

N–O Bond Homolysis of an Iron(II) TEMPO Complex Yields an Iron(III) Oxo Intermediate

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S Supporting Information

ABSTRACT: The reaction of TEMPO with the iron(I) synthon $\text{PhB}(\text{MesIm})_3\text{Fe}(\text{COE})$ leads to formation of the κ^1 -TEMPO complex $\text{PhB}(\text{MesIm})_3\text{Fe}(\text{TEMPO})$. Structural and spectroscopic data establish the complex contains divalent iron bound to a nitroxido anion and is isoelectronic to an iron(II) peroxo complex. Thermolysis of the complex results in N–O bond homolysis, leading to the formation of an iron(III) oxo intermediate. The oxo intermediate is active in oxygen atom transfer reactions and can be trapped by the triphenylmethyl radical to give the iron(II) alkoxo complex $\text{PhB}(\text{MesIm})_3\text{Fe}(\text{OCPh}_3)$.

Nonheme iron dioxygenases and their model complexes have attracted interest as potential green oxidants.¹ Oxoferryl species are proposed as the key oxidizing intermediates in the oxidation mechanism of these species. There is spectroscopic evidence for the $[\text{Fe}^{\text{IV}}=\text{O}]$ unit in a number of metalloenzymes.² In the case of model complexes, the $[\text{Fe}^{\text{IV}}=\text{O}]$ unit has also been characterized by single-crystal X-ray crystallography for $S = 1^3$ and $S = 2^4$ spin states.⁵

The reactivity of synthetic iron(IV) oxo complexes has been extensively investigated.⁶ Depending on the supporting ligand, these complexes oxidize a range of substrates by a number of mechanisms. The hydroxylation of alkanes and oxidation of alcohols in particular are proposed to involve initial hydrogen atom abstraction by the iron(IV) oxo complex.⁵

An isolable iron(III) oxo complex, $[\text{Fe}^{\text{III}}\text{H}_3\text{buea}(\text{O})]^{2-}$, has been reported, where H_3buea is the tripodal tris[(*N*-tert-butylureaylato)-*N*-ethylene]aminato ligand.⁷ Spectroscopic and computational investigations are consistent with a single Fe–O σ -bond that is stabilized by a hydrogen bonding network.⁸ It is possible that the hydrogen bonding network attenuates the reactivity of the oxo ligand, which is reflected in the relatively low thermodynamic driving force toward hydrogen atom transfer.⁹ In addition to this complex, electrochemical and spectroscopic measurements implicate the formation of iron(III) oxo species upon one-electron reduction of iron(IV) oxo complexes. These iron(III) oxos can be stabilized by Lewis acids.¹⁰

Herein, we provide kinetic, reactivity, and computational evidence for an iron(III) oxo species that is formed by the

thermolysis of a high spin iron(II) peroxide analogue. The iron(III) oxo intermediate, which is not stabilized by hydrogen bonding or Lewis acids, can be trapped by a carbon-centered radical to provide an iron(II) alkoxo complex and is also capable of two electron oxygen atom transfer.

Reaction of the iron(I) synthon $\text{PhB}(\text{MesIm})_3\text{Fe}(\text{COE})^{11}$ with TEMPO (where $\text{PhB}(\text{MesIm})_3$ = phenyltris(1-mesitylimidazol-2-ylidene)borate, COE = *cis*-cyclooctene, TEMPO = 2,2',6,6'-tetramethylpiperidinyloxy radical) leads to the formation of the yellow complex $\text{PhB}(\text{MesIm})_3\text{Fe}(\text{TEMPO})$ **1**, a rare example of a late transition metal TEMPO complex.¹² The solid state structure of **1** (Figure 1A) reveals a four-coordinate

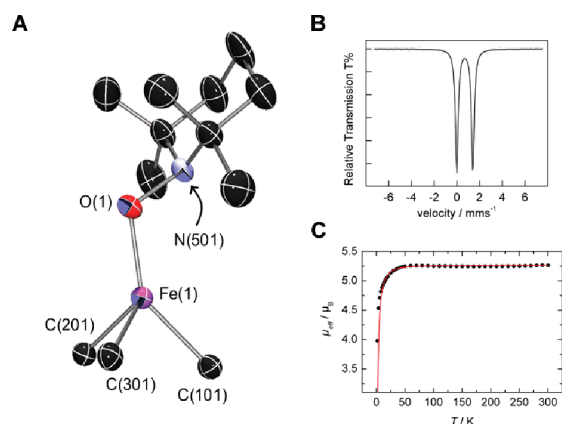


Figure 1. (A) X-ray crystal structure of **1**. Thermal ellipsoids shown at 50% probability, hydrogen atoms, and most of the tris(carbene)borate ligand omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)–O(1) 1.8710(1); Fe(1)–C(101) 2.099(2); Fe(1)–C(301) 2.135(2); Fe(1)–C(201) 2.139(2); O(1)–N(501) 1.449(2); N(501)–O(1)–Fe(1) 114.8(1); C(101)–Fe(1)–C(301) 89.17(8); C(101)–Fe(1)–C(201) 88.14(8); C(301)–Fe(1)–C(201) 87.69(8). (B) Mössbauer spectrum of **1** recorded at 77 K. Spectral parameters: $\delta = 0.70 \text{ mm s}^{-1}$ with $|\Delta E_Q| = 1.42 \text{ mm s}^{-1}$. (C) Variable temperature dc susceptibility data of **1** under an applied field of 1 T. The red line is a fit to the data, yielding the parameters $g = 2.15$, $|D| = 8.5 \text{ cm}^{-1}$.

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iron atom bound to the oxygen atom of a κ^1 -TEMPO ligand.¹³ The long N—O bond length (1.499(2) Å) and pyramidalized nitrogen atom (sum of angles = 334°) of TEMPO are most consistent with the reduction of TEMPO to [TEMPO][−],¹⁴ while the Fe—C bond lengths and C—Fe—C bond angles are similar to other high spin four-coordinate iron(II) tris(carbene)borate complexes.^{11,15} These structural data therefore suggest that the iron(I) synthon reduces TEMPO by one electron, yielding a high spin, four-coordinate iron(II) nitroxide complex.

Mössbauer spectroscopic and SQUID magnetometry measurements confirm this oxidation state assignment. At 77 K, a single quadrupole doublet is observed in the zero-field ⁵⁷Fe Mössbauer spectrum at $\delta = 0.70$ mm s^{−1} with $|\Delta E_Q| = 1.42$ mm s^{−1} (Figure 1B). These spectral parameters are similar to those observed for other high spin iron(II) tris(carbene)borate complexes, e.g. for PhB(MesIm)₃FeCl, $\delta = 0.66$ mm s^{−1}, $|\Delta E_Q| = 1.83$ mm s^{−1}.¹⁵ Between 50 and 300 K, the magnetic moment of **1** is temperature-independent with $\mu_{\text{eff}} = 5.26 \mu_B$ (Figure 1C). Together, these data support the assignment of a mononuclear high spin ($S = 2$) iron(II) center in complex **1**.

The solid state structure of **1** is maintained in solution. Thirteen paramagnetically shifted resonances are observed in the ¹H NMR spectrum (see Supporting Information). Interestingly, the number and relative integrations of these resonances suggest that the TEMPO ligand is locked in the chair conformation that is observed in the solid state structure, presumably a consequence of the highly congested environment near the metal center. The solution magnetic moment ($\mu_{\text{eff}} = 4.7(3) \mu_B$), determined by the Evans' method, is also consistent with a high spin ($S = 2$) state.

The combined structural and spectroscopic data therefore support the assignment of a divalent iron center bound to an anionic TEMPO ligand. The TEMPO ligand in **1** may be considered as an analogue of the peroxide ligand; thus, this complex is a model for the [Fe—OOR] unit, an intermediate in the activation of O₂ by iron-containing metalloenzymes.¹⁶ It is known that the O—O bond in these species is readily cleaved, leading to the formation of an oxidizing iron oxo intermediate.^{1,17,18}

Thermolysis of **1** results in the formation of stoichiometric amounts of 2,2',6,6'-tetramethylpiperidine along with multiple paramagnetic products. The rate at which **1** disappears was monitored by ¹H NMR in C₆D₆ (8–46 mM). The reaction was found to be first order with respect to the iron complex ($k_1 = (4.46 \pm 0.06) \times 10^{-4} \text{ s}^{-1}$ at 68 °C), consistent with an intramolecular reaction. It is likely that thermolysis of **1** results in homolysis of the N—O bond, similar to other examples involving N—O bond cleavage in TEMPO.^{19,20} The resulting aminyl radical then abstracts hydrogen atoms from adventitious H• sources to yield 2,2',6,6'-tetramethylpiperidine. Homolysis of the N—O bond in **1** implicates the formation of an iron(III) oxo intermediate, similar to other TEMPO deoxygenation reactions that afford Re(V) and U(V) oxo complexes, respectively.²⁰

This proposal is supported by electronic structure theory. Specifically, density functional theory calculations with the B3LYP exchange-correlation functional and SDD basis set reveal that the formation of an iron(III) oxo complex by N—O bond homolysis of **1** is thermodynamically favorable in THF solution. Thus, for the formation of PhB(MesIm)₃Fe=O ($S = 5/2$) along with the 2,2',6,6'-tetramethylpiperidiny radical, $\Delta G = -7.3$ kcal/mol.²¹ By contrast, N—O bond heterolysis to give

an iron(IV) oxo species and the 2,2',6,6'-tetramethylpiperidiny anion is not thermodynamically favorable, with $\Delta G \geq +44.7$ kcal/mol in THF.

The optimized structure of PhB(MesIm)₃Fe=O ($S = 5/2$, the lowest energy spin state) reveals the complex to have an approximately 3-fold symmetry (Figure 2A). The Fe—O bond

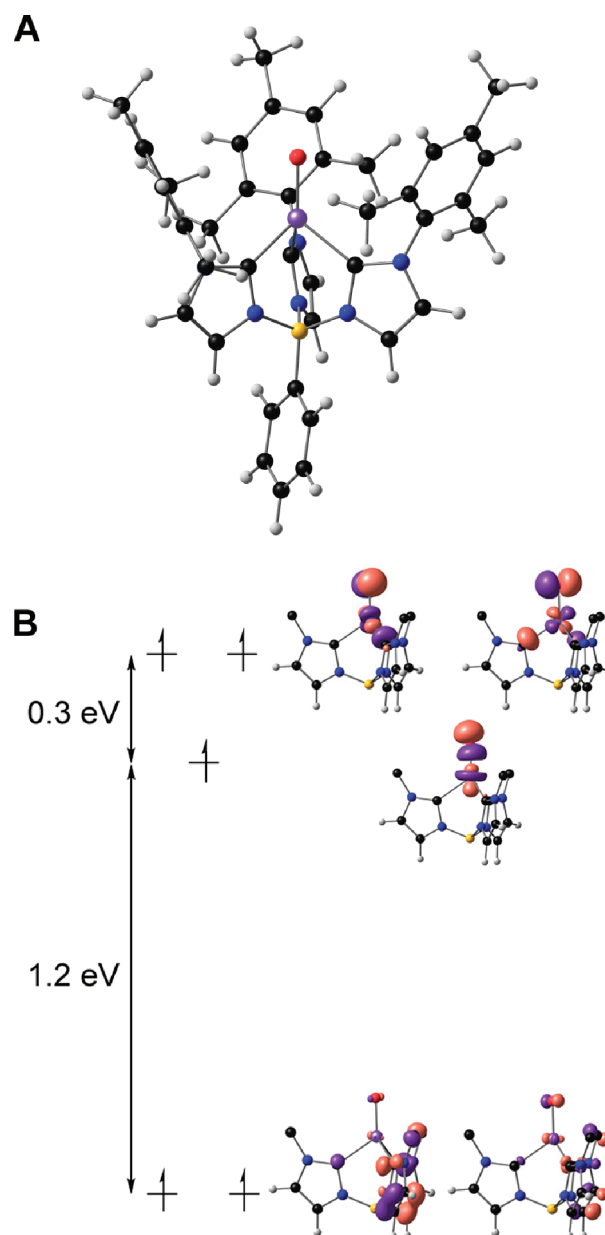
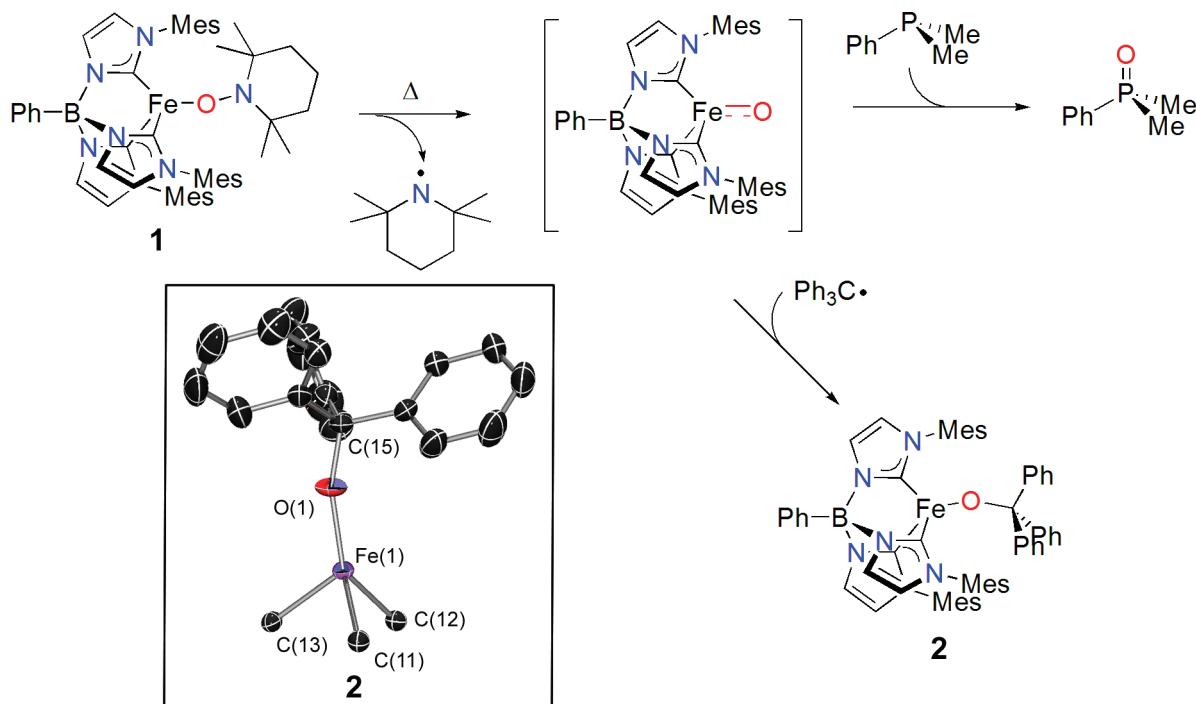


Figure 2. (A) DFT optimized structure of PhB(MesIm)₃Fe=O ($S = 5/2$). Selected bond length (Å) and angle (deg): Fe—O 1.717; B—Fe—O 176.6. (B) Molecular orbital diagram for PhB(MesIm)₃Fe=O ($S = 5/2$). Tris(carbene)borate mesityl substituents and phenyl group have been omitted for clarity.

(1.717 Å) is longer than observed in iron(IV) oxo complexes, which are in the range 1.639(5)–1.680(1) Å.^{3,4,22} However, this bond is shorter than in the iron(III) complex [Fe^{III}H₃buea(O)]^{2−} 1.813(3) Å, which has a single σ -bond,⁸ and thus the Fe—O bond order in PhB(MesIm)₃Fe=O is likely to be between 1 and 2. The frontier orbitals are calculated to be similar to those reported for four-coordinate iron(III) imido complexes (Figure 2B).²³ Notably, the three highest occupied

Scheme 1. Synthesis and reactivity of $\text{PhB}(\text{MesIm})_3\text{Fe}=\text{O}^a$ 

^aInset: Molecular structure of complex 2, thermal ellipsoids shown at 50% probability. Selected bond lengths (Å) and angles (deg): Fe(1)–O(1) 1.814(1); Fe(1)–C(11) 2.118(1); Fe(1)–C(12) 2.118(1); Fe(1)–C(13) 2.098(1); O(1)–C(15) 1.388(2); Fe(1)–O(1)–C(15) 160.8(1); C(11)–Fe(1)–C(12) 89.03(5); C(11)–Fe(1)–C(13) 88.11(5); C(12)–Fe(1)–C(13) 89.20(5).

orbitals show substantial Fe–O antibonding character, suggesting an Fe–O bond order of 3/2. The spin density at the oxo ligand (0.85) indicates that oxyl radical character also likely contributes to the electronic structure.

The iron(III) oxo intermediate can be trapped by the triphenylmethyl radical. Thus, heating 1 in the presence of $\text{Ph}_2\text{C}=\text{C}_6\text{H}_5\text{CPh}_3$,²⁴ a source of the triphenylmethyl radical, results in quantitative formation of the alkoxo complex $\text{PhB}(\text{MesIm})_3\text{FeOCPh}_3$ 2 along with stoichiometric 2,2',6,6'-tetramethylpiperidine. The complex was characterized in the solid state by single crystal X-ray crystallography, revealing a four-coordinate iron alkoxo complex (Scheme 1, inset). The ^1H NMR spectrum of 2 is consistent with the solid state structure; eleven paramagnetically shifted resonances with appropriate relative integrations are observed in the spectrum. The magnetic moment of the complex, $\mu_{\text{eff}} = 4.7(3)$ BM, as measured by Evans' method, is consistent with high spin iron(II).

The rate at which 1 decomposes is unchanged when thermolysis is conducted in the presence of excess $\text{Ph}_2\text{C}=\text{C}_6\text{H}_5\text{CPh}_3$ ($k_{\text{obs}} = (7.1 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$).²⁵ These results are highly suggestive of a mechanism that involves rate limiting formation of an iron(III) oxo complex by N–O bond homolysis, followed by a rapid reaction with the triphenylmethyl radical to yield 2 (Scheme 1).

Finally, the iron(III) oxo intermediate is active in two-electron oxygen atom transfer reactions. While no reaction is observed with either cyclooctene or PPh_3 , the latter presumably due to steric constraints,²⁶ PMe_2Ph is oxidized to the corresponding phosphine oxide in 50% yield (Scheme 1).

In conclusion, structural and spectroscopic characterization of a four-coordinate iron(II) TEMPO complex reveal it to be isoelectronic to an iron(II) peroxide. Kinetic experiments,

supported by electronic structure theory, show that, upon thermolysis, N–O bond homolysis occurs to produce an iron(III) oxo intermediate, a reaction pathway that is analogous to that of iron peroxides.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental and computational details. 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) Selected reviews: (a) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L. *Chem. Rev.* **2004**, *104*, 939. (b) Que, L. *Acc. Chem. Res.* **2007**, *40*, 493.

- (2) (a) Bollinger, J. M.; Price, J. C.; Hoffart, L. M.; Barr, E. W.; Krebs, C. *Eur. J. Inorg. Chem.* **2005**, 4245. (b) Krebs, C.; Price, J. C.; Baldwin, J.; Saleh, L.; Green, M. T.; Bollinger, J. M. *Inorg. Chem.* **2005**, 44, 742. (c) Hoffart, L. M.; Barr, E. W.; Guyer, R. B.; Bollinger, J. M.; Krebs, C. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, 103, 14738. (d) Galonić, D. P.; Barr, E. W.; Walsh, C. T.; Bollinger, J. M.; Krebs, C. *Nat. Chem. Biol.* **2007**, 3, 113. (e) Eser, B. E.; Barr, E. W.; Frantom, P. A.; Saleh, L.; Bollinger, J. M.; Krebs, C.; Fitzpatrick, P. F. *J. Am. Chem. Soc.* **2007**, 129, 11334. (f) Fujimori, D. G.; Barr, E. W.; Matthews, M. L.; Koch, G. M.; Yonce, J. R.; Walsh, C. T.; Bollinger, J. M.; Krebs, C.; Riggs-Gelasco, P. J. *J. Am. Chem. Soc.* **2007**, 129, 13408. (g) Krebs, C.; Fujimori, D. G.; Walsh, C. T.; Bollinger, J. M. *Acc. Chem. Res.* **2007**, 40, 484. (h) Grzyska, P. K.; Appelman, E. H.; Hausinger, R. P.; Proshlyakov, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, 107, 3982.
- (3) (a) Rohde, J.-U.; In, J.-H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Münck, E.; Nam, W.; Que, L. *Science* **2003**, 299, 1037. (b) Klinker, E. J.; Kaizer, J.; Brennessel, W. W.; Woodrum, N. L.; Cramer, C. J.; Que, L. *Angew. Chem., Int. Ed.* **2005**, 44, 3690. (c) Thibon, A.; England, J.; Martinho, M.; Young, V. G., Jr.; Frisch, J. R.; Guillot, R.; Girerd, J.-J.; Münck, E.; Que, L., Jr.; Banse, F. *Angew. Chem., Int. Ed.* **2008**, 47, 7064.
- (4) (a) England, J.; Guo, Y.; Farquhar, E. R.; Young, V. G.; Münck, E.; Que, L. *J. Am. Chem. Soc.* **2010**, 132, 8635. (b) Lacy, D. C.; Gupta, R.; Stone, K. L.; Greaves, J.; Ziller, J. W.; Hendrich, M. P.; Borovik, A. S. *J. Am. Chem. Soc.* **2010**, 132, 12188.
- (5) Hohenberger, J.; Ray, K.; Meyer, K. *Nat. Commun.* **2012**, 3, 720.
- (6) Selected review: Nam, W. *Acc. Chem. Res.* **2007**, 40, 522.
- (7) MacBeth, C. E.; Golombek, A. P.; Young, V. G.; Yang, C.; Kucera, K.; Hendrich, M. P.; Borovik, A. S. *Science* **2000**, 289, 938.
- (8) (a) MacBeth, C. E.; Gupta, R.; Mitchell-Koch, K. R.; Young, V. G.; Lushington, G. H.; Thompson, W. H.; Hendrich, M. P.; Borovik, A. S. *J. Am. Chem. Soc.* **2004**, 126, 2556. (b) Dey, A.; Hocking, R. K.; Larsen, P.; Borovik, A. S.; Hodgson, K. O.; Hedman, B.; Solomon, E. I. *J. Am. Chem. Soc.* **2006**, 128, 9825.
- (9) (a) Gupta, R.; Borovik, A. S. *J. Am. Chem. Soc.* **2003**, 125, 13234. (b) Shook, R. L.; Borovik, A. S. *Inorg. Chem.* **2010**, 49, 3646.
- (10) (a) Sastri, C. V.; Oh, K.; Lee, Y. J.; Seo, M. S.; Shin, W.; Nam, W. *Angew. Chem., Int. Ed.* **2006**, 45, 3992. (b) Collins, M. J.; Ray, K.; Que, L. *Inorg. Chem.* **2006**, 45, 8009. (c) Lee, Y.-M.; Kotani, H.; Suenobu, T.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2008**, 130, 434. (d) Fukuzumi, S.; Morimoto, Y.; Kotani, H.; Naumov, P.; Lee, Y.-M.; Nam, W. *Nat. Chem.* **2010**, 2, 756. (e) Comba, P.; Fukuzumi, S.; Kotani, H.; Wunderlich, S. *Angew. Chem., Int. Ed.* **2010**, 49, 2622. (f) Morimoto, Y.; Kotani, H.; Park, J.; Lee, Y.-M.; Nam, W.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, 133, 403.
- (11) Nieto, I.; Ding, F.; Bontchev, R. P.; Wang, H.; Smith, J. M. *J. Am. Chem. Soc.* **2008**, 130, 2716.
- (12) Hettler, D. G. H.; Kaiser, J.; Reijerse, E.; Peters, T. P. J.; Thewissen, S.; Blok, A. N. J.; Smits, J. M. M.; de Gelder, R.; de Briun, B. *J. Am. Chem. Soc.* **2005**, 127, 1895.
- (13) Two molecules with similar metrical parameters are observed in the asymmetric unit.
- (14) Mahanthappa, M. K.; Huang, K.-W.; Cole, A. P.; Waymouth, R. M. *Chem. Commun.* **2002**, 502. The N–O bond length in TEMPO is 1.283(9) Å; see: Capiomont, A.; Lajžerowicz-Bonnetau, J. *Acta Crystallogr.* **1974**, B30, 2160.
- (15) Scepaniak, J. J.; Harris, T. D.; Vogel, C. S.; Sutter, J.; Meyer, K.; Smith, J. M. *J. Am. Chem. Soc.* **2011**, 133, 3824.
- (16) (a) Katona, G.; Carpentier, P.; Nivière, V.; Amara, P.; Adam, V.; Ohana, J.; Tsanov, N.; Bourgeois, D. *Science* **2007**, 316, 449. (b) Kovaleva, E. G.; Lipscomb, J. D. *Science* **2007**, 316, 453.
- (17) Selected reviews: (a) Decker, A.; Solomon, E. I. *Curr. Opin. Chem. Biol.* **2005**, 9, 152. (b) Que, L.; Tolman, W. B. *Nature* **2008**, 455, 333.
- (18) Cho, J.; Jeon, S.; Wilson, S.; Liu, L. V.; Kang, E. A.; Braymer, J. J.; Lim, M. H.; Hedman, B.; Hodgson, K. O.; Valentine, J. S.; Solomon, E. I.; Nam, W. *Nature* **2011**, 478, 502.
- (19) Selected examples: (a) Lucarini, M.; Marchesi, E.; Pedulli, G. F.; Chatgililoglu, C. *J. Org. Chem.* **1998**, 63, 1687. (b) Iwamoto, T.; Masuda, H.; Ishida, S.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2003**, 125, 9300.
- (20) (a) Lippert, C. A.; Soper, J. D. *Inorg. Chem.* **2010**, 49, 3682. (b) Fortier, S.; Kaltsoyannis, N.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2011**, 133, 14224.
- (21) The reaction is also found to be thermodynamically favorable for other possible spin states of the product, $\Delta G = -2.1$ kcal/mol ($S = 1/2$); $\Delta G = -1.5$ kcal/mol ($S = 3/2$). See Supporting Information for details.
- (22) Further information on the other spin states is provided in the Supporting Information.
- (23) (a) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, 125, 322. (b) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, 125, 10782. (c) Mehn, M. P.; Brown, S. D.; Jenkins, D. M.; Peters, J. C.; Que, L. *Inorg. Chem.* **2006**, 45, 7417. (d) Nieto, I.; Ding, F.; Bontchev, R. P.; Wang, H.; Smith, J. M. *J. Am. Chem. Soc.* **2008**, 130, 2716. (e) Moret, M. E.; Peters, J. C. *Angew. Chem., Int. Ed.* **2011**, 50, 2063.
- (24) (a) Gomberg, M. *J. Am. Chem. Soc.* **1900**, 22, 757. (b) Lankamp, H.; Nauta, W. T.; MacLean, C. *Tetrahedron Lett.* **1968**, 2, 249. (c) McBride, J. M. *Tetrahedron* **1974**, 30, 2009.
- (25) For the dissociation of $\text{Ph}_2\text{C}=\text{C}_6\text{H}_5\text{CPh}_3$, $k = 3.8 \text{ s}^{-1}$ at 68°C : (a) Ziegler, K. *Liebigs Ann.* **1942**, 551, 127. (b) Ziegler, K.; Orth, Ph.; Weber, K. *Liebigs Ann.* **1933**, 504, 131.
- (26) Bigi, J. P.; Harman, W. H.; Lassalle-Kaiser, B.; Robles, D. M.; Stich, T. A.; Yano, J.; Britt, R. D.; Chang, C. J. *J. Am. Chem. Soc.* **2012**, 134, 1536.