Photolytic or Oxidative Fragmentation of Trityl Diazeniumdiolate ($O_2N_2CPh_3^-$): Evidence for both C–N and N–N Bond Cleavage

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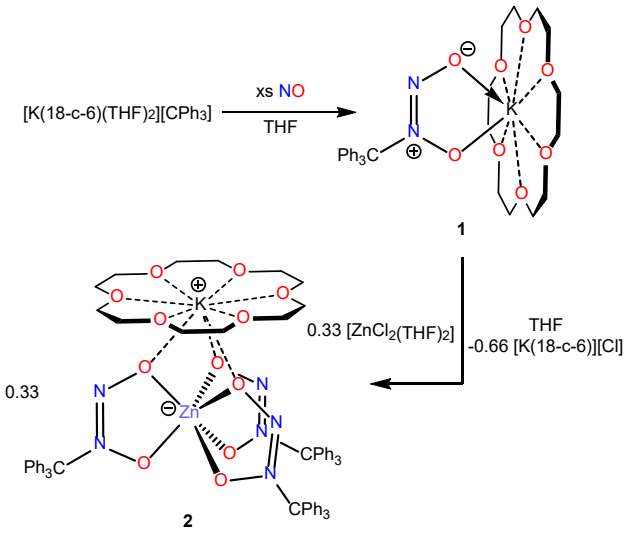
ABSTRACT: Exposure of [K(18-crown-6)(THF)$_2$][CPh_3] to an atmosphere of NO cleanly generates [K(18-crown-6)][$O_2N_2CPh_3$] (**1**) in excellent yields. Subsequent reaction of [$ZnCl_2$(THF)$_2$] with 3 equiv of **1** affords the *C*-diazeniumdiolate complex, [K(18-crown-6)][Zn($O_2N_2CPh_3$)$_3$] (**2**). Both **1** and **2** were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and their structures were confirmed by X-ray crystallography. Photolysis of **2** using 371 nm light resulted in formation of three trityl-containing products, namely, Ph_3CH, 9-phenylfluorene, and *N*,*O*-ditritylhydroxylamine (**3**). In addition, we detected N_2O, as well as small amounts of NO in the reaction mixture. In contrast, oxidation of **2** with 1.2 equiv of [Ag(MeCN)$_4$][PF_6] resulted in formation of O(CPh_3)$_2$ as the major trityl-containing product; N_2O was also detected in the reaction mixture, but NO was not apparently formed in this case. The observation of these fragmentation products indicates that the [$O_2N_2CPh_3$]$^-$ ligand is susceptible to both C–N bond and N–N bond cleavage. Moreover, the different product distributions suggest that [$O_2N_2CPh_3$]$^-$ is susceptible to different modes of fragmentation.

Nitric oxide (NO) is an important intracellular signaling molecule that has an enormous influence on the cardiovascular system.[1, 2] As such, the discovery and development of NO delivery agents has been explored extensively.[3-8] Although there are multiple classes of delivery agents, *N*-diazeniumdiolates (*N*-DAZDs) remain one of the most promising, having already advanced to clinical testing in some cases.[9-11] *N*-DAZDs are characterized by the presence of an *N*-bound ONNO linkage and are known to release NO upon application of a variety of stimuli, including light.[4-6, 12-14]

Despite being the most developed subclass, *N*-DAZDs can generate potentially carcinogenic *N*-nitroso compounds upon NO release.[3, 12, 13, 15-19] The development of new NO-releasing *C*-DAZDs could overcome this drawback.[3] However, *C*-DAZDs generally decompose by N_2O release and not NO formation.[4, 20-22] Nonetheless, some are known to release NO under certain conditions. For example, cupferronate ([O_2N_2Ph]$^-$) and its derivatives have been reported to release NO upon photolysis.[23-29] They can also release NO upon oxidation.[30-32] The *C*-DAZD motif is found in some siderophores, which reportedly can release NO, as well.[33, 34]

To alleviate the paucity of NO-releasing *C*-DAZDs, we focused on the identity of the *C* substituent. In particular, we sought to isolate a *C*-DAZD featuring the redox-active triphenylmethyl (trityl) group. This substituent can exist in anionic and cationic forms,[35, 36] and also as a neutral radical, which is in equilibrium with Gomberg's dimer.[37-39] We have previously used the favorable redox properties of this group to generate metal-ligand multiple bonds[40-44] and polychalcogenide complexes[45] via C–E (E = O, S) bond cleavage. Additionally, the trityl complexes [M^{II}(CPh_3)$_2$] (M = Fe, Ni) have proven to be good M(0) synthons due to the facile formation of ·CPh_3.[46, 47] Accordingly, we reasoned that the C–N bond of a trityl *C*-DAZD would be especially susceptible to cleavage, enhancing its ability to release NO. Herein, we report the synthesis and characterization of the first *C*-DAZD complex supported by a trityl group, as well as its response to photolysis and oxidation.

To synthesize the trityl *C*-DAZD motif, a deep red THF solution of [K(18-crown-6)(THF)$_2$][CPh_3][43] was exposed to an atmosphere of NO with vigorous stirring. Upon NO addition, the red solution quickly bleached to pale yellow. Work-up of the reaction mixture afforded [K(18-crown-6)][$O_2N_2CPh_3$] (**1**) in 92 % yield (Scheme 1). This synthetic method takes advantage of the nucleophilic carbon in the trityl anion, a common strategy in the preparation of *C*-DAZDs.[4, 48-51] Compound **1** is moderately soluble in benzene, toluene, and THF, but very soluble in CH_2Cl_2. With **1** in hand, we considered the synthesis of a Zn trityl DAZD complex, namely [K(18-crown-6)][Zn($O_2N_2CPh_3$)$_3$] (**2**). This complex could ostensibly release 6 equiv of NO per molecule, making it an attractive therapeutic. Thus, reaction of [$ZnCl_2$(THF)$_2$] with 3 equiv of **1** in THF, generated a turbid reaction mixture from which colorless **2** could be isolated in 84 % yield after work-up (Scheme 1). Complex **2** is insoluble in aliphatic solvents, sparingly soluble in Et_2O, and soluble in benzene, toluene, THF, and CH_2Cl_2. It is stable to ambient light for weeks under an inert atmosphere at room temperature; furthermore, it does not react with water (Figure S10).



Scheme 1. Synthesis of trityl *C*-DAZD complexes 1 and 2.

Complexes **1** and **2** were both characterized by X-ray crystallography. The solid-state structure for **1** reveals a trityl *C*-DAZD fragment with a *O,O*-κ² binding mode (Figure 1, top). Its N–N and C–N distances are 1.304(4) Å and 1.510(4) Å, respectively, whereas its N–O distances are 1.299(3) and 1.282(3) Å (Table 1). For comparison, the N–N and C–N distances in **1** are similar to those of $[Al(O_2N_2Cy)_3]$[52] (N–N = 1.264(4) Å, C–N = 1.486(5) Å) and $[Fe(O_2N_2Ph)_3]$[53] (N–N = 1.30 Å, C–N = 1.42 Å). The N–O bond lengths in **1** also compare well with those of $[Al(O_2N_2Cy)_3]$ (1.329(4) and 1.320(4) Å) and $[Fe(O_2N_2Ph)_3]$ (1.33 and 1.32 Å).

Complex **2** crystallized in the monoclinic space group *C*2/*c* as a toluene and 18-crown-6 solvate, **2**·2C₇H₈·0.5C₁₂H₂₄O₆ (Figure 1, bottom). The Zn center in **2** is coordinated by three trityl *C*-DAZD ligands, also via the *O,O*-κ² binding mode, to give a distorted octahedral coordination geometry. In addition, each trityl group is oriented toward the same hemisphere, generating a *C*₃-symmetric complex. In contrast, one R substituent in both $[Al(O_2N_2Cy)_3]$ and $[Fe(O_2N_2Ph)_3]$ is oriented toward the opposite hemisphere of the other two. The different stereochemistry of **2** is most likely due to the presence of the $[K(18\text{-crown-6})]^+$ ion, which binds to one oxygen atom of each *C*-DAZD ligand. The Zn–O distances in **2** range from 2.022(6) to 2.101(5) Å, which are comparable to that of [Na][Zn(acac)₃] (2.076(1) Å).[54] Additionally, the average N–N (1.27 Å) and C–N distances (1.50 Å) in **2** are similar to those in **1**, $[Al(O_2N_2Cy)_3]$, and $[Fe(O_2N_2Ph)_3]$. Finally, its average N–O distance (1.31 Å) also compares well with the aforementioned complexes.

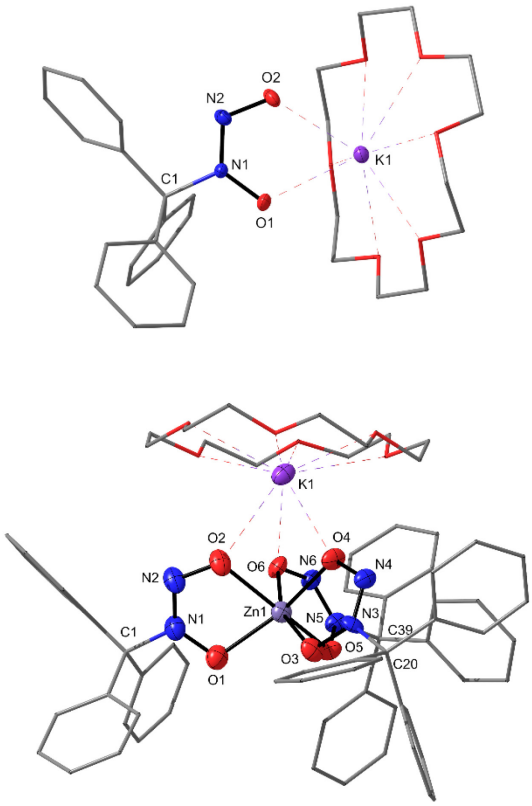


Figure 1. Solid-state structures of **1** (top) and **2**·2C₇H₈·0.5C₁₂H₂₄O₆ (bottom). Thermal ellipsoids drawn at 50% probability. Solvate molecules and hydrogen atoms omitted for clarity. Trityl and 18-crown-6 groups shown in wireframe.

Table 1. Selected bond lengths and angles for **1** and **2**·2C₇H₈·0.5C₁₂H₂₄O₆. O_{prox} denotes the oxygen atoms closest to the trityl substituent, whereas O_{dist} denotes those farthest from it. The same notation is used for nitrogen atoms.

Bond/angle	1	**2**·2C₇H₈·0.5C₁₂H₂₄O₆
M–O_{prox} (Å)	2.688(2)	2.022(6), 2.050(4), 2.076(4)
M–O_{dist} (Å)	2.598(2)	2.101(5), 2.073(5), 2.100(5)
N_{prox}–O_{prox} (Å)	1.299(3)	1.307(8), 1.310(8), 1.314(8)
N_{dist}–O_{dist} (Å)	1.282(3)	1.310(9), 1.305(7), 1.297(7)
N_{prox}–N_{dist} (Å)	1.304(4)	1.278(9), 1.266(9), 1.278(8)
N_{prox}–C (Å)	1.510(4)	1.50(1), 1.497(9), 1.502(8)
O_{prox}–M–O_{dist} (°)	57.78(6)	75.8(2), 74.9(2), 74.9 (2)

The ^{1}H NMR spectrum of **1** in C_6D_6 features resonances at 7.80 and 7.13 ppm, assignable to *o*-CH and overlapping *m*- and *p*-CH environments, respectively. These resoances are present in the expected 2:3 ratio. Similarly, the ^{1}H NMR spectrum of **2** in C_6D_6 features resonances at 7.48, 7.02, and 6.98 ppm, which are assignable to the *o*-, *p*-, and *m*-CH environments, respectively. Finally, the UV-vis spectrum of

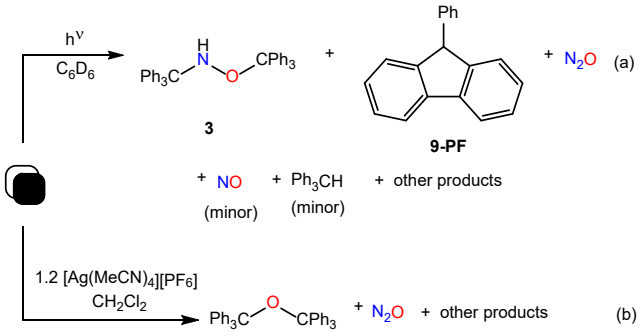
2 (0.18 mM) in C_6H_6 reveals an intense peak in the UV region, but with minimal absorption past 340 nm, consistent with its d^{10} electronic configuration.

Despite its poor absorption properties in the visible region, the photochemistry of complex **2** was surveyed. Irradiation of a colorless solution of **2** in C_6D_6 with a 371 nm LED source for 9 d resulted in formation of a pale brown solution, concomitant with deposition of a tan brown solid.[55] Analysis of this solution by ^{1}H NMR spectroscopy revealed the complete consumption of **2**, along with the presence of three new trityl-containing products: 9-phenylfluorene (9-PF), Ph_3CH, and $Ph_3CN(H)OCPh_3$ (**3**) (Scheme 2a), as evidenced by diagnostic EH (E = C, N) resonances at 4.81, 5.42, and 5.91 ppm, respectively.[46, 56, 57] These three species are present in 23%, 7%, and 48% yields (calculated on the basis of trityl equivalents; Figure S7), respectively, as determined by integration against an internal standard (C_6Me_6). Notably, no other trityl-containing products were observed in this spectrum, including Gomberg's dimer, Ph_3COH, $Ph_3CN(H)OH$,[56] or Ph_3CNH_2. Our assignments were further confirmed by $^{13}C\{^1H\}$ NMR spectroscopy. In particular, the $^{13}C\{^1H\}$ NMR spectrum of the reaction mixture features resonances at 89.71 and 74.38 ppm, which are assignable to the two unique $C_{quaternary}$ environments of **3** (Figures S8 and S13). Also present in this spectrum were resonances at 57.31 and 54.92 ppm, which are assignable to the methine CH environments of Ph_3CH and 9–PF, respectively.[46, 57] Further analysis of the reaction mixture revealed the presence N_2O, which is formed in 51% yield (calculated assuming a maximum of 3 equiv. N_2O produced), according to analysis by GC-MS (Figure S32). We also observe formation of NO in the reaction mixture; however, it is only formed in 0.12% yield (calculated assuming a maximum of 3 equiv. NO produced), according to analysis with a Nitric Oxide Analyzer (Figure S38). Finally, heating a C_6D_6 solution of **2** to 52 °C in the absence of light resulted in no reaction (Figure S11), even after 7 d, demonstrating that product formation is photo-initiated, even though **2** barely absorbs in the visible region.

While we cannot yet fully balance Scheme 2a, it is apparent that **3** is derived from N-N bond cleavage, whereas N_2O and 9-PF are derived from C-N bond cleavage. Moreover, the NH proton on **3** is likely derived from a $Ph_3C\cdot$ fragment, which is known to undergo facile H-atom abstraction to form 9-PF.[58] This suggestion nicely accounts for the formation of **3** and 9-PF in a ca. 1:1 molar ratio in the final reaction mixture. We also note that Ph_3CH is predominately formed during the later stages of the reaction (Figure S7), suggesting that it may form upon photo-degradation of **3**. Consistent with this hypothesis, photolysis of a sample of independently-prepared **3** in C_6D_6 does result in formation of both Ph_3CH and 9-PF, among other products, as assayed by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy (see Figures S14 and S15).

We also surveyed the response of complex **2** to oxidation. Thus, addition of 1.2 equiv of $[Ag(MeCN)_4][PF_6]$ to a CH_2Cl_2 solution of **2** resulted in formation of a deep brown suspension, consistent with Ag^0 formation (Scheme 2b). Analysis of the reaction mixture with $^{13}C\{^1H\}$ NMR spectroscopy revealed the presence of one major trityl-containing product, namely, $O(CPh_3)_2$ (Scheme 2),[59] which was identified by its diagnostic $C_{quaternary}$ resonance at 90.26 ppm. This species is present in 43% yield (calculated on the basis of trityl equivalents; Figure S19). A second minor, trityl-containing product is also present in this sample, but it could not be identified. N_2O is also formed during the reaction, as revealed by analysis of the reaction headspace using GC-MS. It is formed in 63% yield (calculated assuming a maximum of 3 equiv. N_2O produced, Figure S33). However, we were unable to detect NO in the reaction mixture, according to a two-vial trapping experiment with [T(OMe)PP]Co.[60] Intriguingly, we see no evidence for products derived from N-N bond cleavage in the reaction mixture, as both $O(CPh_3)_2$ and N_2O are evidently derived from C-N bond cleavage. Their formation, along with the absence of NO, **3**, and 9-PF, demonstrates that an entirely different mechanism of trityl hyponitrite fragmentation is operative.

For comparison with our trityl diazeniumdiolate results, we synthesized the Zn cupferronate complex, $[Zn(O_2N_2Ph)_2(py)_2]$ (**4**, see SI for full characterization details), and measured its response to photolysis under the same conditions used for complex **2**. Irradiation of **4** did not result in formation of detectable amounts of N_2O (Figure S34); however, it did result in formation of NO (Figure S39). These data are reminiscent of the photolysis of cupferron itself (e.g., $[NH_4][O_2N_2Ph]$), which results in formation NO and azoxybenzene, but no N_2O.[23] That said, complex **4** proved much more robust toward photolysis than **2**, in-line with our initial hypothesis.



Scheme 2. Reactivity of **2** upon photolysis or oxidation.

In summary, we have synthesized and characterized the *C*-DAZD-containing Zn complex, [K(18-crown-6)][$Zn(O_2N_2CPh_3)_3$]. Photolysis of this complex results in formation of N_2O, 9-phenylfluorene, and $Ph_3CN(H)OCPh_3$ as the major products. The presence of 9-phenylfluorene and N_2O in the final reaction mixture suggests that the $[O_2N_2CPh_3]^-$ fragment is susceptible to C–N bond cleavage, as initially anticipated; however, N–N bond cleavage is also occurring, as revealed by the formation of $Ph_3CN(H)OCPh_3$. In contrast, oxidation of [K(18-crown-6)][$Zn(O_2N_2CPh_3)_3$] results solely in observation of the products of C–N bond cleavage, namely, $O(CPh_3)_2$ and N_2O. Both reactions represent new modes of *C*-DAZD fragmentation. While significant NO evolution from this platform was not achieved, the identification of these new fragmentation pathways should allow us to design new *C*-DAZDs that favor NO release.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, crystallographic details (as CIF files), and spectral data for compounds

1–4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Furchgott, R. F.; Zawadzki, J. V., The obligatory role of endothelial cells in the relaxation of arterial smooth muscle by acetylcholine. *Nature* **1980**, *288*, 373-376.
2. Ignarro, L. J.; Byrns, R. E.; Buga, G. M.; Wood, K. S., Endothelium-derived relaxing factor from pulmonary artery and vein possesses pharmacologic and chemical properties identical to those of nitric oxide radical. *Circ. Res.* **1987**, *61*, 866-879.
3. Wang, P. G.; Xian, M.; Tang, X.; Wu, X.; Wen, Z.; Cai, T.; Janczuk, A. J., Nitric Oxide Donors: Chemical Activities and Biological Applications. *Chem. Rev.* **2002**, *102*, 1091-1134.
4. Hrabie, J. A.; Keefer, L. K., Chemistry of the Nitric Oxide-Releasing Diazeniumdiolate ("Nitrosohydroxylamine") Functional Group and Its Oxygen-Substituted Derivatives. *Chem. Rev.* **2002**, *102*, 1135-1154.
5. Miller, M. R.; Megson, I. L., Recent developments in nitric oxide donor drugs. *Br. J. Pharmacol.* **2007**, *151*, 305-321.
6. Paul, S.; Pan, S.; Mukherjee, A.; De, P., Nitric Oxide Releasing Delivery Platforms: Design, Detection, Biomedical Applications, and Future Possibilities. *Mol. Pharm.* **2021**, *18*, 3181-3205.
7. Wright, A. M.; Zaman, H. T.; Wu, G.; Hayton, T. W., Nitric Oxide Release from a Nickel Nitrosyl Complex Induced by One-Electron Oxidation. *Inorg. Chem.* **2013**, *52*, 3207-3216.
8. Ford, P. C., Metal complex strategies for photo-uncaging the small molecule bioregulators nitric oxide and carbon monoxide. *Coord. Chem. Rev.* **2018**, *376*, 548-564.
9. Knox, C. D.; de Kam, P. J.; Azer, K.; Wong, P.; Ederveen, A. G.; Shevell, D.; Morabito, C.; Meehan, A. G.; Liu, W.; Reynders, T.; Denef, J. F.; Mitselos, A.; Jonathan, D.; Gutstein, D. E.; Mitra, K.; Sun, S. Y.; Lo, M. M. C.; Cully, D.; Ali, A., Discovery and Clinical Evaluation of MK-8150, A Novel Nitric Oxide Donor With a Unique Mechanism of Nitric Oxide Release. *J. Am. Heart Assoc.* **2016**, *5*, e003493.
10. Zhong, Y.-L.; Muzzio, D. J.; Weisel, M.; Zhang, L.; Humphrey, G. R.; Maloney, K. M.; Campos, K. R., Development of a Scalable and Safer Synthesis of Diazeniumdiolates. *Org. Process Res. Dev.* **2020**, *24*, 1602-1608.
11. Zhong, Y.-L.; Weisel, M.; Humphrey, G. R.; Muzzio, D. J.; Zhang, L.; Huffman, M. A.; Zhong, W.; Maloney, K. M.; Campos, K. R., Scalable Synthesis of Diazeniumdiolates: Application to the Preparation of MK-8150. *Org. Lett.* **2019**, *21*, 4210-4214.
12. Pavlos, C. M.; Cohen, A. D.; D'Sa, R. A.; Sunoj, R. B.; Wasylenko, W. A.; Kapur, P.; Relyea, H. A.; Kumar, N. A.; Hadad, C. M.; Toscano, J. P., Photochemistry of 1-(*N*,*N*-Diethylamino)diazen-1-ium-1,2-diolate: An Experimental and Computational Investigation. *J. Am. Chem. Soc.* **2003**, *125*, 14934-14940.
13. Pavlos, C. M.; Xu, H.; Toscano, J. P., Controlled photochemical release of nitric oxide from O_2-substituted diazeniumdiolates. *Free Radic. Biol. Med.* **2004**, *37*, 745-752.
14. Weinstain, R.; Slanina, T.; Kand, D.; Klán, P., Visible-to-NIR-Light Activated Release: From Small Molecules to Nanomaterials. *Chem. Rev.* **2020**, *120*, 13135-13272.
15. Keefer, L. K.; Nims, R. W.; Davies, K. M.; Wink, D. A., "NONOates" (1-substituted diazen-1-ium-1,2-diolates) as nitric oxide donors: Convenient nitric oxide dosage forms. In *Methods in Enzymology*, Academic Press: 1996; Vol. 268, pp 281-293.
16. Ragsdale, R. O.; Karstetter, B. R.; Drago, R. S., Decomposition of the Adducts of Diethylamine and Isopropylamine with Nitrogen(II) Oxide. *Inorg. Chem.* **1965**, *4*, 420-422.
17. Barnes, J. M.; Magee, P. N., Some Toxic Properties of Dimethylnitrosamine. *Br. J. Ind. Med.* **1954**, *11*, 167-174.
18. Mirvish, S. S., *N*-nitroso compounds: Their chemical and in vivo formation and possible importance as environmental carcinogens. *J. Toxicol. Environ. Health* **1977**, *2*, 1267-1277.
19. Spiegelhalder, B.; Preussmann, R., Contamination of toiletries and cosmetic products with volatile and nonvolatile *N*-nitroso carcinogens. *J. Cancer Res. Clin. Oncol.* **1984**, *108*, 160-163.
20. Ishwara Bhat, J.; Clegg, W.; Maskill, H.; J. Elsegood, M. R.; D. Menneer, I.; C. Miatt, P., *N*-Nitroso-*N*,*O*-dialkylhydroxylamines: preparation, structure, and mechanism of the hydronium ion catalysed solvolytic nitrous oxide extrusion reaction. *J. Chem. Soc., Perkin Trans. 2* **2000**, *0*, 1435-1446.
21. Yandovskii, V. N.; Gidaspov, B. V.; Tselinskii, I. V., The Formation of the Azoxy-group in Reactions Involving Anions with Nitrogen–Nitrogen Bonds. *Russ. Chem. Rev.* **1980**, *49*, 237.
22. S. Evans, A.; P. Toscano, J., The Chemistry of NO- and HNO-Producing Diazeniumdiolates. In *PATAI'S Chemistry of Functional Groups*, John Wiley & Sons, Ltd: 2010.
23. Hwu, J. R.; Yau, C. S.; Tsay, S.-C.; Ho, T.-I., Thermal- and photo-induced transformations of N-aryl-*N*-nitrosohydroxylamine ammonium salts to azoxy compounds. *Tetrahedron Lett.* **1997**, *38*, 9001-9004.
24. Hou, Y.; Xie, W.; Janczuk, A. J.; Wang, P. G., *O*-Alkylation of Cupferron: Aiming at the Design and Synthesis of Controlled Nitric Oxide Releasing Agents. *J. Org. Chem.* **2000**, *65*, 4333-4337.
25. Hou, Y.; Xie, W.; Ramachandran, N.; Mutus, B.; Janczuk, A. J.; Wang, P. G., *O*-Alkylation chemistry of neocupferron. *Tetrahedron Lett.* **2000**, *41*, 451-456.
26. Blangetti, M.; Fraix, A.; Lazzarato, L.; Marini, E.; Rolando, B.; Sodano, F.; Fruttero, R.; Gasco, A.; Sortino, S., A Non-metal-Containing Nitric Oxide Donor Activated with Single-Photon Green Light. *Chem. Eur. J.* **2017**, *23*, 9026-9029.

27. Keefer, L. K., Fifty Years of Diazeniumdiolate Research. From Laboratory Curiosity to Broad-Spectrum Biomedical Advances. *ACS Chem. Biol.* **2011**, *6*, 1147-1155.

28. Levy, E. S.; Morales, D. P.; Garcia, J. V.; Reich, N. O.; Ford, P. C., Near-IR mediated intracellular uncaging of NO from cell targeted hollow gold nanoparticles. *Chem. Commun.* **2015**, *51*, 17692-17695.

29. Kunkely, H.; Vogler, A., Photoredox reaction of iron(III) cupferronate. Release of NO induced by ligand-to-metal charge transfer excitation. *Inorg. Chim. Acta* **2003**, *346*, 275-277.

30. Lawless, J. G.; Hawley, M. D., Electrochemical oxidation of cupferron. *Anal. Chem.* **1968**, *40*, 948-951.

31. Hou, Y.; Chen, Y.; A. Amro, N.; Wadu-Mesthrige, K.; R. Andreana, P.; Liu, G.-y.; G. Wang, P., Nanomolar scale nitric oxide generation from self-assembled monolayer modified gold electrodes. *Chem. Commun.* **2000**, 1831-1832.

32. McGill, A. D.; Zhang, W.; Wittbrodt, J.; Wang, J.; Schlegel, H. B.; Wang, P. G., *para*-substituted N-Nitroso-*N*-oxybenzenamine ammonium salts: a new class of redox-sensitive nitric oxide releasing compounds. *Bioorg. Med. Chem.* **2000**, *8*, 405-412.

33. Hermenau, R.; Ishida, K.; Gama, S.; Hoffmann, B.; Pfeifer-Leeg, M.; Plass, W.; Mohr, J. F.; Wichard, T.; Saluz, H.-P.; Hertweck, C., Gramibactin is a bacterial siderophore with a diazeniumdiolate ligand system. *Nat. Chem. Biol.* **2018**, *14*, 841-843.

34. Hermenau, R.; Mehl, J. L.; Ishida, K.; Dose, B.; Pidot, S. J.; Stinear, T. P.; Hertweck, C., Genomics-Driven Discovery of NO-Donating Diazeniumdiolate Siderophores in Diverse Plant-Associated Bacteria. *Angew. Chem. Int. Ed.* **2019**, *58*, 13024-13029.

35. Buncel, E.; Menon, B., Carbanion mechanisms. 9. Spectrophotometric study of triphenylmethyl alkali metal salts. Contact and solvent-separated ion pairs in ethereal solvents. *J. Org. Chem.* **1979**, *44*, 317-320.

36. Hinz, A.; Labbow, R.; Reiß, F.; Schulz, A.; Sievert, K.; Villinger, A., Synthesis and structure of tritylium salts. *Struct. Chem.* **2015**, *26*, 1641-1650.

37. Gomberg, M., AN INSTANCE OF TRIVALENT CARBON: TRIPHENYLMETHYL. *J. Am. Chem. Soc.* **1900**, *22*, 757-771.

38. Gomberg, M., ON TRIVALENT CARBON. *J. Am. Chem. Soc.* **1901**, *23*, 496-502.

39. Lankamp, H.; Nauta, W. T.; MacLean, C., A new interpretation of the monomer-dimer equilibrium of triphenylmethyl- and alkylsubstituted-diphenyl methyl-radicals in solution. *Tetrahedron Lett.* **1968**, *9*, 249-254.

40. Baeza Cinco, M. Á.; Wu, G.; Kaltsoyannis, N.; Hayton, T. W., Synthesis of a "Masked" Terminal Zinc Sulfide and Its Reactivity with Brønsted and Lewis Acids. *Angew. Chem. Int. Ed.* **2020**, *59*, 8947-8951.

41. Hartmann, N. J.; Wu, G.; Hayton, T. W., Synthesis of a "Masked" Terminal Nickel(II) Sulfide by Reductive Deprotection and its Reaction with Nitrous Oxide. *Angew. Chem. Int. Ed.* **2015**, *54*, 14956-14959.

42. Hartmann, N. J.; Wu, G.; Hayton, T. W., Trapping of an Ni^{II} Sulfide by a Co^{I} Fulvene Complex. *Organometallics* **2017**, *36*, 1765-1769.

43. Smiles, D. E.; Wu, G.; Hayton, T. W., Synthesis of Uranium–Ligand Multiple Bonds by Cleavage of a Trityl Protecting Group. *J. Am. Chem. Soc.* **2014**, *136*, 96-99.

44. Smiles, D. E.; Wu, G.; Kaltsoyannis, N.; Hayton, T. W., Thorium–ligand multiple bonds via reductive deprotection of a trityl group. *Chem. Sci.* **2015**, *6*, 3891-3899.

45. E. Smiles, D.; Wu, G.; W. Hayton, T., Reactivity of $[U(CH_2SiMe_2NSiMe_3)(NR_2)_2]$ (R = $SiMe_3$) with elemental chalcogens: towards a better understanding of chalcogen atom transfer in the actinides. *New J. Chem.* **2015**, *39*, 7563-7566.

46. Touchton, A. J.; Wu, G.; Hayton, T. W., Generation of a Ni_3 Phosphinidene Cluster from the Ni(0) Synthon, $Ni(\eta^3\text{-}CPh_3)_2$. *Organometallics* **2020**, *39*, 1360-1365.

47. Touchton, A. J.; Wu, G.; Hayton, T. W., Synthesis of Bis(trityl)iron(II) and Formation of the Iron(0)-Stabilized *o*,*o*-Isomer of Gomberg's Dimer. *Organometallics* **2021**, *40*, 4045-4049.

48. Traube, W., Ueber Isonitramin- und Oxazo-Fettsäuren. *Ber. Dtsch. Chem. Ges* **1895**, *28*, 1785-1797.

49. Müller, E.; Metzger, H., Über Nitrosoverbindungen, V. Mitteil.: Einwirkung von Nitrosylchlorid oder Stickstoffmonoxyd auf Cyclohexylmagnesiumchlorid und auf Benzylmagnesiumchlorid. *Chem. Ber.* **1956**, *89*, 396-406.

50. Amirkhai.ili, S.; Conway, A. J.; Smith, J. D., Nitric oxide complexes of trimethylaluminium. *J. Organom. Chem.* **1978**, *149*, 407-411.

51. Arulsamy, N.; Bohle, D. S.; Holman, C. L.; Perepichka, I., *E* versus *Z* Diazeniumdiolation of Acetoacetate-Derived Carbanions. *J. Org. Chem.* **2012**, *77*, 7313-7318.

52. Klebe, G.; Hadicke, E.; Boehn, K. H.; Reuther, W.; Hickmann, E., Die Molekül- und Kristallstruktur der Kupfer-, Aluminium-und Kaliumkomplexe des Cyclohexyl-hydroxy-diazeniumoxids. *Z. Kristallogr.* **1996**, *211*, 798-803.

53. Van der Helm, D.; Merritt, L. L.; Degeilh, R.; MacGillavry, C. H., The crystal structure of iron cupferron $Fe(O_2N_2C_6H_5)_3$. *Acta Crystallogr.* **1965**, *18*, 355-362.

54. Choujaa, H.; Johnson, A. L.; Kociok-Köhn, G.; Molloy, K. C., Synthesis of heterobimetallic tungsten acetylacetonate/alkoxide complexes and their application as molecular precursors to metal tungstates. *Polyhedron* **2013**, *59*, 85-90.

55. During photolysis, the reaction mixture reached a temperature of 45 °C

56. Canle L, M.; Clegg, W.; Demirtas, I.; Elsegood, M. R. J.; Haider, J.; Maskill, H.; Miatt, P. C., *N*-Tritylhydroxylamines: preparations, structures, base strengths, and reactions with nitrous acid and perchloric acid. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1742-1747.

57. Xie, L.-H.; Hou, X.-Y.; Hua, Y.-R.; Tang, C.; Liu, F.; Fan, Q.-L.; Huang, W., Facile Synthesis of Complicated 9,9-Diarylfluorenes Based on $BF_3{\cdot}Et_2O$-Mediated Friedel–Crafts Reaction. *Org. Lett.* **2006**, *8*, 3701-3704.

58. Letsinger, R. L.; Collat, R.; Magnusson, M., The Formation of 9-Phenylfluorene and Triphenylmethane by Disproportionation of Triphenylmethyl. *J. Am. Chem. Soc.* **1954**, *76*, 4185-4186.

59. Gomberg, M., TRIPHENYLMETHYL. XXII. ETHERS OR OXIDES IN THE TRIPHENYLMETHANE SERIES. *J. Am. Chem. Soc.* **1913**, *35*, 200-210.

60. Stauffer, M.; Sakhaei, Z.; Greene, C.; Ghosh, P.; Bertke, J. A.; Warren, T. H., Mechanism of O-Atom Transfer from Nitrite: Nitric Oxide Release at Copper(II). *Inorg. Chem.* **2021**, *60*, 15968–15974.

SYNOPSIS TOC. Photolysis of the trityl diazeniumdiolate complex [K(18-crown-6)][Zn($O_2N_2CPh_3$)$_3$] results in formation of N_2O, 9-phenylfluorene, and $Ph_3CN(H)OCPh_3$ as the major products, whereas oxidation results in formation of $O(CPh_3)_2$ and N_2O. Both reactions represent new modes of diazeniumdiolate fragmentation.