

Chemistry of Nitrosyliron Complexes Supported by a β -Diketiminato Ligand

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Several nitrosyl complexes of Fe and Co have been prepared using the sterically hindered Ar-nacnac ligand (Ar-nacnac = anion of [(2,6-diisopropylphenyl)NC(Me)₂CH]. The dinitrosyliron complexes [Fe(NO)₂(Ar-nacnac)] (**1**) and (Bu₄N)[Fe(NO)₂(Ar-nacnac)] (**2**) react with [Fe^{III}(TPP)Cl] (TPP = tetraphenylporphine dianion) to generate [Fe^{II}(NO)(TPP)] and the corresponding mononitrosyliron complexes. The factors governing NO transfer with dinitrosyliron complexes (DNICs) **1** and **2** are evaluated, together with the chemistry of the related mononitrosyliron complex, [Fe(NO)Br(Ar-nacnac)] (**4**). The synthesis and properties of the related cobalt dinitrosyl [Co(NO)₂(Ar-nacnac)] (**3**) is also discussed for comparison to DNICs **1** and **2**. The solid-state structures of several of these compounds as determined by X-ray crystallography are reported.

Introduction

The potential for dinitrosyliron complexes (DNICs) to serve as storage and transfer units for nitric oxide (NO) in vivo has stimulated interest in biomimetic chemistry that reveals the principles underlying such reactivity.¹ Much of this interest stems from the demonstration that DNICs can participate in a host of physiological processes normally mediated by NO gas.^{2–8} DNICs also hold promise as therapeutic delivery agents of NO.^{9–14} The release of free NO by iron nitrosyls has been examined in detail, yet very

little work has been devoted to understanding the mechanism of NO transfer from DNICs.^{15–18} In a biological context, the transfer of NO can be tedious to study since the nature of a DNIC can be difficult to ascertain. Broadly defined, DNICs are any member of a class of compounds containing the {Fe(NO)₂} unit,¹⁹ although the moniker DNIC is typically reserved for thiolate-bound, mononuclear complexes of the type [Fe(NO)₂(SR)₂][–].^{20,21} Biologically, the [–]SR anion typically derives from cysteinate residues in proteins or mobile units such as glutathione, although examples of biological DNICs with nonthiolate ligands are also known.^{22,23}

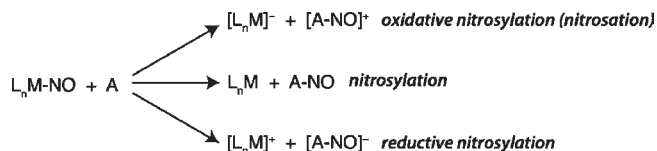
Formation of DNICs in vivo occurs through interaction of NO with chelatable pools of ferrous iron²⁴ or by attack of NO on protein-based iron centers such as iron–sulfur clusters.^{25–31} Mononuclear DNICs that result are denoted {Fe(NO)₂}⁹ in the Enemark–Feltham notation³² and display a characteristic $g_{\text{avg}} = 2.03$ EPR signal arising from an

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- (1) Vanin, A. F. *Nitric Oxide* **2009**, 21, 1–13.
- (2) Alencar, J. L.; Chalupsky, K.; Sarr, M.; Schini-Kerth, V.; Vanin, A. F.; Stoclet, J.-C.; Muller, B. *Biochem. Pharmacol.* **2003**, 66, 2365–2374.
- (3) Vanin, A. F. *Biochemistry (Moscow)* **1998**, 63, 782–793.
- (4) Vanin, A. F.; Stukan, R. A.; Manukhina, E. B. *Biochim. Biophys. Acta, Protein Struct. Mol. Enzymol.* **1996**, 1295, 5–12.
- (5) Boese, M.; Mordvintsev, P. I.; Vanin, A. F.; Busse, R.; Mülsch, A. *J. Biol. Chem.* **1995**, 270, 29244–29249.
- (6) Chen, Y.-J.; Ku, W.-C.; Feng, L.-T.; Tsai, M.-L.; Hsieh, C.-H.; Hsu, W.-H.; Liaw, W.-F.; Hung, C.-H.; Chen, Y.-J. *J. Am. Chem. Soc.* **2008**, 130, 10929–10938.
- (7) Mokh, V. P.; Poltorakov, A. P.; Serezhenkov, V. A.; Vanin, A. F. *Nitric Oxide* **2010**, 22, 266–274.
- (8) Bosworth, C. A.; Toledo, J. C., Jr.; Zmijewski, J. W.; Li, Q.; Lancaster, J. R., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, 106, 4671–4676.
- (9) Chang, H.-H.; Huang, H.-J.; Ho, Y.-L.; Wen, Y.-D.; Huang, W.-N.; Chiou, S.-J. *Dalton Trans.* **2009**, 6396–6402.
- (10) Weckler, S. R.; Hutchinson, J.; Ford, P. C. *Inorg. Chem.* **2006**, 45, 1192–1200.
- (11) Wen, Y.-D.; Ho, Y.-L.; Shiau, R.-J.; Yeh, J.-K.; Wu, J.-Y.; Wang, W.-L.; Chiou, S.-J. *J. Organomet. Chem.* **2010**, 695, 352–359.
- (12) Sanina, N. A.; Roudneva, T. N.; Shilov, G. V.; Morgunov, R.; Ovanesyan, N. S.; Aldoshin, S. M. *Dalton Trans.* **2009**, 1703–1706.
- (13) Ostrowski, A. D.; Ford, P. C. *Dalton Trans.* **2009**, 10660–10669.
- (14) Dillinger, S. A. T.; Schmalke, H. W.; Fox, T.; Berke, H. *Dalton Trans.* **2007**, 3562–3571.

- (15) Lu, T.-T.; Chen, C.-H.; Liaw, W.-F. *Chem.—Eur. J.* **2010**, 16, 8088–8095.
- (16) Chiang, C.-Y.; Darensbourg, M. J. *Biol. Inorg. Chem.* **2006**, 11, 359–370.
- (17) Ueno, T.; Suzuki, Y.; Fujii, S.; Vanin, A. F.; Yoshimura, T. *Biochem. Pharmacol.* **2002**, 63, 485–493.
- (18) Hsieh, C.-H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2010**, 132, 14118–14125.
- (19) Butler, A. R.; Glidewell, C.; Li, M.-H. *Adv. Inorg. Chem.* **1988**, 32, 335–393.
- (20) Butler, A. R.; Megson, I. L. *Chem. Rev.* **2002**, 102, 1155–1165.
- (21) Chiang, C. Y.; Miller, M. L.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2004**, 126, 10867–10874.
- (22) Cesareo, E.; Parker, L. J.; Pedersen, J. Z.; Nuccetelli, M.; Mazzetti, A. P.; Pastore, A.; Federici, G.; Caccuri, A. M.; Ricci, G.; Adams, J. J.; Parker, M. W.; Lo Bello, M. *J. Biol. Chem.* **2005**, 280, 42172–42180.
- (23) Lee, M.; Arosio, P.; Cozzi, A.; Chasteen, N. D. *Biochemistry* **1994**, 33, 3679–3687.
- (24) Toledo, J. C., Jr.; Bosworth, C. A.; Hennon, S. W.; Mahtani, H. A.; Bergonia, H. A.; Lancaster, J. R., Jr. *J. Biol. Chem.* **2008**, 283, 28926–28933.

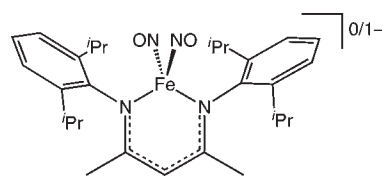
Scheme 1. Different Scenarios for Transfer of NO between Donor (L_nM) and Acceptor (A)



$S = 1/2$ ground state.³³ The precise electronic structure of $\{Fe(NO)_2\}^9$ DNICs remains a point of contention, and descriptions ranging from $\{HS-Fe(I)\}-\{^2(NO\cdot)\}_2$, to $\{HS-Fe(III)\}-\{^3(NO^-)\}_2$, to $\{Fe(-I)\}-\{^1(NO^+)\}_2$, where HS denotes “high-spin”, have been proffered.^{34–39} A more detailed knowledge of DNIC electronic structure is important for understanding both the nature of the metal–nitrosyl bond and the mechanism of NO transfer. Such information would also facilitate comparison with the chemistry of nitrosothiols, which are generally agreed to play an important role in NO-mediated processes.^{40,41}

Implicit to a discussion of NO-transfer reactivity is the question of NO redox state. Three different scenarios are possible for transfer of the nitrosyl group from donor to acceptor, formally involving NO^+ , NO^\bullet , and NO^- and resulting in oxidative nitrosylation (nitrosation), nitrosylation, or reductive nitrosylation of the acceptor moiety, respectively (Scheme 1). With nitrosothiols, reductive nitrosylation is unlikely because the reaction would require formation of RS^+ . With metal nitrosyls, however, transfer of each redox form of NO must be considered. An added layer of complexity to the chemistry of DNICs is their ability to participate in redox chemistry prior to NO transfer. DNICs containing the $\{Fe(NO)_2\}^9$ unit display an electrochemically reversible one-electron reduction to the diamagnetic $\{Fe(NO)_2\}^{10}$ state. With π -acidic ligands such as carbonyls, phosphines, and certain nitrogen-based ligands, such reduced species have

Chart 1. Chemical Structures of Compounds **1** and **2**



1 - charge neutral
2 - anionic (cation = Bu_4N^+ or PPN^+)

been isolated and characterized.⁴² With thiolate (RS^-) ligands, however, chemical reduction of the $\{Fe(NO)_2\}^9$ DNIC leads to dissociation of disulfide ($RSSR$) and dimerization to form a valence-delocalized $\{Fe(NO)_2\}^9-\{Fe(NO)_2\}^{10}$ species.^{43,44}

Recently, we reported the synthesis of a pair of homologous DNIC redox partners, $\{Fe(NO)_2\}^{9/10}$, containing a sterically hindered β -diketiminato ligand (Chart 1, compounds **1** and **2**).⁴⁵ The identical ligand sets in these DNICs permit an evaluation of the effect that iron redox state plays on their structures and reactivity. One very interesting observation from this study is that the isomer shifts (δ) in the Mössbauer spectra of the two DNICs are nearly identical, δ 0.19(2) and 0.23(2) mm/s for **1** and **2**, respectively, which is unexpected for a metal-centered reduction.³⁴ This result clearly reveals the intricate nature of the electronic structure of $\{Fe(NO)_2\}$ units and indicates that redox reactions of DNICs are more complex than anticipated from simple metal-based processes.

In the present work, we have used these well-defined DNICs to investigate the mechanism of NO transfer. The β -diketiminato ligand, Ar-nacnac (Ar = 2,6-diisopropylphenyl),^{46,47} is critical to this study because it helps stabilize both the DNIC starting materials and the products of NO transfer. Moreover, the nitrogen-rich coordination environment afforded by the Ar-nacnac ligand is a reasonable approximation of the histidine residue nitrogen-donor atoms.^{48,49}

Results

Dinitrosyl Complexes. The synthesis and characterization of DNICs **1** and **2** were described previously.⁴⁵ Each compound has pseudotetrahedral coordination geometry, with the $\{Fe(NO)_2\}$ unit residing in a pocket created by the sterically demanding diisopropylphenyl substituents. Compounds **1** and **2** are thermally robust and display sharp melting points at temperatures above 150 °C. Compound **1** is stable in air for short periods of time, whereas compound **2** oxidizes rapidly in the presence of dioxygen to generate **1** (Figure S1 in the Supporting Information, SI). Both compounds display an electrochemically reversible one-electron couple at -1.34 V vs

- (25) Ren, B.; Duan, X.; Ding, H. *J. Biol. Chem.* **2009**, *284*, 4829–4835.
(26) Duan, X.; Yang, J.; Ren, B.; Tan, G.; Ding, H. *Biochem. J.* **2009**, *417*, 783–789.
(27) Ren, B.; Zhang, N.; Yang, J.; Ding, H. *Mol. Microbiol.* **2008**, *70*, 953–964.
(28) Rogers, P. A.; Eide, L.; Klungland, A.; Ding, H. *DNA Repair* **2003**, *2*, 809–817.
(29) Foster, M. W.; Cowan, J. A. *J. Am. Chem. Soc.* **1999**, *121*, 4093–4100.
(30) Sellers, V. M.; Johnson, M. K.; Dailey, H. A. *Biochemistry* **1996**, *35*, 2699–2704.
(31) Reddy, D.; Lancaster, J. R., Jr.; Cornforth, D. P. *Science* **1983**, *221*, 769–770.
(32) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339–406.
(33) Vanin, A. F.; Serezhnikov, V. A.; Mikoyan, V. D.; Genkin, M. V. *Nitric Oxide* **1998**, *2*, 224–234.
(34) Ye, S.; Neese, F. *J. Am. Chem. Soc.* **2010**, *132*, 3646–3647.
(35) Tsai, M.-C.; Tsai, F.-T.; Lu, T.-T.; Tsai, M.-L.; Wei, Y.-C.; Hsu, I.-J.; Lee, J.-F.; Liaw, W.-F. *Inorg. Chem.* **2009**, *48*, 9579–9591.
(36) Hopmann, K. H.; Conradie, J.; Ghosh, A. *J. Phys. Chem. B* **2009**, *113*, 10540–10547.
(37) Conradie, J.; Quarless, D. A., Jr.; Hsu, H.-F.; Harrop, T. C.; Lippard, S. J.; Koch, S. A.; Ghosh, A. *J. Am. Chem. Soc.* **2007**, *129*, 10446–10456.
(38) Tsai, F.-T.; Chiou, S.-J.; Tsai, M.-C.; Tsai, M.-L.; Huang, H.-W.; Chiang, M.-H.; Liaw, W.-F. *Inorg. Chem.* **2005**, *44*, 5872–5881.
(39) Bryar, T. R.; Eaton, D. R. *Can. J. Chem.* **1992**, *70*, 1917–1926.
(40) Mutus, B. In *Nitric Oxide Donors*; Wang, P. G.; Cai, T. B., Taniguchi, N., Eds.; Wiley-VCH Verlag GmbH & Co KGaA: Weinheim, Germany, 2005; pp 91–109.
(41) Ng, E. S. M.; Kubes, P. *Can. J. Physiol. Pharmacol.* **2003**, *81*, 759–764.
(42) Atkinson, F. L.; Blackwell, H. E.; Brown, N. C.; Connelly, N. G.; Crossley, J. G.; Orpen, A. G.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1996**, 3491–3502.

- (43) Lu, T.-T.; Tsou, C.-C.; Huang, H.-W.; Hsu, I.-J.; Chen, J.-M.; Kuo, T.-S.; Wang, Y.; Liaw, W.-F. *Inorg. Chem.* **2008**, *47*, 6040–6050.
(44) Tsou, C.-C.; Lu, T.-T.; Liaw, W.-F. *J. Am. Chem. Soc.* **2007**, *129*, 12626–12627.
(45) Tonzetich, Z. J.; Do, L. H.; Lippard, S. J. *J. Am. Chem. Soc.* **2009**, *131*, 7964–7965.
(46) Holland, P. L. *Acc. Chem. Res.* **2008**, *41*, 905–914.
(47) Puiui, S. C.; Warren, T. H. *Organometallics* **2003**, *22*, 3974–3976.
(48) Wang, X.; Sundberg, E. B.; Li, L.; Kantardjieff, K. A.; Herron, S. R.; Lim, M.; Ford, P. C. *Chem. Commun.* **2005**, 477–479.
(49) Reginato, N.; McCrory, C. T. C.; Pervitsky, D.; Li, L. *J. Am. Chem. Soc.* **1999**, *121*, 10217–10218.

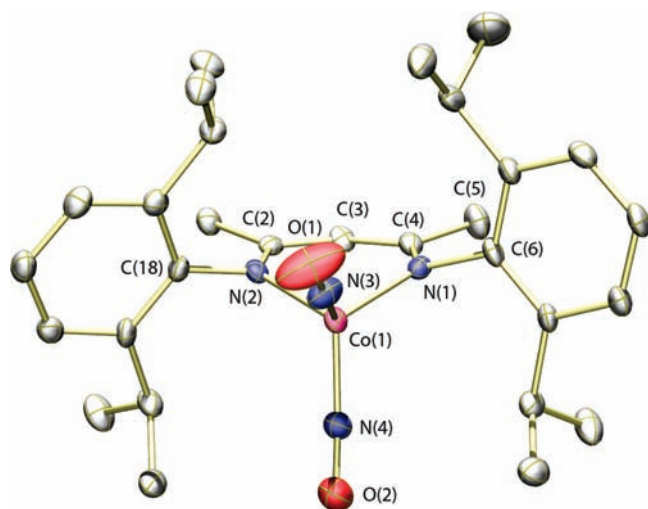


Figure 1. Thermal ellipsoid (50%) rendering of one of the two crystallographically independent molecules of **3** in the asymmetric unit. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Co(1)–N(1) = 1.955(4); Co(1)–N(2) = 1.957(4); Co(1)–N(3) = 1.633(3); Co(1)–N(4) = 1.695(4); N(3)–O(1) = 1.165(5); N(4)–O(2) = 1.166(5); Co(1)–N(3)–O(1) = 173.0(4); Co(1)–N(4)–O(2) = 150.1(4); N(3)–Co(1)–N(4) = 110.5(2).

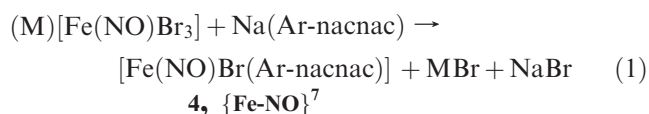
Fc/Fc⁺ in tetrahydrofuran (Figure S2). This potential is higher than that observed for DNICs containing thiolate ligands, reflecting the neutral charge of **1**. Other examples of neutral DNICs with mixed histidine/thiolate ligands have comparable potentials for the {Fe(NO)₂}^{9/10} couple.⁵⁰

As a means of comparison to compounds **1** and **2**, the cobalt analogue, [Co(NO)₂(Ar-nacnac)], was prepared. A variety of {Co(NO)₂}¹⁰ species have been reported previously, and these compounds are generally similar to the corresponding {Fe(NO)₂}⁹ species.^{51,52} The dicobalt precursor, [Co(NO)₂(μ-Cl)]₂,⁵³ was chosen as a starting material for the synthesis of [Co(NO)₂(Ar-nacnac)]. Reaction of Na(Ar-nacnac) with [Co(NO)₂(μ-Cl)]₂ in THF or diethyl ether afforded the desired {Co(NO)₂}¹⁰ species, **3**, in moderate yield after recrystallization from pentane. The compound is diamagnetic as expected for a {M(NO)₂}¹⁰ species, giving a sharp, well-resolved ¹H NMR spectrum at 25 °C in benzene-*d*₆. Much like compounds **1** and **2**, compound **3** displays two intense IR peaks arising from the two nitrosyl ligands. These peaks appear at 1801 and 1706 cm⁻¹ in benzene-*d*₆ and should be compared with values of 1761 and 1709 cm⁻¹ for **1** and 1627 and 1567 cm⁻¹ for **2**. The solid-state structure of **3** is displayed in Figure 1 (see Table 1 for refinement details). Compound **3** crystallizes with two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Like **1** and **2**, compound **3** displays pseudotetrahedral geometry at the metal center, with the flanking diisopropylphenyl groups creating a pocket for the {Co(NO)₂}¹⁰ unit. The geometric parameters about the nitrosyl ligands compare well with those in **1** and **2** but with slightly shorter N–O bond lengths (average of

1.16 Å) consistent with the poorer π-back-bonding ability of Co(I) versus Fe(I) and Fe(0).

Compound **3** was examined by cyclic voltammetry (CV) to determine whether the {Co(NO)₂}⁹ state could be accessed electrochemically. The cyclic voltammogram displayed no reversible oxidation in THF but did exhibit a quasi-reversible cathodic process at –1.80 V (Figure 2). Reduction of the {Co(NO)₂}¹⁰ core is surprising considering that a putative {Co(NO)₂}¹¹ species would have 19 electrons. Chemical reduction of **3** was attempted with K₂C₈ in benzene. IR, UV–vis, and EPR spectra of the resulting reduced species are all consistent with a {Co(NO)₂}¹¹ complex (see the SI). A new optical band appeared at 607 nm upon reduction. Addition of dry air to this reduced species resulted in disappearance of the band at 607 nm and regeneration of **3**, as judged by UV–vis spectroscopy (Figure S5). The IR bands of **3** disappear upon reduction, being replaced with lower energy bands <1600 cm⁻¹. Unfortunately, the {Co(NO)₂}¹¹ complex could not be isolated. The K⁺ ions appear to be important in stabilizing the reduced species, because attempts to replace them by treatment with Bu₄NCl and PPNCl [PPN = cation of μ-nitridobis(triphenylphosphine)] failed, resulting in decomposition.

Mononitrosyl Complexes. The success of the β-diketiminato in stabilizing compounds containing both {Fe(NO)₂}⁹ and {Fe(NO)₂}¹⁰ units prompted us to evaluate its potential as a ligand for the {Fe–NO}⁷ unit. Furthermore, mononitrosyliron complexes (MNICs) are relevant to NO-transfer chemistry because they represent logical byproducts of nitrosyl loss from DNICs. The synthesis of a compound containing the {Fe–NO}⁷ unit was accomplished by salt metathesis of the lithium or sodium dikeiminato with the mononitrosyl precursor, (M)[Fe(NO)Br₃] (eq 1, M = Et₄N or PPN). Upon addition of the dikeiminato salt to [Fe(NO)Br₃]⁻, an immediate color change from yellow-brown to dark green occurred, indicating formation of a new species. The precise nature of this initial complex is unknown but most likely corresponds to a dibromo complex having the formula (M)[Fe(NO)Br₂(Ar-nacnac)] (**4'**). After several hours at 25 °C, Et₄NCl or PPNCl precipitated and the supernatant changed from green to dark brown, indicating formation of the desired compound, [Fe(NO)Br(Ar-nacnac)] (**4**). Prolonged reaction times were detrimental to both the yield and purity of **4** due to competing disproportionation to form **1** (vide infra).



MNIC **4** is a dark-brown crystalline solid that is soluble in common organic solvents including alkanes. Its IR spectrum displays an intense peak at 1777 cm⁻¹ (benzene-*d*₆) corresponding to the ν_{NO} fundamental (see the SI). Substitution with ¹⁵NO leads to a 34 cm⁻¹ red shift, consistent with a simple harmonic oscillator (calculated Δν_{NO} = 32 cm⁻¹). As with other mononuclear {Fe–NO}⁷ species, **4** is paramagnetic. Its EPR spectrum at 77 K in a 2-MeTHF glass is consistent with an S = 3/2 ground state (see the SI). Such a spin state for a four-coordinate

(50) Tsai, M.-L.; Liaw, W.-F. *Inorg. Chem.* **2006**, *45*, 6583–6585.

(51) Haymore, B.; Feltham, R. D. *Inorg. Synth.* **1973**, *14*, 81–89.

(52) Tennyson, A. G.; Dhar, S.; Lippard, S. J. *J. Am. Chem. Soc.* **2008**, *130*, 15087–15098.

(53) Sacco, A.; Rossi, M.; Nobile, C. F. *Ann. Chim. (Rome)* **1967**, *57*, 499–507.

Table 1. X-ray Data Collection and Refinement Parameters for Compounds 3–6^a

	3	4	5	6
empirical formula	C ₂₉ H ₄₁ CoN ₄ O ₂	C ₂₉ H ₄₁ BrFeN ₃ O	C ₃₃ H ₄₉ BrFeN ₂ O	C ₂₉ H ₄₁ FeN ₂ Br ₂
formula weight (g/mol)	536.59	583.41	625.50	633.31
temperature (K)	100(2)	110(2)	110(2)	100(2)
crystal system, space group	triclinic, <i>P</i> $\bar{1}$	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	monoclinic, <i>P</i> 2 ₁ / <i>n</i>
unit cell dimensions	<i>a</i> = 12.590(2) Å <i>b</i> = 16.240(3) Å <i>c</i> = 16.649(3) Å α = 111.071(3)° β = 99.370(3)° γ = 109.899(3)°	<i>a</i> = 12.442(3) Å <i>b</i> = 20.007(5) Å <i>c</i> = 13.102(3) Å β = 115.805(4)°	<i>a</i> = 10.1792(6) Å <i>b</i> = 14.7884(8) Å <i>c</i> = 21.7305(13) Å β = 93.3570(10)°	<i>a</i> = 12.5714(10) Å <i>b</i> = 19.9181(16) Å <i>c</i> = 13.2247(11) Å β = 116.9340(10)°
volume (Å ³)	2824.8(8)	2936.2(12)	3265.6(3)	2952.2(4)
<i>Z</i> , calculated density (g/cm ³)	4, 1.262	4, 1.320	4, 1.272	4, 1.425
absorption coefficient (mm ⁻¹)	0.639	1.899	1.711	3.237
<i>F</i> (000)	1144	1220	1320	1300
crystal size (mm)	0.13 × 0.06 × 0.05	0.28 × 0.17 × 0.13	0.40 × 0.24 × 0.20	0.24 × 0.18 × 0.14
θ range (deg)	1.39–24.71	1.89–29.57	1.67–25.03	1.86–26.33
limiting indices	–14 ≤ <i>h</i> ≤ 14, –19 ≤ <i>k</i> ≤ 19, –19 ≤ <i>l</i> ≤ 19	–17 ≤ <i>h</i> ≤ 17, –27 ≤ <i>k</i> ≤ 27, –18 ≤ <i>l</i> ≤ 18	–12 ≤ <i>h</i> ≤ 12, –17 ≤ <i>k</i> ≤ 17, –25 ≤ <i>l</i> ≤ 25	–15 ≤ <i>h</i> ≤ 15, –24 ≤ <i>k</i> ≤ 24, –16 ≤ <i>l</i> ≤ 16
reflections collected/unique	42 216/9575	64 961/8235	52 989/5786	52 094/5987
[<i>R</i> (int) = 0.1065]		[<i>R</i> (int) = 0.0628]	[<i>R</i> (int) = 0.0290]	[<i>R</i> (int) = 0.0302]
completeness to θ (%)	99.5	100	99.9	99.6
absorption correction	empirical	empirical	empirical	empirical
max and min transmission	0.9688 and 0.9215	0.7904 and 0.6184	0.7259 and 0.5476	0.6600 and 0.5105
data/restraints/parameters	9575/0/653	8235/62/354	5786/0/346	5987/0/317
GOF on <i>F</i> ²	1.018	1.294	1.265	1.043
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0599, <i>wR</i> 2 = 0.1235	<i>R</i> 1 = 0.0554, <i>wR</i> 2 = 0.1103	<i>R</i> 1 = 0.0431, <i>wR</i> 2 = 0.0992	<i>R</i> 1 = 0.0203, <i>wR</i> 2 = 0.0506
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1132, <i>wR</i> 2 = 0.1465	<i>R</i> 1 = 0.0691, <i>wR</i> 2 = 0.1138	<i>R</i> 1 = 0.0446, <i>wR</i> 2 = 0.0999	<i>R</i> 1 = 0.0236, <i>wR</i> 2 = 0.0520
largest diff peak and hole (e/Å ³)	0.852 and –0.524	0.466 and –0.523	0.936 and –0.574	0.609 and –0.292

^a Refinement method was full-matrix least squares on *F*²; wavelength = 0.71073 Å. *R*1 = $\sum||F_o| - |F_c||/\sum|F_o|$; *wR*2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]\}^{1/2}$.

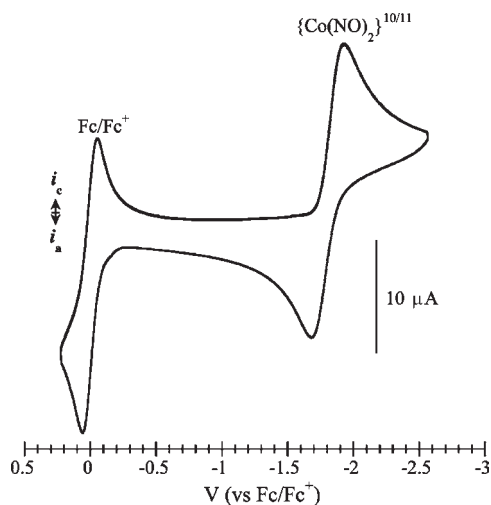


Figure 2. Cyclic voltammogram of compound **3** in THF at a glassy carbon electrode (0.1 M Bu₄BAR₄^F supporting electrolyte; 50 mV/s scan rate). Fc/Fc⁺ indicates the ferrocene reference couple.

{Fe–NO}⁷ species is not uncommon and has been observed for both [Fe(NO)Br₃][–] and [Fe(NO)(S-*t*-Bu)₃][–].^{54,55}

The solid-state structure of **4** is displayed in Figure 3 (see Table 1 for refinement details). Much like compounds **1** and **2**, compound **4** is pseudotetrahedral with a

N–Fe–N bite angle of 96.49(10)° for the Ar-nacnac ligand. The Br and NO groups are disordered in the crystal lattice but were modeled satisfactorily with occupancies of 67% and 33% for the major and minor components, respectively. In addition, the thermal ellipsoid for the oxygen atom of the NO group is elongated in a plane perpendicular to the N–O bond vector. This elongation may be a consequence of slight nonlinearity of the Fe–N–O bond angle that could not be effectively modeled due to the proximity of the disordered bromine atom. The geometric parameters about the iron nitrosyl unit (see Figure 3 caption) are similar to those reported for other {Fe–NO}⁷ species.^{54,56} The Mössbauer spectrum of **4** (see the SI) displays a single quadrupole doublet with an isomer shift of 0.33(2) mm/s and a quadrupole splitting of 0.92(2) mm/s. The isomer shift compares moderately well with that of 0.26(2) mm/s reported for [Fe(NO)(S-*t*-Bu)₃][–]⁵⁴ but is substantially lower than values for five- and six-coordinate *S* = 3/2 {Fe–NO}⁷ species, which typically fall between 0.62 and 0.77 mm/s.⁵⁷

(54) Harrop, T. C.; Song, D.; Lippard, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 3528–3529.

(55) Connelly, N. G.; Gardner, C. J. *Chem. Soc., Dalton Trans.* **1976**, 1525–1527.

(56) Lu, T.-T.; Chiou, S.-J.; Chen, C.-Y.; Liaw, W.-F. *Inorg. Chem.* **2006**, *45*, 8799–8806.

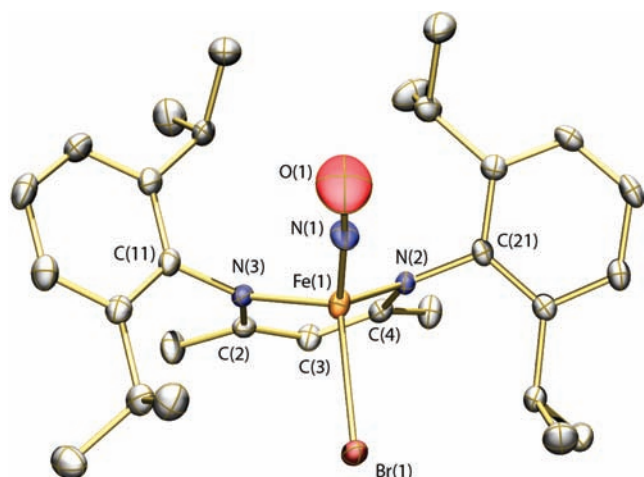


Figure 3. Thermal ellipsoid (50%) rendering of the solid-state structure of **4**. The major component of the disordered structure is pictured. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)–N(1) = 1.644(5); Fe(1)–N(2) = 1.971(2); Fe(1)–N(3) = 1.938(2); N(1)–O(1) 1.217(6); Fe(1)–Br(1) = 2.4136(9); O(1)–N(1)–Fe(1) = 175.5(6); N(1)–Fe(1)–Br(1) = 115.22(15).

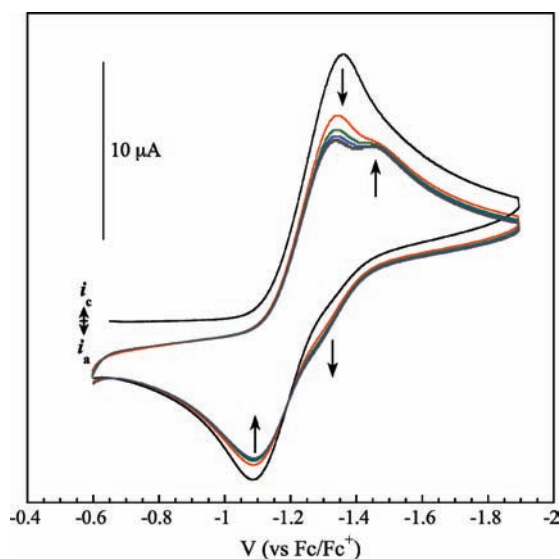


Figure 4. Cyclic voltammogram (100 mV/s) of compound **4** indicating disproportionation of the {Fe–NO}⁸ species to {Fe(NO)₂}¹⁰ and “Fe(II)”. The traces were recorded at a glassy carbon electrode in THF with 0.1 M Bu₄NPF₆ as supporting electrolyte.

The cyclic voltammogram of **4** in THF displays a quasi-reversible one-electron reduction at –1.23 V (vs Fc/Fc⁺) corresponding to the {Fe–NO}^{7/8} couple. Upon cycling of this couple at 100 mV/s, a new species formed having a midpoint potential of –1.34 V (Figure 4). This value corresponds to the {Fe(NO)₂}^{9/10} couple previously observed for compounds **1** and **2**, suggesting that the {Fe–NO}⁸ species is unstable with respect to transformation to a DNIC.

The electrochemical results with **4** were corroborated chemically using Cp*₂Co (Cp* = pentamethylcyclopentadiene) as a reductant. Upon addition of Cp*₂Co to solutions of **4** in benzene-*d*₆, an immediate change in color

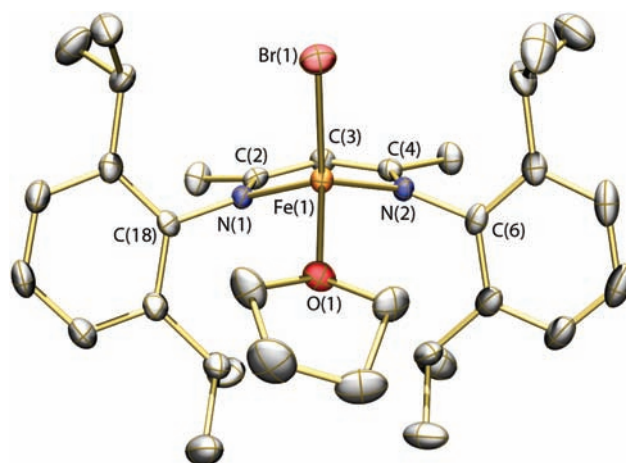
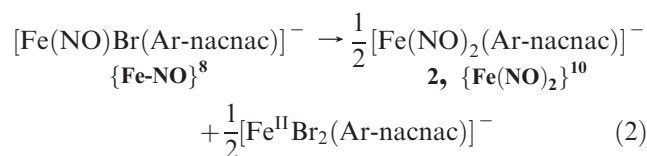
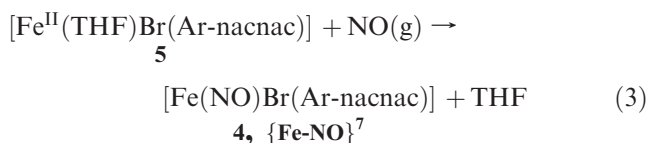


Figure 5. Thermal ellipsoid (50%) rendering of the solid-state structure of **5**. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)–N(1) 2.010(3); Fe(1)–N(2) 1.999(3); Fe(1)–O(1) 2.062(3); Fe(1)–Br(1) 2.4114(6); Br(1)–Fe(1)–O(1) = 98.50(7).

from dark brown to yellow-brown was observed. NMR and IR spectra of the reaction mixtures confirmed the presence of **2** along with a new paramagnetic Fe species. Simple stoichiometry requires the formation of a new Fe(II) species, as indicated in eq 2.



An iron(II) bromide complex could be prepared independently by reaction of the sodium salt of the β -diketiminate ligand with anhydrous FeBr₂ in THF. This new compound, **5**, was isolated as a yellow THF adduct after crystallization from THF/pentane (Figure 5). Divalent iron halide species similar to **5** have been prepared previously as dimers in the absence of a coordinating solvent.⁵⁸ The ¹H NMR features of **5** are nearly identical to those observed for the Fe(II) species formed by reduction of **4**, suggesting that **5**, or a related complex such as the dibromide anion shown in eq 2, is generated concomitant with **2** during disproportionation of the putative {Fe–NO}⁸ species. Compound **5** loses THF in vacuo to form an orange species, which is most likely the dimeric [Fe₂(μ-Br)₂(Ar-nacnac)₂] (**5'**). Dimeric **5'** has poor solubility in noncoordinating solvents but dissolves readily in THF to regenerate **5**. Compound **5** also serves as a convenient synthon for MNIC **4**, which forms by simple addition of NO gas (eq 3). In this manner, the ¹⁵N analogue of **4** can be prepared directly from ¹⁵NO(g).



Disproportionation of the {Fe–NO}⁸ unit accounts for the observation that samples of recrystallized **4** contain

(57) Hauser, C.; Glaser, T.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2000**, *122*, 4352–4365.

(58) Eckert, N. A.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2004**, *43*, 3306–3321.

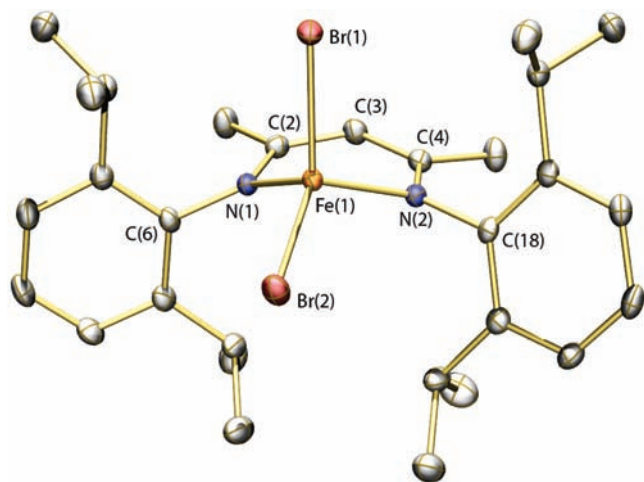
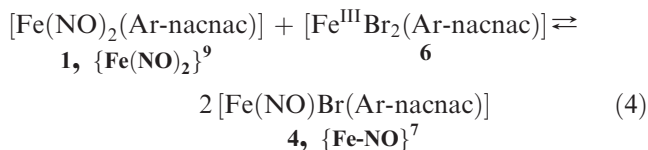


Figure 6. Thermal ellipsoid (50%) rendering of the solid-state structure of **6**. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)–N(1) = 1.9459(13); Fe(1)–N(2) = 1.9730(13); Fe(1)–Br(1) = 2.3446(3); Fe(1)–Br(2) = 2.3188(3); Br(1)–Fe(1)–Br(2) = 116.068(11).

small amounts of **1**, since the {Fe–NO}⁷ complex may be reasonably supposed to disproportionate to **1** and an Fe(III) species in an analogous fashion to its reduced counterpart, albeit at a much slower rate. To test this hypothesis, the Fe(III) complex [FeBr₂(Ar-nacnac)] (**6**) was prepared.⁵⁹ Isolation and purification of [Fe^{III}Br₂(Ar-nacnac)] was complicated by competing reduction of Fe(III) by the Ar-nacnac ligand.⁶⁰ Nevertheless, small quantities of **6** could be isolated, and the solid-state structure is displayed in Figure 6 (see also Table 1). Upon mixing solutions of compounds **1** and **6** at ambient temperature, partial conversion to MNIC **4** was observed by IR spectroscopy over 24 h. This observation suggests that all three species, **1**, **4**, and **6**, can interconvert (eq 4), with the equilibrium lying predominantly toward **4**. Upon reduction, a similar situation exists involving compounds **2** and **5** and the {Fe–NO}⁸ complex, but in this instance the equilibrium lies entirely toward **2** and **5** (eq 2).



NO-Transfer Reactions. NO-transfer experiments were undertaken with DNICs **1** and **2** using [Fe^{III}(TPP)Cl] (TPP = *meso*-tetraphenylporphine) as the NO acceptor. This porphyrin complex was chosen because of the documented importance of iron heme compounds to the biological chemistry of NO and the precedent for transfer of NO from DNICs to iron porphyrins.^{16,17,61} Furthermore, porphyrin compounds have intense optical bands that facilitate reaction monitoring by UV–vis spectroscopy. Addition of **1** to THF or benzene solutions of [Fe^{III}(TPP)Cl] resulted in little to no reaction at 25 °C

(59) Panda, A.; Stender, M.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909–3916.

(60) Shimokawa, C.; Itoh, S. *Inorg. Chem.* **2005**, *44*, 3010–3012.

(61) Harrop, T. C.; Song, D.; Lippard, S. J. *J. Inorg. Biochem.* **2007**, *101*, 1730–1738.

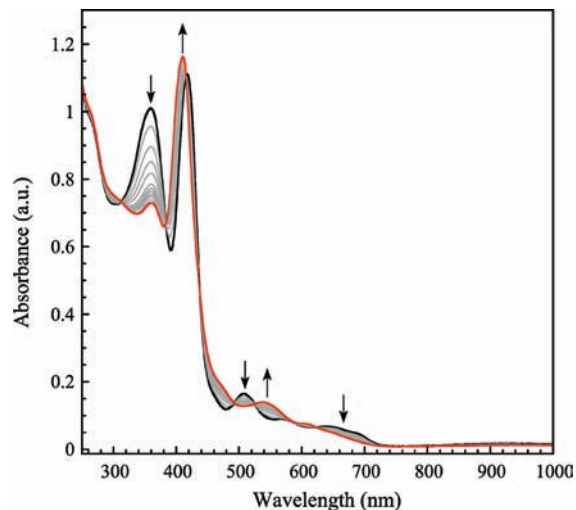
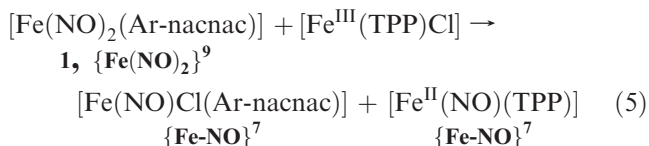


Figure 7. UV–vis spectral changes associated with the reaction of [Fe(NO)₂(Ar-nacnac)] with [Fe^{III}(TPP)Cl] in THF with exposure to ordinary room light.

over several hours in the absence of light. Upon heating (from 50 to 80 °C) and/or irradiation with room light, however, a new Fe(TPP) species formed within 1 h. When the reaction was followed by optical spectroscopy, a clean conversion to the new iron porphyrin species was detected, with several isosbestic points indicating an A → B type process (Figure 7). UV–vis and IR spectral studies confirmed the identity of the new species as the nitrosylated {Fe–NO}⁷ porphyrin, [Fe^{II}(NO)(TPP)].⁶² IR spectroscopy also identified a new NO-containing compound with a ν_{NO} stretch near 1770 cm⁻¹. This value agrees well with that found for compound **4** (vide supra) and most likely corresponds to the related MNIC, [Fe(NO)Cl(Ar-nacnac)]. These results indicate that NO transfer from **1** to [Fe^{III}(TPP)Cl] formally involves transfer of NO⁻ with reductive nitrosylation of the ferric porphyrin. Upon transfer of NO⁻ from DNIC **1**, the corresponding {Fe–NO}⁷ MNIC is generated, a process that can be described by the stoichiometry displayed in eq 5.



Initial kinetic studies of the reaction employing excess **1** at several temperatures > 50 °C displayed complex behavior that could not be fit to a pseudo-first-order process (e.g., Figure 8). Although inconclusive, the data suggest that NO transfer from **1** is unimolecular in DNIC concentration and independent of [Fe^{III}(TPP)Cl]. For example, halving the DNIC concentration led to an ~50% decrease in reaction rate, whereas halving the [Fe^{III}(TPP)Cl] concentration led to no discernible change. These observations are consistent with a mechanism that involves rate-limiting dissociation of NO[•] or NO⁻ from **1** followed by rapid capture of the nitrosyl (or nitroxyl) fragment by [Fe^{III}(TPP)Cl] and immediate transfer of Cl[•] or Cl⁻ to the resulting {Fe–NO}⁸ or {Fe–NO}⁷ species,

(62) Scheidt, W. R.; Ellison, M. K. *Acc. Chem. Res.* **1999**, *32*, 350–359.

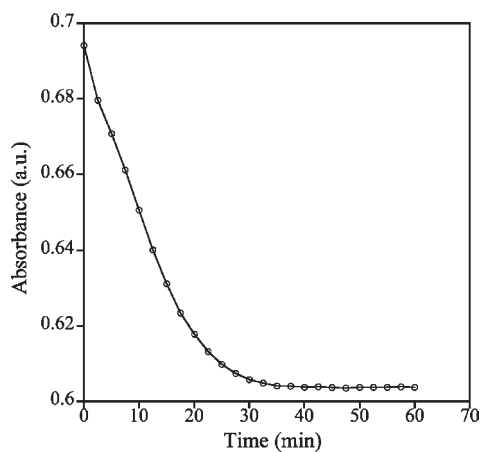


Figure 8. Representative kinetic trace (single wavelength, 419 nm) for the reaction of 95 μM **1** with 4.7 μM $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ in toluene at 60 $^{\circ}\text{C}$.

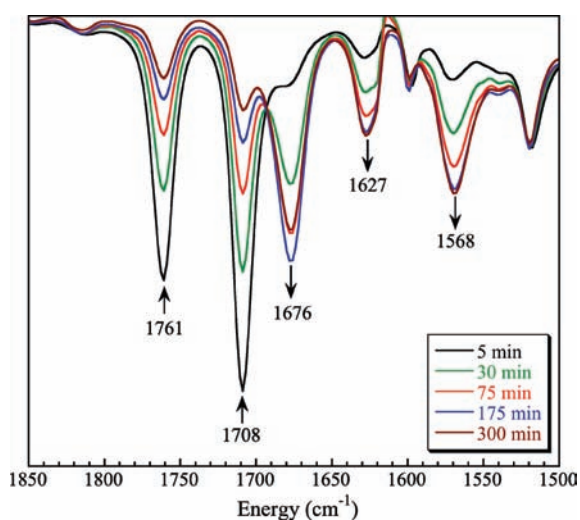
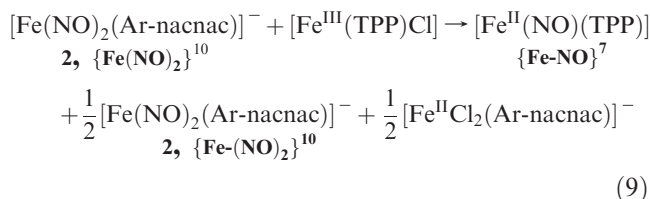
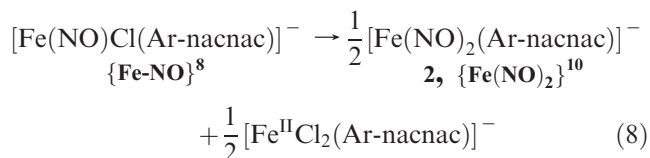
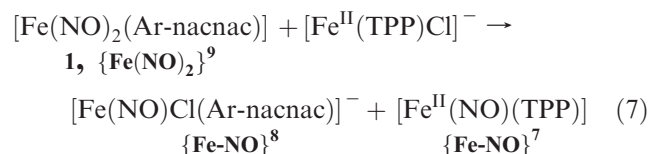
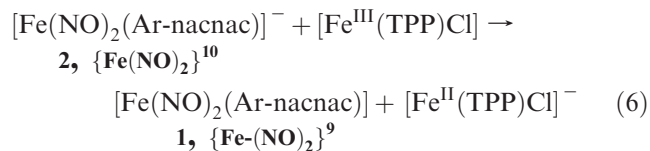


Figure 9. IR spectral changes associated with the reaction of $(\text{Bu}_4\text{N})[\text{Fe}(\text{NO})_2(\text{Ar-nacnac})]$ with $[\text{Fe}(\text{TPP})\text{Cl}]$ in C_6D_6 at 25 $^{\circ}\text{C}$. The decrease in intensity of the peak at 1676 cm^{-1} after 300 min is due to precipitation of $[\text{Fe}(\text{NO})(\text{TPP})]$.

respectively. Other mechanistic scenarios involving subsequent fast electron-transfer steps are also consistent with the data. On the basis of the observed decomposition route of the $\{\text{Fe}-\text{NO}\}^8$ species, however, we favor a pathway involving direct formation of $\{\text{Fe}-\text{NO}\}^7$ from **1**.

In order to compare the effect of DNIC redox state on NO-transfer reactivity, the reaction of **2** with $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ was also examined. As with DNIC **1**, reaction of the ferric porphyrin with DNIC **2** cleanly afforded $[\text{Fe}^{\text{II}}(\text{NO})(\text{TPP})]$. In contrast to reactions with **1**, however, NO transfer with **2** proceeded in the absence of light and/or heat over the course of 4 h in benzene- d_6 . Compound **2** is consumed immediately upon reaction with $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$, as judged by IR spectroscopy (Figure 9). UV-vis spectroscopy confirmed that reduction of $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ takes place prior to NO transfer to generate **1** (Figure 9: 1761 and 1708 cm^{-1}) and the ferrous porphyrin $[\text{Fe}^{\text{II}}(\text{TPP})]$ (eq 6). This result is not surprising considering the redox potential of **2** ($E_{1/2} = -1.34$ V). After initial electron transfer, peaks corresponding to **1** diminish, with concomitant growth of features due to

$[\text{Fe}^{\text{II}}(\text{NO})(\text{TPP})]$ (1676 cm^{-1}) and **2** (1627 and 1569 cm^{-1}). The appearance of **2** differs from the results for **1**, which revealed formation of **4** as a byproduct of NO transfer (vide supra). In the reaction with an iron(II) porphyrin, however, **1** must formally transfer 1 equiv of NO^{\bullet} (not NO^-) to yield $[\text{Fe}^{\text{II}}(\text{NO})(\text{TPP})]$. Transfer of NO^{\bullet} from **1** generates an $\{\text{Fe}-\text{NO}\}^8$ species (eq 7) that immediately disproportionates to give **2** (eq 8). Such a reaction sequence explains the observed IR spectral changes in Figure 9 with the net stoichiometry displayed in eq 9.



NO transfer from **1** to independently prepared $[\text{Fe}^{\text{II}}(\text{TPP})]$ did not occur under the reactions conditions employed above for **2** and $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ (eqs 7 and 8). When Bu_4NCl was added to the reaction mixture, however, NO transfer proceeded as before over 4 h at ambient temperature. This result suggests that chloride may facilitate transfer of NO^{\bullet} from **1** to $[\text{Fe}^{\text{II}}(\text{TPP})]$. The role of chloride is not yet known, and kinetic experiments employing **2** and $[\text{Fe}(\text{TPP})\text{Cl}]$ could not be followed by UV-vis spectroscopy because the reaction proceeded too sluggishly at the concentrations required for optical spectroscopy, $\sim 5\text{--}10$ μM in porphyrin. This fact suggests that, unlike the reaction of **1** with $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$, the rate-limiting step for reaction of **1** with $[\text{Fe}^{\text{II}}(\text{TPP})]$ and Cl^- is overall bimolecular. Whether the reaction depends on the concentration of Cl^- or $[\text{Fe}^{\text{II}}(\text{TPP})]$ is unknown at this time. A transition state or intermediate involving a chloride bridge is an attractive hypothesis, given the possibility for the DNIC/MNIC to adopt a five-coordinate geometry (vide supra, compound **4**).

Discussion

The transfer of NO ligands from DNICs to various acceptors has been demonstrated previously with several synthetic DNICs.^{15,16,61} In many of these systems, the form

of NO (NO^\bullet , NO^+ , or NO^-) formally being transferred from the DNIC to the acceptor is dictated by the stability of the resulting nitrosylated or nitrosated product. Such dependence was noted previously in a study of NO transfer from a cobalt nitrosyl to a variety of different metal complexes.⁶³ The reactivity suggests that NO-transfer reactions are dictated by the thermodynamic requirements of the acceptor and that different forms of NO may be released or transferred from the DNIC depending on the nature of the acceptor. Biologically, this characteristic of DNICs may be important because the NO acceptor may require NO^\bullet (heme sites), NO^- (oxidized heme sites), or NO^+ (thiols, amines, and alcohols).

In the present work, we demonstrate a net formal transfer of both NO^- , $\{\text{Fe}(\text{NO})_2\}^9$ to $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$, and NO^\bullet , $\{\text{Fe}(\text{NO})_2\}^9$ to $[\text{Fe}^{\text{II}}(\text{TPP})]$. In each case, the mechanism is distinct and the qualitative reaction rates under similar conditions are quite different. Formal transfer of NO^- from **1** to $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ operates by a unimolecular process with rate-limiting loss of NO^\bullet or NO^- . This mechanism is consistent with the observation that light irradiation increases the NO-transfer rate because excitation of electrons to M–N antibonding orbitals should accelerate loss of a nitrosyl or nitroxyl ligand. In contrast, transfer of NO^\bullet from **1** to $[\text{Fe}^{\text{II}}(\text{TPP})]$ appears to be a bimolecular process. Furthermore, transfer of NO^\bullet does not occur in the absence of Cl^- . This fact suggests that coordination of a Lewis base to the DNIC may be required for the transfer of NO^\bullet or perhaps that ligands capable of bridging two metal centers are important in mediating transfer of NO^\bullet between a DNIC and its metal targets.

In addition to NO-transfer reactions between DNICs and porphyrins, the related chemistry of MNICs was examined in the present work and deserves comment. Both four-coordinate $\{\text{Fe}-\text{NO}\}^7$ and $\{\text{Fe}-\text{NO}\}^8$ compounds disproportionate, forming DNICs and Fe(III) ($\{\text{Fe}-\text{NO}\}^7$) or Fe(II) ($\{\text{Fe}-\text{NO}\}^8$) compounds. In the case of the former, $\{\text{Fe}-\text{NO}\}^7$ compound, this reaction appears to be reversible judging by the fact that DNIC **1** and $[\text{Fe}^{\text{III}}\text{Br}_2(\text{Ar}-\text{nacnac})]$ (**6**) disproportionate in solution at 25 °C. Similar reactivity also occurs with four-coordinate MNICs containing thiolate ligands. These species can disproportionate, leading to DNICs and iron(III) thiolates.¹⁹ Such reactivity contrasts with that of five- and six-coordinate MNICs, which are stable with respect to disproportionation.

Reduction of **4** to give the unstable $\{\text{Fe}-\text{NO}\}^8$ species is intriguing, given its possible relevance to the mechanism of NO-scavenging reductases (sNORs).⁶⁴ These enzymes contain adjacent carboxylate-bridged $\{\text{Fe}-\text{NO}\}^7$ centers in their NO-bound state. In one proposed mechanism, reduction of both iron centers leads to formation of the corresponding $\{\text{Fe}-\text{NO}\}^8$ species. These reduced nitrosyls then revert back to diiron(II) species in the presence of protons with concomitant release of N_2O and H_2O . In the case of compound **4**, reduction to $\{\text{Fe}-\text{NO}\}^8$ leads to formation of a DNIC and *not* to chemistry at the NO ligands. The fact that Fe(II) is generated in the process, however, lends credence to the proposal

that sNOR activity could occur through the intermediacy of an $\{\text{Fe}-\text{NO}\}^8$ species.^{65,66}

Conclusions

The NO-transfer chemistry of two DNICs supported by a sterically demanding β -diketiminato ligand has been explored using iron porphyrins as NO acceptors. The $\{\text{Fe}(\text{NO})_2\}^9$ DNIC, **1**, is capable of reductively nitrosylating $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ at elevated temperatures or in the presence of light to afford $[\text{Fe}^{\text{II}}(\text{NO})(\text{TPP})]$ and the corresponding $\{\text{Fe}-\text{NO}\}^7$ complex, **4**. Preliminary kinetic measurements of this reaction point to a rate-limiting step involving dissociation of NO^\bullet or NO^- from **1**. The analogous reaction of the $\{\text{Fe}(\text{NO})_2\}^{10}$ DNIC, **2**, also affords $[\text{Fe}^{\text{II}}(\text{NO})(\text{TPP})]$, but in this instance, rapid electron transfer from **2** to $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ precedes NO transfer. The resulting $\{\text{Fe}(\text{NO})_2\}^9$ DNIC then nitrosylates the iron(II) porphyrin, generating a $\{\text{Fe}-\text{NO}\}^8$ species that immediately disproportionates to **2** and an NO-free Fe(II) complex, **5**. This chemistry was verified by the synthesis of MNIC **4** and examination of its redox chemistry. In addition to iron, a four-coordinate $\{\text{Co}(\text{NO})_2\}^{10}$ species, **3**, was isolated and fully characterized. The structural and spectroscopic properties of **3** are similar to those of the iron analogues, **1** and **2**. Compound **3** undergoes a quasi-reversible one-electron reduction to the putative $\{\text{Co}(\text{NO})_2\}^{11}$ species.

Experimental Section

General Comments. Manipulations of air- and moisture-sensitive materials were performed under an atmosphere of nitrogen gas using standard Schlenk techniques or in an MBraun glovebox under an atmosphere of purified nitrogen. Tetrahydrofuran (THF), diethyl ether, pentane, benzene, and toluene were purified by passage through activated alumina⁶⁷ and then stored over 4-Å molecular sieves prior to use. Benzene-*d*₆ and THF-*d*₈ were dried over sodium ketyl and vacuum-distilled prior to use.

Materials. Compounds **1** and **2**,⁴⁵ $(\text{M})[\text{Fe}(\text{NO})\text{Br}_3]$,⁵⁵ $[\text{Fe}^{\text{II}}(\text{TPP})]$,⁶⁸ $[\text{Co}(\mu\text{-Cl})(\text{NO})_2]_2$,⁵³ KC_8 , anhydrous $\text{Fe}^{\text{II}}\text{Br}_2$, and Cp^*_2Co were synthesized according to published procedures. $\text{Na}(\text{Ar}-\text{nacnac})\cdot 2\text{THF}$ was prepared by deprotonation of $\text{H}(\text{Ar}-\text{nacnac})$ with $\text{NaN}(\text{SiMe}_3)_2$ in THF followed by crystallization from pentane. $\text{Li}(\text{Ar}-\text{nacnac})$ was prepared by deprotonation of $\text{H}(\text{Ar}-\text{nacnac})$ with $t\text{-BuLi}$ followed by crystallization from pentane at –30 °C. $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]$ and anhydrous $\text{Fe}^{\text{III}}\text{Br}_3$ were purchased from Strem Chemicals and used as received. Nitric oxide (NO; Matheson, 99%) was purified by passage through an Ascarite column (NaOH fused on silica gel) and a 6-ft coil filled with silica gel cooled to –78 °C.⁶⁹ Purified NO gas was stored and transferred under an inert atmosphere using standard gas storage bulbs and gastight syringes, respectively. For NO-transfer reactions, care was taken to prevent light exposure by covering reaction glassware in aluminum foil or by performing experiments in a darkened glovebox.

Physical Measurements. ¹H NMR spectra were recorded on a Varian INOVA spectrometer operating at 500 MHz. FT-IR spectra were recorded with a Thermo Nicolet Avatar 360 spectrophotometer running the OMNIC software; solid samples were pressed into KBr disks, and solution samples were prepared in THF or benzene-*d*₆ in an airtight Graseby-Specac

(63) Ungermaun, C. B.; Caulton, K. G. *J. Am. Chem. Soc.* **1976**, *98*, 3862–3868.

(64) Kurtz, D. M., Jr. *Dalton Trans.* **2007**, 4115–4121.

(65) Hayashi, T.; Caranto, J. D.; Wampler, D. A.; Kurtz, D. M., Jr.; Moënne-Loccoz, P. *Biochemistry* **2010**, *49*, 7040–7049.

(66) Silaghi-Dumitrescu, R.; Ng, K. Y.; Viswanathan, R.; Kurtz, D. M., Jr. *Biochemistry* **2005**, *44*, 3572–3579.

(67) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(68) Hu, C.; Noll, B. C.; Schulz, C. E.; Scheidt, W. R. *Inorg. Chem.* **2007**, *46*, 619–621.

(69) Lim, M. D.; Lorković, I. M.; Ford, P. C. *Methods in Enzymology*; Academic Press: New York, 2005; Vol. 396, pp 3–17.

solution cell with CaF₂ windows and 0.1 mm spacers. UV-vis spectra were recorded on a Cary-50 spectrophotometer in air-tight Teflon-capped quartz cells. Samples for ⁵⁷Fe Mössbauer studies were prepared by grinding solids with Apiezon-N grease. Samples were placed in a 90 K cryostat during measurement. All isomer shift (δ) and quadrupole splitting (ΔE_Q) values are reported with respect to ⁵⁷Fe-enriched metallic iron foil that was used for velocity calibration. The displayed spectrum was folded to enhance the signal-to-noise ratio. Fits of the data were calculated by the *WMOSS* version 2.5 plot and fit program.⁷⁰ X-band EPR spectra were recorded on a Bruker EMX EPR spectrometer. Temperature control was maintained with a quartz finger dewar (77 K). Spectra were recorded in 4-mm-o.d. quartz EPR tubes capped with a tight-fitting rubber septum. Electrochemical measurements were performed at 25 °C on a VersaSTAT3 Princeton Applied Research potentiostat running the V3-Studio electrochemical analysis software. A three-electrode setup was employed comprising a glassy carbon working electrode, a platinum wire auxiliary electrode, and a 0.1 M Ag/Ag⁺ reference electrode. Triply recrystallized Bu₄NPF₆ or Bu₄NBAR₄^F (Ar^F = 3,5-bis(trifluoromethyl)phenyl) was used as the supporting electrolyte. All electrochemical data were referenced internally to the ferrocene/ferrocenium couple at 0.00 V. Elemental analyses were performed by Midwest Micro-lab, LLC, Indianapolis, IN.

X-ray Data Collection and Structure Solution Refinement. Crystals of **3–6** suitable for X-ray diffraction were mounted in Paratone N oil using 30 μ m aperture MiTeGen MicroMounts (Ithaca, NY) and frozen under a nitrogen cold stream maintained by a KRYO-FLEX low-temperature apparatus. Data were collected on a Bruker SMART APEX CCD X-ray diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) controlled by the *APEX2* software package (version 2010.1-2). Data reduction was performed with *SAINTE*.⁷¹ Empirical absorption corrections were applied with *SADABS*,⁷² and the structure was checked for higher symmetry by the *PLATON* software.⁷³ The structures were solved by direct methods with refinement by full-matrix least squares based on F^2 using *SHELXTL-97*.⁷⁴ All non-hydrogen atoms were located and their positions refined anisotropically. Hydrogen atoms were assigned to idealized positions and given thermal parameters equal to either 1.5 (methyl hydrogen atoms) or 1.2 (non-methyl hydrogen atoms) times the thermal parameters of the atoms to which they were attached.

Crystals of **3–6** were grown by slow cooling of a saturated solution of each complex in pentane. No incorporation of solvent occurred in any of the crystal lattices. The asymmetric unit of complex **3** contains two independent molecules having the same molecular structure. Complex **4** was modeled with a positional disorder between the NO and Br[−] ligands. The NO and Br[−] ligands were observed to be positionally disordered in a difference Fourier map and the occupancy factors of the two disordered components refined to 67% and 33%. Further information is provided in the Supporting Information. Table 1 reports crystallographic data and additional refinement details.

[Co(NO)₂(Ar-nacnac)] (3). To 0.200 g (0.650 mmol) of [Co(μ -Cl)(NO)₂]₂ in 5 mL Et₂O was added a solution of 0.555 g (1.30 mmol) of Na(Ar-nacnac)·2THF in 10 mL of Et₂O. The resulting brown-yellow solution was allowed to stir at ambient temperature for 2 h. All volatiles were removed in vacuo, and the resulting residue was extracted into 10 mL of pentane. After

filtration through a plug of Celite, the pentane solution was concentrated in vacuo to 3 mL and allowed to stand at −30 °C for 24 h. Compound **5** precipitated as 0.527 g (0.75%) of brown cubes in two crops. ¹H NMR (benzene-*d*₆): δ 7.07 (m, 6 ArH), 5.15 (s, 1 CH), 3.16 (sep, 4 CHMe₂), 1.73 (s, 6 Me), 1.23 (d, 12 CHMe₂), 1.15 (d, 12 CHMe₂). IR (benzene-*d*₆, cm^{−1}): 3057, 2963, 2928, 2869, 1801 (ν_{NO}), 1706 (ν_{NO}), 1554, 1522, 1458, 1438, 1399, 1316, 1177. CV (THF): $E_{1/2} = -1.80$ V {Co(NO)₂}^{10/11}; $E_{\text{ox}} = +0.53$ V. UV-vis (THF) [λ_{max} , nm (ϵ , M^{−1} cm^{−1}): 322 (6700), 360 (5700), 415 (sh), 570 (sh). Anal. Calcd for C₂₉H₄₁CoN₄O₂: C, 64.91; H, 7.70; N, 10.44. Found: C, 64.09; H, 7.58; N, 10.17.

[Fe(NO)Br(Ar-nacnac)] (4). Procedure A: To 0.114 g (0.250 mmol) of (Et₄N)[Fe(NO)Br₃] dissolved in 10 mL of THF was added a solution of 0.106 g (0.250 mmol) of Li(Ar-nacnac) in 5 mL of THF. The solution immediately changed from yellow-brown to dark forest green upon addition of the diketiminate salt. The reaction was allowed to stir for an additional 2 h at ambient temperature, during which time the forest-green solution changed to a dark-brown mixture. All volatiles were removed in vacuo, and the residue was extracted into 15 mL of pentane. The extract was filtered through a plug of Celite to remove Et₄NBr and LiCl. The resulting pentane solution was concentrated in vacuo to 5 mL and allowed to stand at −30 °C for 24 h. During this time, compound **3** precipitated in two crops as 0.0886 g (61%) of brown cubes. See below for spectral data.

Procedure B: To 0.0530 g (0.099 mmol) of compound **4** in 2 mL of THF was added 2.5 mL (~0.10 mmol) of NO gas via syringe. The solution immediately changed from bright yellow to dark brown. The solution was allowed to stir at ambient temperature for 20 min. All volatiles were removed in vacuo, and the residue was extracted into 5 mL of pentane. After filtration through glass filter paper, the pentane solution was concentrated in vacuo to 2 mL and allowed to stand at −30 °C for 24 h. During this time, compound **3** precipitated as 0.0247 g (50%) of brown cubes. Mp: 190–195 °C. ¹H NMR (benzene-*d*₆): δ 33.7 (2 H), 27.1 (2 H), 13.5 (v br, 1H), 4.5 (2 H), 3.7 (12 H), 2.8 (12 H), 1.4 (2 H), −21.2 (2 H), −33.2 (6 H). IR (benzene-*d*₆, cm^{−1}): 3060, 2965, 2927, 2869, 1777 (ν_{NO}), 1519, 1463, 1437, 1371, 1317, 1174, 1106, 1022; 1743 (ν_{isNO}). EPR (X-band, 2-MeTHF): 77 K $g_1 = 4.62$, $g_2 = 3.41$, $g_3 = 1.96$. CV (THF): $E_{1/2} = -1.23$ V {Fe-NO}^{7/8}. UV-vis (THF) [λ_{max} , nm (ϵ , M^{−1} cm^{−1}): 313 (19 000), 417 (sh), 552 (1800)]. ⁵⁷Fe Mössbauer: $\delta = 0.33(2)$ mm/s, $\Delta E_Q = 0.92(2)$ mm/s, $\Gamma = 0.44(2)$ mm/s. Anal. Calcd for C₂₉H₄₁BrFeN₃O: C, 59.70; H, 7.08; N, 7.20. Found: C, 60.19; H, 6.98; N, 7.41.

[Fe(THF)Br(Ar-nacnac)] (5). To 0.167 g (0.774 mmol) of anhydrous Fe^{II}Br₂ in 20 mL of THF was added 0.454 g (0.776 mmol) of Na(Ar-nacnac)·2THF. The mixture was allowed to stir at ambient temperature for 2 h, during which time the color changed from orange to brown-yellow. The mixture was filtered through a plug of Celite to remove NaBr. All volatiles were removed in vacuo. The resulting residue was washed with pentane, causing formation of a yellow precipitate. The solid was isolated by filtration and washed with pentane to give 0.377 g (85%) of **5** as a yellow powder. Storing the filtrate at −30 °C for 24 h afforded an additional 0.030 g of yellow needles that were used for X-ray diffraction. ¹H NMR (THF-*d*₈): δ 19.0, 7.0, 5.1, 1.1, 0.8, −8.8, −38.9, −68.9, −80.2. UV-vis (THF) [λ_{max} , nm (ϵ , M^{−1} cm^{−1}): 331 (4200), 428 (sh)]. UV-vis (toluene) [λ_{max} , nm (ϵ , M^{−1} cm^{−1}): 325 (11 500), 389 (3500), 520 (670)]. CV (THF): $E_{1/2} = -0.61$ V. Anal. Calcd for C₃₃H₄₉BrFeN₂O: C, 63.37; H, 7.90; N, 4.48. Found: C, 63.31; H, 7.68; N, 4.51.

[Fe^{III}Br₂(Ar-nacnac)] (6). This compound could only be prepared in small quantities by reaction of equimolar amounts of Na(Ar-nacnac)·2THF and anhydrous FeBr₃ in toluene. After stirring for 2 h at ambient temperature, all volatiles were removed in vacuo, affording a dark-forest-green residue. Extraction of

(70) Kent, T. A. *WMOSS*, version 2.5; Mössbauer Spectral Analysis Software, WEB Research Co.; Minneapolis, MN, 1998.

(71) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112–122.

(72) Sheldrick, G. M. *SADABS: Area-Detector Absorption Correction*; University of Göttingen: Göttingen, Germany, 2001.

(73) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2000.

(74) Sheldrick, G. M. *SHELXTL97: Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

this residue into pentane generated a dark-green solution and a large quantity of brown insoluble material, Fe(II) byproducts formed by reduction of Fe(III) by the diketiminate salt. The pentane solution was filtered through a plug of Celite, concentrated in vacuo, and allowed to stand at $-35\text{ }^{\circ}\text{C}$ for 24 h. After this time, small green cubes of **6** appeared (typically $<10\text{ mg}$). These cubes were suitable for X-ray diffraction, but repeated elemental analysis and solution magnetic susceptibility measurements indicated that **6** contained diamagnetic impurities, most likely the coupled Ar-nacnac ligand. EPR (X-band, 2-MeTHF): 77 K $g = 9.02, 5.24, 3.55, 2.60, 2.04, 1.30$ (see the SI). CV (THF): $E_{1/2} = -0.61\text{ V}$.

General Procedure for NO-Transfer Reactions. Solutions of **1** or **2** in THF (UV-vis) or benzene- d_6 (IR) were prepared in the glovebox at appropriate concentrations ($\sim 100\text{ }\mu\text{ M}$ for UV and $\sim 20\text{ mM}$ for IR). These solutions were then combined with a

solution of the desired iron porphyrin compound in a vial or quartz cuvette. Reactions were allowed to proceed in the absence of light as much as possible. For UV-vis reactions conducted in the presence of light irradiation, the cuvette was exposed to fluorescent room light for 3 min intervals between spectra.

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Supporting Information Available: Additional figures, complete spectra, crystallographic data, and fully labeled thermal ellipsoid diagrams for compounds **3–6**, as well as the corresponding CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.