have tentatively assigned these resonances to a bimetallic Cu(I) product, $[(ArNC^{Me}C(\mathit{N}O)C^{Me}\mathit{N}Ar)Cu]_2$ (**7**). In contrast to the photolysis of **1** and **2**, the major trityl-containing species in the Cu reaction is $Ph_3CN(\mathit{H})OCPh_3$, formed in 53% yield, while Ph_3CH and 9-phenylfluorene are present in only 4% yields each (yields calculated on the basis of trityl equivalents). The ^{31}P NMR spectrum of the mixture (Figure S10) shows resonances assignable to $[^{Me}LCu(PPh_3)]$, **6**, and Ph_3PO. The latter species is formed in 15% yield (calculated on the basis of PPh_3 equivalents). Additionally, N_2O is generated during the photolysis, as ascertained via solution-phase IR spectroscopy (ν_{NN} = 2222 cm^{-1}).[52] Finally, analysis of the reaction headspace using a NO analyzer revealed formation of NO, but in only 0.2% yield (Figure S32).



Scheme 3. Photolysis of complex **3**.

To explain the observed product distribution, we propose that photolysis of **3** results in an initial C–N bond cleavage, forming $\cdot CPh_3$ and the putative hyponitrite complex, $[^{Me}LCu(ONNO)]$. The latter species is reduced by PPh_3 to form $[^{Me}LCu]$, Ph_3PO, and N_2O, whereas the former species reacts with intact **3** to generate $Ph_3CN(\cdot)OCPh_3$ as well as NO and $[^{Me}LCu]$. $[^{Me}LCu]$ is then captured by PPh_3 to generate known $[^{Me}LCu(PPh_3)]$.[58] Finally, addition of NO across the γ-C and Cu atoms of $[^{Me}LCu(PPh_3)]$ or $[^{Me}LCu]$ results in formation of a tripodal κ^3-*O*,*N*,*N* Cu(I) intermediate, from which an H atom is scavenged by $Ph_3CN(\cdot)OCPh_3$ to yield $Ph_3CN(\mathit{H})OCPh_3$ and complexes **6** or **7**. In support of the proposed mechanism, we note that similar tripodal κ^3-*O*,*N*,*N* intermediates have been documented in the reactions of β-diketiminates with a variety of unsaturated substrates.[59–65] Moreover, Grützmacher and co-workers have recently shown that a transiently-formed rhodium(III) hyponitrite complex reacts with H_2 to form H_2O and N_2O,[66] suggesting that $[^{Me}LCu(ONNO)]$ could be capable of O-atom transfer to PPh_3. Finally, the mechanism is consistent with the trace amounts of NO formed during the reaction, as all NO equivalents should be consumed by N_2O formation or ligand nitrosation. In an effort to confirm the formulations of **6** and **7**, we recorded an ESI-mass spectrum, recorded in CH_3CN in positive ion mode, of the photolyzed reaction mixture (Figures S33-S38). The spectrum features a prominent peak at 769.60 *m*/*z*, which is assignable to $[\mathbf{6}\text{–}2H]^+$ (calcd 769.32 *m*/*z*). Also observed in the spectrum is a species that can be formulated as $[(ArNC^{Me}C(\mathit{N}O)C^{Me}\mathit{N}Ar)Cu_2(PPh_3)_2]^+$, as evidenced by the peak at 1096.72 *m*/*z* (calcd 1096.36 *m*/*z*). We suggest this species is formed upon fragmentation and dimerization of **6**. We also recorded an ESI-mass spectrum of the photolyzed reaction mixture in negative ion mode (Figures S39 and S40). This spectrum features a peak at 544.26 *m*/*z*, which is assignable to $[\mathbf{6}\text{–}PPh_3\text{+}Cl]^-$ (calcd 544.22 *m*/*z*), and further supports our formulation of complex **6**. Unfortunately, in neither spectrum do we observe a peak that could be assigned to complex **7** (calcd 1020.39 *m*/*z*).

Attempts to isolate **6** or **7** directly from the reaction mixture were unsuccessful; however, photolysis of **3** in the presence of 2 equiv of PPh_3 resulted in formation of a pink solution from which $[(ArNC^{Me}C(\mathit{N}O)C^{Me}\mathit{N}Ar)Cu(PPh_3)_2]$ (**8**) was isolated as bright pink crystals. The solid-state structure of complex **8** confirms that the γ-C position of the ^{Me}L ligand has been nitrosated and that the new nitroso group is coordinated to the Cu center (Figure S19). A similar binding mode is observed in $[^{Me*}LCu(ArNC^{Me}C(\mathit{N}O)C^{Me}\mathit{N}Ar)]$ (Ar = 2,6-$Me_2C_6H_3$).[67] Importantly, its characterization demonstrates that the ^{Me}L ligand can act as a NO sink, as outlined in Scheme 3. Furthermore, it adds to previous reports of reactivity between β-diketiminate ligands and NO.[59,67] Finally, its structural characterization supports our formulation of **6** and implies that complex **8** should, in principle, be formed by reaction of **6** with another equiv of PPh_3. Gratifyingly, addition of a second equivalent of PPh_3 to a photolyzed mixture of complex **3** and 1 equiv of PPh_3 led to consumption of **6** and formation of **8**, according to ^1H NMR spectroscopy (Figure S13). Complex **7** does not react with PPh_3 under these conditions. Lastly, we note that complex **7** is also formed when **3** is photolyzed in the absence of PPh_3 (Figure S17), demonstrating that it does not contain PPh_3. Additionally, complex **7** is the only γ-nitrosated product formed in this reaction, according to the ^1H NMR spectrum of the reaction mixture. Yet, despite all attempts, complex **7** could still not be isolated. While its exact formulation remains unclear, we prefer a bimetallic formulation containing a bridging nitrosated ^{Me}L ligand, which is inert to phosphine coordination, most likely because all the coordination sites are occupied by the multidentate nitrosated diketiminate ligand.

CONCLUSIONS

We have synthesized and characterized a series of β-diketiminate-supported *C*-diazeniumdiolate complexes $[^{Me}LM(O_2N_2CPh_3)]$ (M = Fe, Co, Cu). When the Fe and Co analogues are photolyzed, the corresponding dinitrosyl complexes $[^{Me}LM(NO)_2]$ are formed in good yields, via a putative

O,*O*-κ^2 hyponitrite [^{Me}LM(ONNO)] intermediate. These reactions are remarkable examples of hyponitrite cleavage to nitric oxide, which is the microscopic reverse of hyponitrite formation in Nitric Oxide Reductase. In contrast, when the Cu analogue is photolyzed, no metal nitrosyl complexes were obtained and only minute quantities of NO were detected. Instead, the Cu(I) complexes, [^{Me}LCu(PPh_3)], [(ArNC^{Me}C(*N*O)C^{Me}*N*Ar)Cu(PPh_3)], and [(ArNC^{Me}C(*N*O)C^{Me}*N*Ar)Cu]$_2$ were formed, in addition to N_2O, Ph_3PO, and Ph_3CN(*H*)$OCPh_3$. Overall, this work demonstrates that the use of a co-ligand can significantly alter the disassembly pathways of *C*-diazeniumdiolates, as initially surmised. In addition, the change in product distribution demonstrates that *C*-diazeniumdiolate disassembly is highly metal-dependent. While NO release in each case is thwarted by either metal or ligand nitrosylation, these results suggest that through judicious selection of the metal and/or co-ligand, efficient NO release from the *C*-diazeniumdiolate fragment could be possible.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, crystallographic data, and spectral data for complexes **1**–**8** (CIF, PDF)

Accession Codes

CCDC 2260891–2260894 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Photolysis of the *C*-diazeniumdiolate complexes, $[^{Me}LM(O_2N_2CPh_3)]$ ($^{Me}L = \{(2,6\text{-}^iPr_2C_6H_3)NC(Me)\}_2CH$; M = Fe, Co), results in complete disassembly of their *C*-diazeniumdiolate ligands to yield $[^{Me}LM(NO)_2]$, via a proposed hyponitrite intermediate