

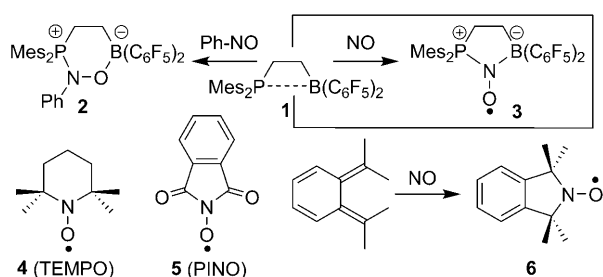
Frustrated Lewis Pairs

Capture of NO by a Frustrated Lewis Pair: A New Type of Persistent N-Oxyl Radical**

Allan Jay P. Cardenas, Brooks J. Culotta, Timothy H. Warren,* Stefan Grimme,* Annika Stute, Roland Fröhlich, Gerald Kehr, and Gerhard Erker*

Frustrated Lewis Pairs (FLPs) show a rapidly increasing spectrum of interesting chemical reactions.^[1] They have been reported to activate dihydrogen under mild conditions and to serve as metal free hydrogenation catalysts toward specific organic substrates.^[2] FLPs add to numerous unsaturated substrates such as alkenes and alkynes, carbonyl compounds, azides and even CO₂ or N₂O.^[3,4] For instance, the intramolecular P/B-FLP **1** adds to nitrosobenzene to form the six-membered heterocycle **2**.^[5]

Nitric oxide (NO) is an important messenger molecule and regulator in biological systems.^[6] We find that the reactive frustrated Lewis pair **1** cleanly and rapidly reacts with this essential small molecule to form the persistent heterocyclic N-oxyl radical “P/B-FLP-NO” (**3**). Compound **3** represents a novel type of N-oxyl radical related to the ubiquitous TEMPO radical (**4**) and its congeners (e.g. **5** (PINO)^[7] and **6**,^[8] see Scheme 1).^[9] Herein we describe the synthesis, characterization, and O-based reactivity of this novel type of N-oxyl radical derived from a frustrated Lewis pair and nitric oxide.



Scheme 1. Synthesis of P/B-FLP-NO (**3**) with related N-oxyl radicals.

Treatment of a yellow solution of the FLP Mes₂PCH₂CH₂B(C₆F₅)₂ (**1**)^[10] (in situ generated from Mes₂PCH=CH₂ and Piers' borane [HB(C₆F₅)₂]^[11]) in fluorobenzene with 1 equiv NO_{gas} gave rise to an intense green solution from which blue crystals of the P/B-FLP-NO product **3** were isolated in 58% yield by precipitation with pentane (Scheme 1). X-ray crystal structure analysis of **3** (Figure 1)

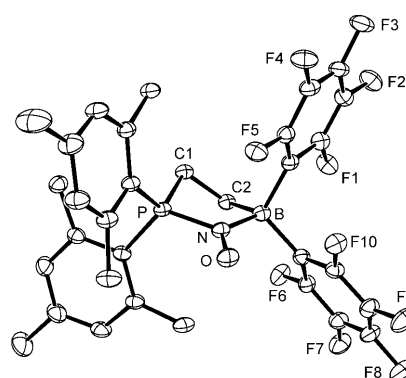


Figure 1. X-ray structure of P/B-FLP-NO (**3**).^[33]

revealed that both the phosphorus and the boron atoms have formed bonds to the nitrogen atom of the incorporated NO molecule (P–N: 1.7127(14) Å, B–N: 1.592(2) Å, P–N–B: 114.27(10)°). The N–O bond distance in **3** of 1.2962(17) Å is significantly lengthened relative to that of free NO (1.151 Å);^[12] it is similar to that found in N-oxyl radicals R₂N–O• such as TEMPO (**4**: 1.284(8) Å)^[13] and *t*Bu₂N–O• (1.28(2) Å (gas phase)^[14]).

The odd-electron species **3** exhibits an X-band EPR signal at room temperature in fluorobenzene solution consistent with coupling of the electron spin to the ¹⁴N nucleus as well as to ³¹P and ¹¹B nuclei (Figure 2). Simulation of the symmetric pattern about *g* = 2.0089 gives *A*(¹⁴N) = 18.5 MHz, *A*(³¹P) = 48.5 MHz, and *A*(¹¹B) = 9.1 MHz (contribution from ¹⁰B neglected). While *A*(¹⁴N) is markedly lower than in the related nitroxides TEMPO^[15] and *t*Bu₂NO^[16] (43.5 and 43.3 MHz in toluene, respectively), DFT calculations at the TPSS0^[17] level employing a def2-TZVP AO basis (fully decontracted for P, N, B atoms) predict very similar hyperfine interactions (*A*(¹⁴N) = 16.7, *A*(³¹P) = 46.9, *A*(¹¹B) = 10 MHz) to those used to successfully simulate the experimental EPR spectrum. To experimentally confirm these assignments, we prepared the isotopomer P/B-FLP-¹⁵NO (**3**-¹⁵N) by addition of ¹⁵NO (generated from the reaction of *t*BuO¹⁵NO, [Cp₂Fe], and TMS-OTf; see Supporting Information, Scheme S1) to a

[*] A. J. P. Cardenas, B. J. Culotta, Prof. T. H. Warren
Department of Chemistry, Georgetown University
Box 571227, Washington, DC 20057-1227 (USA)
E-mail: thw@georgetown.edu

Prof. Dr. S. Grimme, Dipl.-Chem. A. Stute, Dr. R. Fröhlich, Dr. G. Kehr,
Prof. Dr. G. Erker
Organisch-Chemisches Institut der Universität Münster
Corrensstrasse 50, 48149 Münster (Germany)
E-mail: grimmes@uni-muenster.de
erker@uni-muenster.de

[**] We acknowledge funding from the National Science Foundation (CHE-0957606 to T.H.W.; CHE-0840453 to Georgetown for an EPR spectrometer) and the Deutsche Forschungsgemeinschaft (S.G., G.E.).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201101622>.

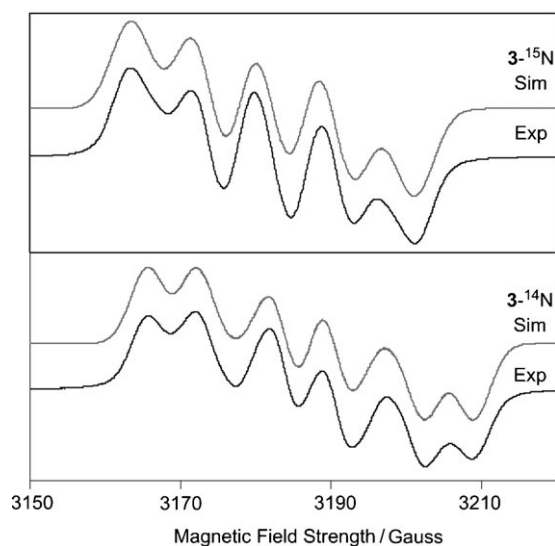


Figure 2. X-band EPR spectra (fluorobenzene, room temperature) and simulations for P/B-FLP-NO $\cdot$ (3 - ^{14}N , bottom; 3 - ^{15}N , top).

solution of $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$. The EPR spectrum of 3 - ^{15}N (Figure 2) is best simulated with $A(^{15}\text{N}) = 25.5$ MHz very close to the anticipated value of 26.0 MHz based on the relative gyromagnetic ratios of ^{15}N and ^{14}N .

The optical absorption spectrum of 3 in fluorobenzene (Figure 3) features a maximum at $\lambda = 705$ nm ($6.7(1) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) that is quite distinct from typical nitroxides

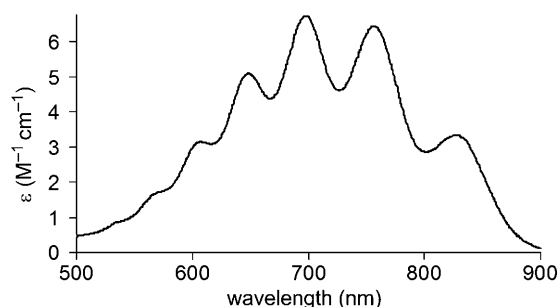
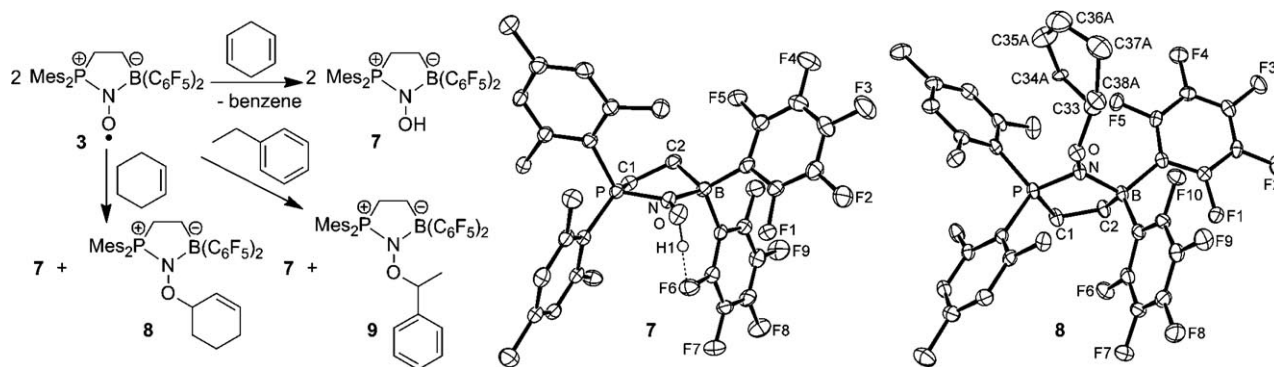


Figure 3. Visible spectrum of P/B-FLP-NO $\cdot$ (3) in fluorobenzene at room temperature.

such as TEMPO ($\lambda_{\text{max}} = 460$ nm ($10.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in MeCN).^[18] This band exhibits detailed vibrational fine structure with an average spacing of $1109(11) \text{ cm}^{-1}$ for the six most intense peaks. Since difference IR spectra of 3 - ^{14}N and 3 - ^{15}N identify the $\nu(^{14}\text{NO})$ and $\nu(^{15}\text{NO})$ stretches at 1474 and 1457 cm^{-1} (DFT predicts $\nu(^{14}\text{NO})$ in a range 1428 – 1472 cm^{-1} (delocalized)), the vibronic spacing observed in the visible spectrum likely reflects the excited state of 3 . Time-dependent DFT calculations indicate that this weak transition ($f = 0.0002$) possesses $n \rightarrow \pi^*$ character (Supporting Information, Figure S12).

While NO itself is a very poor H-atom acceptor owing to the very modest H–NO bond strength of approximately 47 kcal mol^{-1} in nitroxyl (HNO),^[19] the FLP-NO adduct 3 engages readily in H-atom abstraction reactions (Scheme 2). Reaction of P/B-FLP-NO $\cdot$ (3) with 1,4-cyclohexadiene (C–H bond dissociation energy (BDE) ca. 76 kcal mol^{-1})^[19] rapidly quenches the blue color of 3 to give the corresponding diamagnetic product P/B-FLP-NOH (7). This species may be isolated in 67 % yield as colorless crystals by vapor diffusion of heptane into a benzene solution of 7 . X-ray crystal structure analysis of 7 reveals a significant lengthening of the N–O distance to $1.422(2) \text{ \AA}$ in 7 (from $1.2962(17) \text{ \AA}$ in 3) consistent with a decrease in N–O bond order. A similar lengthening of the N–O distance occurs upon reduction of TEMPO to TEMPOH (N–O: $1.450(2)$ – $1.462(2) \text{ \AA}$).^[20] The conversion of 3 into 7 is accompanied by a decrease in the P–N bond length in 7 to $1.6315(18) \text{ \AA}$ while the B–N distance of $1.561(3) \text{ \AA}$ in 7 remains similar to that found in 3 , slightly opening the P–N–B angle to $118.39(15)^\circ$. The hydroxy H-atom was refined and shows a close contact to one of the F atoms on an adjacent C_6F_5 ring ($\text{H1} \cdots \text{F6} = 2.218 \text{ \AA}$).

NMR spectroscopic characterization of the diamagnetic species 7 in $[\text{D}_1]\text{chloroform}$ reveals multiplets in the ^1H NMR spectrum at $\delta = 2.83$ and 1.76 ppm corresponding to the backbone PCH_2 and BCH_2 groups along with a broad singlet at $\delta = 4.76$ ppm for the NOH group. $^{31}\text{P}\{^1\text{H}\}$ and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra possess signals at $\delta = 46.8$ ppm ($\nu_{1/2} = 40 \text{ Hz}$) and -5.8 ($\nu_{1/2} = 150 \text{ Hz}$) ppm, respectively. The IR spectrum of 7 in the solid state shows a relatively sharp band for the $\nu(^{14}\text{NO-H})$ stretch at 3527 cm^{-1} along with the $\nu(^{14}\text{NO})$ stretch at 1110 cm^{-1} ($\nu(^{15}\text{NO}) = 1082 \text{ cm}^{-1}$).



The P/B-FLP-NO[•] radical **3** abstracts H-atoms from stronger C–H bonds as well. Exposure of **3** to excess cyclohexene (C–H BDE $\approx$ 82 kcal mol^{−1})^[19] results in clean H-atom abstraction (HAA) to form **7** along with the new product **8** (³¹P NMR: δ = 47.4 ppm; ¹¹B NMR: δ = −5.5 ppm in [D₁]chloroform) in a 1:1 ratio (Scheme 2). With excess cyclohexene, the loss of **3** follows clean first-order kinetics in which the observed rate constant k_{obs} essentially doubles from $9.04 \times 10^{-4} \text{ s}^{-1}$ to $2.16 \times 10^{-3} \text{ s}^{-1}$ with a doubling of the concentration of cyclohexene from 2.47 M to 4.94 M in fluorobenzene to give a second order rate constant $k_{\text{cyclohexene}}$ (25 °C) = $4.0(4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Isolation of the new product **8** by crystallization (Scheme 2) of the mixture from methanol allows for its characterization as P/B-FLP-NO(2-cyclohexenyl). This species is similar in structure to P/B-FLP-NOH (**7**) with a N–O bond length of 1.445(2) Å and similar metrical parameters about the P–N–B linkage (P–N 1.6516(17) Å, B–N 1.586(3) Å, P–N–B 116.99(13)°).

Mechanistic studies employing the reactive *N*-oxyl radical PINO (**5**) in cyclohexene functionalization had revealed two concurrent pathways. The first is a stepwise HAA/radical combination sequence that results in the formation of a new O–C bond. Addition of the PINO radical to the C=C double bond, however, followed by abstraction of an allylic H-atom to give the functionalized product represents a competing pathway.^[7] Without such mechanistic ambiguity, **3** also undergoes HAA with the significantly stronger C–H bonds of ethylbenzene (C–H BDE $\approx$ 85 kcal mol^{−1})^[19] following clean pseudo first-order kinetics in **3** employing excess ethylbenzene substrate (4–7 M) in fluorobenzene to give $k_{\text{ethylbenzene}}$ (25 °C) = $5.6(3) \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. The reaction of **3** with excess ethylbenzene gives a 1:1 ratio of **7** along with the new O-functionalized product P/B-FLP-NO(1-CH(Me)Ph) (**9**; Scheme 2) as monitored by ³¹P NMR (δ = 48.1 ppm in [D₁]chloroform).

To better understand the electronic structure of **3** along with the heightened HAA reactivity of **3** relative to typical nitroxides such as TEMPO,^[21] we examined **3** and **7** by theoretical methods. The DFT structural optimizations have been performed at the dispersion corrected (DFT-D3^[22] method) TPSS^[17] level using very large quadruple-zeta AO basis sets.^[23] The computed structures and predicted spectroscopic properties agree very well with experimental data. For instance, the computed N–O, P–N, and B–N distances for **3** are 1.283, 1.732, and 1.608 Å compared to values of 1.2962(17), 1.7127(14), and 1.592(2) Å determined by X-ray. Single-point thermochemical calculations at the even higher B2PLYP-D3/def2-QZVP level of theory^[24] reveal the binding of NO to P/B-FLP (**1**) in its closed (quenched) four-membered ring conformation to give P/B-FLP-NO[•] (**3**) is quite exothermic with ΔE = −24.6 kcal mol^{−1} ($\Delta G(298)$ = −11.9 kcal mol^{−1}).

While the steric environment of the *N*-oxyl moiety of **3** is more congested than in TEMPO, analysis of the electronic structure of **3** reveals a basic similarity to TEMPO (Figure 4a and Supporting Information S11–S12). The N–P bond in **3** is essentially a single bond with a Wiberg Bond Order (WBO)^[3c,f,25] of 1.07 while the N–B interaction is of donor–acceptor type (WBO = 0.73). As in TEMPO, the N–O unit

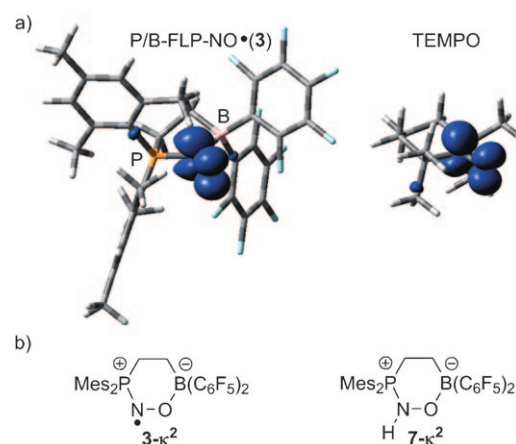
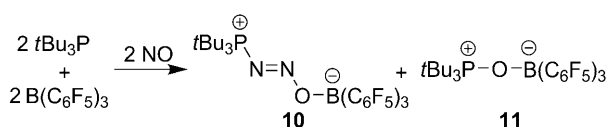


Figure 4. a) Spin density plot of **3** and TEMPO (isospin = 0.001). b) Alternative structures considered for **3** and **7** with P–N–O–B linkages.

has a singly occupied π^* SOMO and a concomitantly small WBO of 1.15 (1.21 in TEMPO). The Mulliken spin-density populations at O and N in **3** are 0.54 and 0.34 e^- , respectively, slightly more biased towards O as compared to the corresponding values in TEMPO (0.50 and 0.44 e^- , respectively). Identified through both simulation and calculation, the hyperfine couplings present in the EPR spectrum of **3** (Figure 2) clearly reflect the lower spin-density at the N atom in **3**. This perturbation in electronic structure enhances the H-atom abstracting ability of **3** to form **7**. P/B-FLP-NOH (**7**) has a calculated O–H bond dissociation enthalpy (BDH) of 77.3 kcal mol^{−1} (at 298 K) which is about 10 kcal mol^{−1} larger than the corresponding values for TEMPO–H at the same level of theory (BDH = 67.2 kcal mol^{−1}). These calculated values for TEMPO–H compare well with experimental values in benzene (bond dissociation free energy (BDFE) 70.2, BDE = 65.2 kcal mol^{−1}).^[26]

Inspired by the nitrosobenzene adduct **2** that features a six-membered ring with a P–N–O–B linkage (Scheme 1), we computationally considered related κ^2 -isomers of **3** and **7** (Figure 4b). These species are only 8.1 and 5.1 kcal mol^{−1} higher in free energy than the experimentally observed species **3** and **7** that feature κ^1 -NO units. Interestingly, **3-κ²** undergoes a reversal in the spin-density distribution (O: 0.32 e^- , N: 0.52 e^-) as compared to **3**. Isomer **7-κ²** suggests the possibility of trapping the elusive molecule HNO^[27] with **1**, supported by calculations that reveal a particularly tight interaction to give the experimentally observed P/B-FLP-NOH ground state **7** with ΔE = −57.3 kcal mol^{−1} ($\Delta G(298)$ = −41.9 kcal mol^{−1}).

As a point of comparison, we briefly investigated the reaction of the intermolecular FLP *t*Bu₃P/B(C₆F₅)₃ with NO. Bubbling 1 equiv NO_{gas} through a bromobenzene solution of *t*Bu₃P and B(C₆F₅)₃ at room temperature resulted in 40% conversion into a 1:1 mixture of known products FLP–N₂O **10** and phosphine oxide **11** (Scheme 3; ³¹P NMR: δ = 65.8 and 92.2 ppm in [D₆]benzene, respectively).^[4] This reaction follows a course related to the well studied disproportionation of NO to give N₂O and R₃P=O upon reaction of NO with phosphines PR₃.^[28] Thus the ability of the intramolecular FLP



Scheme 3. Reaction of “open” FLP system $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ with NO.

1 to form a P/B chelate with NO plays a pivotal role in the isolation of the NO adduct **3** and its subsequent examination as a new type of N-oxyl radical.

Our new FLP-NO species represents a novel addition to the large and important family of persistent N-oxyl free radicals which have an especially diverse range of applications.^[7,9,29,30] We anticipate that the properties of related FLP-NO species can be tuned by appropriate variation of the Lewis pair components. For instance, modulation of FLP-NO-H and FLP-NO-R bond strengths may lead to selective radical addition and/or HAA reactions. Moreover, a decrease in the strength of the FLP-NO interaction could lead to the reversible binding of NO as well as provide insight into phosphine-based approaches to sense and quantify NO^[31] and HNO.^[32] Our study expands frustrated Lewis pair chemistry to radical species providing access to unprecedented areas of chemistry by the cooperative action of pairs of potent Lewis bases and acids sterically prevented from achieving a strong donor–acceptor interaction in the absence of a mediating molecule.

Received: March 5, 2011

Revised: April 19, 2011

Published online: July 1, 2011

Keywords: frustrated Lewis pairs · H-atom abstraction · nitric oxide · nitroxides · radicals

- [1] D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50; *Angew. Chem. Int. Ed.* **2010**, *49*, 46.
- [2] a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124; b) G. C. Welch, D. W. Stephan, *J. Am. Chem. Soc.* **2007**, *129*, 1880; c) H. Wang, R. Fröhlich, G. Kehr, G. Erker, *Chem. Commun.* **2008**, 5966; d) P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701; e) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 8196; *Angew. Chem. Int. Ed.* **2007**, *46*, 8050; f) P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich, G. Erker, *Angew. Chem.* **2008**, *120*, 7654; *Angew. Chem. Int. Ed.* **2008**, *47*, 7543; g) D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, 2130; h) D. Chen, Y. Wang, J. Klankermayer, *Angew. Chem.* **2010**, *122*, 9665; *Angew. Chem. Int. Ed.* **2010**, *49*, 9475.
- [3] a) J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 5056; *Angew. Chem. Int. Ed.* **2007**, *46*, 4968; b) T. Voss, C. Chen, G. Kehr, E. Nauha, G. Erker, D. W. Stephan, *Chem. Eur. J.* **2010**, *16*, 3005; c) C. M. Mömming, S. Frömel, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 12280; d) C. M. Mömming, G. Kehr, B. Wibbeling, R. Fröhlich, B. Schirmer, S. Grimme, G. Erker, *Angew. Chem.* **2010**, *122*, 2464; *Angew. Chem. Int. Ed.* **2010**, *49*, 2414; e) M. W. P. Bebbington, S. Bontemps, G. Bouhadir, D. Bourissou, *Angew. Chem.* **2007**, *119*, 3397; *Angew. Chem. Int. Ed.* **2007**, *46*, 3333; f) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker, *Angew. Chem.* **2009**, *121*, 6770; *Angew. Chem. Int. Ed.* **2009**, *48*, 6643; g) R. C. Neu, E. Otten, A. Lough, D. W. Stephan, *Chem. Sci.* **2011**, *2*, 170.
- [4] E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918.
- [5] C. M. Mömming, G. Kehr, B. Wibbeling, R. Fröhlich, G. Erker, *Dalton Trans.* **2010**, *39*, 7556.
- [6] a) *Nitric Oxide: Biology and Pathobiology*, 2nd Ed. (Ed.: L. J. Ignarro), Academic, San Diego, **2010**; b) J. F. Kerwin, Jr., J. R. Lancaster, Jr., P. L. Feldman, *J. Med. Chem.* **1995**, *38*, 4343–4362.
- [7] F. Recupero, C. Punta, *Chem. Rev.* **2007**, *107*, 3800.
- [8] H.-G. Korth, K. U. Ingold, R. Sustmann, H. de Groot, H. Sies, *Angew. Chem.* **1992**, *104*, 915; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 891.
- [9] G. Likhtenshtein, J. Yamauchi, S. Nakatsuji, A. I. Smirnov, Tamara, *Nitroxides: Applications in Chemistry, Biomedicine, and Materials Science*, Wiley-VCH, Weinheim, **2008**.
- [10] P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072.
- [11] a) D. J. Parks, R. E. v. H. Spence, W. E. Piers, *Angew. Chem.* **1995**, *107*, 895; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809; b) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492.
- [12] N. L. Nichols, C. D. Hause, R. H. Noble, *J. Chem. Phys.* **1955**, *23*, 57.
- [13] Y. Yonekuta, K. Oyaizu, H. Nishide, *Chem. Lett.* **2007**, *36*, 866.
- [14] B. Andersen, P. Andersen, *Acta Chem. Scand.* **1966**, *20*, 2728.
- [15] E. P. Talsi, N. V. Semikolenova, V. N. Panchenko, A. P. Sobolev, D. E. Babushkin, A. A. Shubin, V. A. Zakharov, *J. Mol. Catal. A* **1999**, *139*, 131.
- [16] B. R. Knauer, J. J. Napier, *J. Am. Chem. Soc.* **1976**, *98*, 4395.
- [17] V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, *J. Chem. Phys.* **2003**, *119*, 12129.
- [18] A. Wu, E. A. Mader, A. Datta, D. A. Hrovat, W. T. Bordon, J. M. Mayer, *J. Am. Chem. Soc.* **2009**, *131*, 11985.
- [19] Y.-R. Luo, *Handbook of Bond Dissociation Energies in Organic Compounds*, CRC, Boca Raton, FL, **2002**.
- [20] E. A. Mader, E. R. Davidson, J. M. Mayer, *J. Am. Chem. Soc.* **2007**, *129*, 5153.
- [21] TEMPO and closely related derivatives require prolonged reaction times (12 h–3 days) at 120–130 °C to observe HAA/radical recombination reactions in neat ethylbenzene: a) T. J. Connolly, J. C. Scaiano, *Tetrahedron Lett.* **1997**, *38*, 1133; b) J. E. Babiarez, G. T. Cunkle, A. D. DeBellis, D. Eveland, S. D. Pastor, S. P. Shum, *J. Org. Chem.* **2002**, *67*, 6831.
- [22] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.
- [23] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [24] S. Grimme, *J. Chem. Phys.* **2006**, *124*, 034108.
- [25] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.
- [26] J. J. Warren, T. A. Tronic, J. M. Mayer, *Chem. Rev.* **2010**, *110*, 6961.
- [27] a) J. M. Fukuto, M. D. Bartberger, A. S. Dutton, N. Paolocci, D. A. Wink, K. N. Houk, *Chem. Res. Toxicol.* **2005**, *18*, 790; b) H. C. Irvine, R. H. Ritchie, J. L. Favaloro, K. L. Andrews, R. E. Widdop, B. K. Kemp-Harper, *Trends Pharmacol. Sci.* **2008**, *29*, 601; c) N. Paolocci, M. I. Jackson, B. E. Lopez, K. Miranda, C. G. Tocchetti, D. A. Wink, A. J. Hobbs, J. M. Fukuto, *Pharmacol. Ther.* **2007**, *113*, 442.
- [28] a) R. Longhi, R. O. Ragsdale, R. S. Drago, *Inorg. Chem.* **1962**, *1*, 768; b) M. D. Lim, I. M. Lorkovic, P. C. Ford, *Inorg. Chem.* **2002**, *41*, 1026.
- [29] *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds* (Ed.: R. G. Hicks), Wiley, Chichester, **2010**.

- [30] a) A. Studer, *Chem. Soc. Rev.* **2004**, 33, 267; b) C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* **2001**, 101, 3661; c) H. Fischer, *Chem. Rev.* **2001**, 101, 3581.
- [31] A. Bakac, M. Schouten, A. Johnson, W. Song, O. Pestovsky, W. Szajna-Fuller, *Inorg. Chem.* **2009**, 48, 6979.
- [32] J. A. Reisz, E. B. Klorig, M. W. Wright, S. B. King, *Org. Lett.* **2009**, 11, 2719.
- [33] CCDC 826363, 826364, 826365, 826366, and 826367 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
-