Superoxonickel Complexes

DOI: 10.1002/anie.200802234

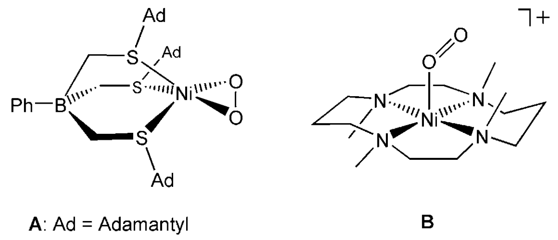
A “Side-on” Superoxonickel Complex $[LNi(O_2)]$ with a Square-Planar Tetracoordinate Nickel(II) Center and Its Conversion into $[LNi(\mu\text{-}OH)_2NiL]$**

*Shenglai Yao, Eckhard Bill, Carsten Milsmann, Karl Wieghardt, and Matthias Driess**

In memory of Dieter Sellmann

Dioxygen activation mediated by transition-metal sites is of importance in numerous stoichiometric and catalytic transformations of organic substrates in biological[1] and industrial processes.[2] Using dioxygen as a primary oxidant (aerobic oxidation) is very attractive because it is cheap and ecologically benign, but it is still difficult to control in a broad range of synthetic systems. It is of particular interest in synthetic chemistry to develop novel metal–dioxygen compounds that are capable of chemoselective C–H bond functionalization without autoxidation and overoxidation of the substrates. Prominent examples in synthetic chemistry comprise homobimetallic Fe, Co, and Cu complexes bearing superoxo (O_2^-), peroxo (O_2^{2-}), hydroperoxo (O_2H^-), and oxo ligands (O^{2-}) as active oxygen species.[3] Many of the most important metal-mediated oxidation catalysts for aerobic oxidation of organic substrates on an industrial scale are based on palladium oxidase systems, some of which have been known for more than a century (Wacker process).[4] The use of stoichiometric and catalytic Pd-mediated aerobic oxidation reactions poses a great challenge for the development of cheaper analogous nickel reagents.

Although $\{NiO_2\}$ intermediates have in fact been inferred to be highly active species in several C–H bond transformations,[5] it seems peculiar that knowledge on nickel–dioxygen complexes is still comparatively scarce. Since Ni^{II} complexes are generally inert toward O_2, the most common approach to $\{NiO_2\}$ compounds involves the reaction of H_2O_2 with Ni^{II} salts to give hydroperoxo and peroxo complexes.[6] An attractive alternative for the synthesis of $\{NiO_2\}$ peroxo complexes is the two-electron reduction of O_2 by Ni^0 complexes.[7] Recently, Riordan and co-workers reported the synthesis of the remarkable nickel superoxo complexes **A**[8] and **B**[9] with five-coordinate Ni^{II} sites (Scheme 1), which resulted from one-electron reduction of O_2 by the respective Ni^I precursors at low temperature. Because **A** and **B** are only stable at low temperatures, they could only be characterized by spectroscopy and DFT calculations. These results show their similar electronic but different geometric structure, namely, “side-on” (**A**) versus “end-on” coordination (**B**) of the O_2 moiety to the Ni center. To our knowledge, no structural data are currently available for nickel superoxo complexes.



Scheme 1. The labile superoxonickel complexes **A** and **B** with “side-on” and “end-on” coordination of O_2, respectively.[8,9]

Herein we report the unexpectedly facile synthesis, isolation, and reactivity of the novel paramagnetic superoxonickel complex **1**, which has a square-planar tetracoordinate Ni^{II} center and an unpaired electron localized on the superoxo ligand. Compound **1** represents the first superoxonickel complex structurally characterized by a single-crystal X-ray diffraction analysis.

Exposure of solutions of the β-diketiminato-(toluene)nickel complex **2** as Ni^I precursor[10a] in toluene to dry dioxygen leads to an immediate color change from red-brown to green, indicating the formation of the novel $\{Ni^{II}O_2\}$ complex **1** (Scheme 2). Fractional crystallization from the reaction solution provides green crystals of **1** in 84 % yield.[11] The composition of **1** was confirmed by EI mass spectrometry and elemental analysis (C, H, N). The complex is sensitive toward protic solvents but remains unchanged in hexane at 60 °C.

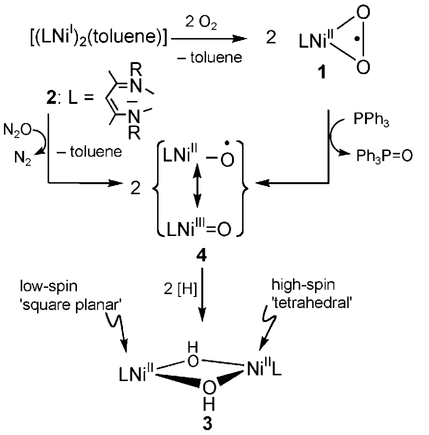
---

[*] Dr. S. Yao, Prof. Dr. M. Driess
Technische Universität Berlin
Institut für Chemie
Metallorganik und Anorganische Materialien, Sekr. C2
Strasse des 17. Juni 135, 10623 Berlin (Germany)
Fax: (+49) 30-314-29732
E-mail: matthias.driess@tu-berlin.de
Homepage: http://www.driess.tu-berlin.de

Dr. E. Bill, Dipl.-Chem. C. Milsmann, Prof. Dr. K. Wieghardt
Max-Planck-Institut für Bioanorganische Chemie
Stiftsstrasse 34-36, 45470 Mülheim/Ruhr (Germany)

[**] Financial support from the Cluster of Excellence “Unifying Concepts in Catalysis” (EXC 314/1) by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Prof. P. Hildebrandt (TU Berlin) and Dr. U. Kuhlmann for Resonance-Raman measurements and Prof. H. Schwarz (TU Berlin) for providing us $^{18}O_2$ samples. L = β-diketiminato.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802234.



Scheme 2. Formation of the superoxonickel(II) complex **1** from **2** and its conversion to **3** via the proposed intermediate **4**. R = 2,6-iPr$_2$C$_6$H$_3$.

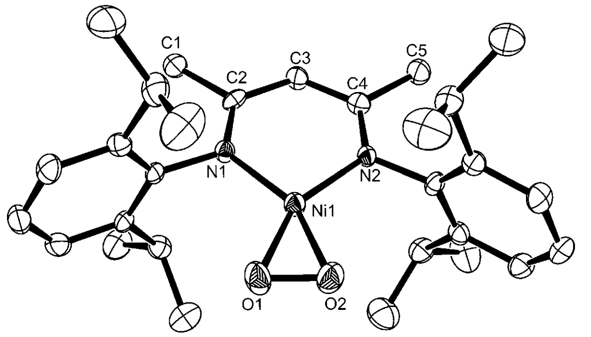


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. Selected distances [pm] and angles [°]: Ni1–O2 181.7(2), Ni1–O1 184.0(2), Ni1–N1 184.7(2), Ni1–N2 184.9(2), O1–O2 134.7(2), N1–C2 133.4(3), N2–C4 134.2(3); O2-Ni1-O1 43.23(7), O2-Ni1-N1 153.55(9), O1-Ni1-N1 110.34(9), O2-Ni1-N2 108.91(9), O1-Ni1-N2 152.13(9), N1-Ni1-N2 97.52(9), O2-O1-Ni1 67.5(1), O1-O2-Ni1 69.3(1).

Single-crystal X-ray diffraction analysis[11] revealed that **1** consists of an almost planar six-membered {C$_3$N$_2$Ni} ring. The Ni atom is planar tetracoordinated, which suggests a low-spin Ni^{II} configuration (Figure 1). The Ni–N bond lengths of 184.7(2) and 184.9(2) pm are significantly shorter than those observed in **2** and related Ni^{II} complexes,[10b–c] indicating considerably more Ni–N π interactions in **1**. The Ni–O bond lengths of 181.7(2) and 184.0(2) pm are similar to those in a {(Ni^{II})$_2$(μ-OH)$_2$} complex with a four-coordinate Ni center[10d] and a {(Ni^{III})$_2$(μ-O)$_2$} complex with a five-coordinate Ni center,[12] as well as the Ni–O bond length of 185 pm in **A**, deduced from Ni EXAFS measurements.[8] The structure is most notable for its short O–O bond length of 134.7(2) pm, which implies superoxo character because peroxo ligands have O–O bond lengths longer than 140 pm.[13] The superoxo character was confirmed by spectroscopic measurements and DFT calculations (see below).[11] The superoxo nature of **1** is also consistent with the ^{16}O–^{16}O stretching vibration mode of 971 cm^{-1} (ν(^{18}O–^{18}O) = 919 cm^{-1}) determined by IR spectroscopy.[11,13]

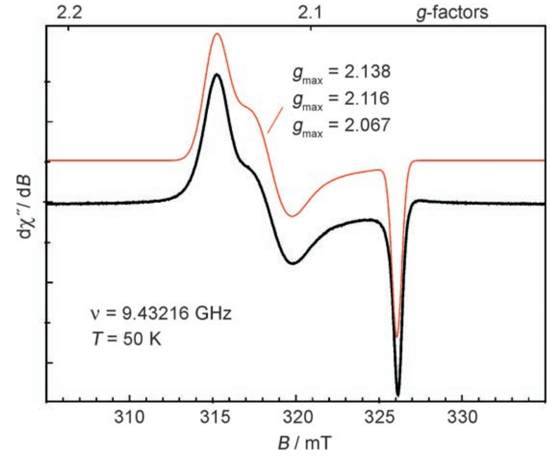


Figure 2. X-band EPR spectrum of **1** in frozen toluene at 50 K.[11] The red line is a powder simulation with anisotropic g values as shown.

The ^{1}H NMR spectrum of **1** shows paramagnetically shifted resonances. X-band EPR measurements of **1** in frozen toluene at 50 K reveal a paramagnetic ground state with spin of $S = \frac{1}{2}$ (Figure 2). The rhombic spectrum has principal g values of 2.138, 2.116, and 2.067, and the corresponding average value $g_{av} = 2.107$ is in agreement with the effective magnetic moment observed for a solid sample in the temperature range 20–300 K ($\mu_{eff} = 1.8\ \mu$B , corresponding to $g_{av} = 2.08$).[11] The anisotropic g values resemble quite closely those of "free" O$_2^-$ in water with g = [2.10, 2.00, 1.98].[14] We infer that the spin is centered on the superoxo ligand, because the Ni^{II} site (d^8) is diamagnetic since its planar coordination is persistent also in solution. A similar rhombic EPR spectrum, but with larger g anisotropy [2.24, 2.19, 2.01], was also observed for Riordan's "side-on" superoxo compound **A**. However, the latter contains a five-coordinate Ni^{II} center, which gives a different electronic structure since the remaining unpaired electron is predominantly located in the d$_{z^2}$ orbital of the Ni center.[8]

The electronic nature of **1** as suggested by its geometric structure and magnetic properties was also confirmed by DFT calculations (Figure 3).[11] The energy-minimized DFT-calculated structure of **1** is in good agreement with that obtained by X-ray diffraction. Interestingly, its hypothetical isomer with a tetrahedral, high-spin Ni^{II} center (**1'**) is disfavored by 19.1 kcal mol^{-1}. The calculations revealed that the HOMO of **1** is a singly occupied π* orbital completely located on the O$_2$ ligand; in other words, **1** is a genuine superoxide. In contrast, the hypothetical isomer **1'** with a tetrahedral Ni center is a paramagnetic superoxo complex with spin of $S = \frac{1}{2}$ located on the Ni site because of antiferromagnetic coupling of the high-spin Ni^{II} center with the O$_2^-$ radical[11] (similar to the situation observed for **A**[8]).

As expected, **1** is a gentle oxygenation reagent as shown by its reaction with PPh$_3$ to afford OPPh$_3$ and the unusual dinuclear, homovalent {(Ni^{II})$_2$(μ-OH)$_2$} complex **3** (Scheme 2). The composition of **3** was proven by EI mass spectrometry and elemental analysis (C, H, N). To our

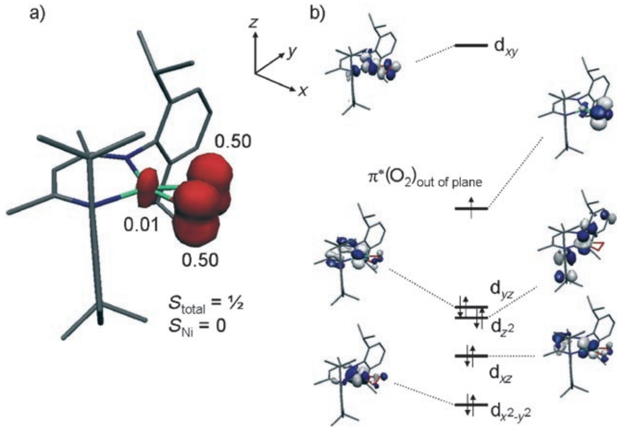


Figure 3. a) DFT-calculated spin density of **1** from Mulliken population analysis; b) DFT-calculated frontier orbitals of **1**.

surprise, **3** adopts an astonishing molecular structure and is paramagnetic as proven by single-crystal X-ray diffraction analysis and magnetic measurements.[11] The dimer consists of two structurally distinct β-diketiminatonickel(II) moieties with planar tetracoordinate (Ni1) and tetrahedral Ni^{II} sites (Ni1′), which are bridged by two μ-hydroxo ligands (Figure 4). This structure is in contrast to an analogous $\{(Ni^{II})_2(\mu\text{-}OH)_2\}$ complex with two almost planar tetracoordinate Ni^{II} centers.[10d]

The different coordination geometries of Ni1 and Ni1′ and their remarkably different Ni−O bond lengths, ranging from 186.1(2) to 196.3(2) pm, are presumably due to steric reasons. In fact, steric release by a smaller aryl group on the nitrogen atom leads to a $\{(Ni^{II})_2(\mu\text{-}OH)_2\}$ derivative with almost planar tetracoordinate Ni^{II} centers and similar Ni−O and Ni−N bond lengths.[10d] The coexistence of planar and tetrahedral Ni^{II} sites in **3** leads to a very unusual example of a homovalent complex with a paramagnetic ground state that is not achieved by ferromagnetic exchange coupling. The effective magnetic moment shows a broad high-temperature plateau at about $\mu_{eff} = 3\ \mu B$, indicating a spin triplet state. The temperature dependence of $\mu_{eff}(T)$ could be readily simulated with a single spin of $S = 1$, average g value of $g_{av} = 2.18$, and a large axial zero-field splitting parameter $D = 66(2)\ cm^{-1}$. Similar values have been found for other mononuclear tetrahedral Ni^{II} complexes, for example, with thiolato-Schiff base ligands ($g = 2.09$, $D = 34\text{–}53\ cm^{-1}$).[15] Thus, the magnetism of **3** originates entirely from the properties of the tetrahedral Ni^{II} site of the complex, whereas the planar site, as expected, is diamagnetic, as confirmed by DFT calculations.[11] Although the mechanism is still unknown, we propose that **3** results from the transient Ni–oxo species **4** ({LNiO}) as primary nickel-containing product, which evidently acts as a hydrogen scavenger and subsequently undergoes dimerization. In line with that, **3** results also as the sole isolable product from the reaction of **2** with N_2O (Scheme 2). Likewise, monooxygenation of **2** by **1** through reaction of **2** with **1** in a molar ratio of 1:1 leads also to **3**.[11]

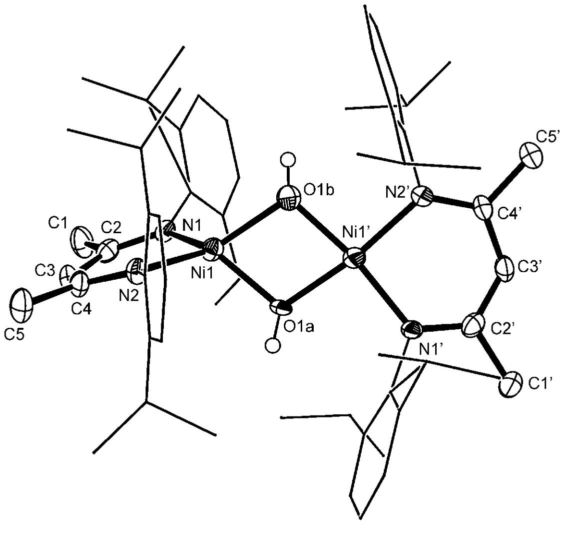


Figure 4. Molecular structure of compound **3**. Thermal ellipsoids (C1–C5, C1′–C5′, N1, N2, N1′, N2′, Ni1, Ni1′, O1a, and O1b) are drawn at 50% probability level. Hydrogen atoms (except for those at O1a and O1b) are omitted for clarity. The atoms labeled with the prime character (′) are at equivalent positions ($-x+1, y, -z+1/2$). Selected distances [pm] and angles [°]: Ni1–O1a 186.1(7), Ni1–O1b 186.5(7), Ni1′–O1a 190.8(7), Ni1′–O1b 196.3(7), Ni1–N2 192.0(4), Ni1–N1 193.1(4); N2-Ni1-N1 94.0(2), N1-Ni1-O1a 94.0(2), O1a-Ni1-O1b 77.3(3), O1a-Ni1′-O1b 73.9(3), O1a-Ni1′-N2′ 112.2(2).

According to DFT calculations, the proposed intermediate **4** shows a short Ni−O bond length of 164 pm and high spin density at the terminal oxo ligand. Both features resemble those of other metal–oxo species, such as the $\{Fe^{IV}{=}O\}$ group in heme and nonheme iron complexes.[16a] The spin density at the oxygen center may be regarded as the result of a large contribution from the Ni^{II}–oxyl configuration to the electronic ground state. Likewise, the calculations reveal virtually equal energies for the two alternative spin states of intermediate **4** ($S = {}^1\!/_2$ and $S = {}^3\!/_2$) and relatively high spin density on the oxygen center in both cases.[11] Interestingly, a direct precedent of **4** is an isolable Ni^{III}–imide analogue [LNi=NR] (R = adamantyl) with radical character at the imino N atom which reacts rapidly with H atom donors to give the corresponding Ni^{II}–amide.[17]

In summary, we report the facile synthesis and structural characterization of the genuine paramagnetic $\{NiO_2\}$ complex **1** with a planar tetracoordinate Ni^{II} center. This is the first complex of its type that is stable at room temperature and in which the single unpaired electron is predominantly located on the "side-on" coordinated dioxygen ligand. The $\{NiO_2\}$ moiety in **1** is a new, promising mild oxygenation agent, which gives the unusual dinuclear, homovalent $\{(Ni^{II})_2(\mu\text{-}OH)_2\}$ complex **3** with planar and tetrahedral Ni^{II} sites. Furthermore, we propose the formation of the nickel–oxo species {LNiO} **4** as an intermediate. Species **4** could paves the way for reaction systems capable of consecutive oxygenation and C−H bond activation reactions by the same reagent. Investigations to prove the existence of **4** and to use **1** for structure–reactivity relationships for oxygenation and C−H activation reactions are currently underway.

Received: May 13, 2008

Keywords: β-diketiminates · magnetic properties · nickel · oxygen · peroxo ligands

---

[1] a) S. Ferguson-Miller, G. T. Babcock, *Chem. Rev.* **1996**, *96*, 2889; b) E. Kim, M. E. Helton, I. M. Wasser, K. D. Karlin, S. Lu, H.-W. Huang, P. Moenne-Loccoz, C. D. Incarvito, A. L. Rheingold, M. Honecker, S. Kaderli, A. D. Zuberbühler, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3623; c) A. Decker, E. I. Solomon, *Curr. Opin. Chem. Biol.* **2005**, *9*, 152.

[2] a) L. Vaska, *Acc. Chem. Res.* **1976**, *9*, 175; b) A. E. Martell, D. T. Sawyer, *Oxygen Complexes and Oxygen Activation by Transition Metals*, Plenum Press, New York, **1988**, pp. 1–341; c) C. Limberg, *Angew. Chem.* **2003**, *115*, 6112; *Angew. Chem. Int. Ed.* **2003**, *42*, 5932; d) T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329; e) Special issue of *Chem. Rev.* for Metal-Oxygen Complexes: *Chem. Rev.* **1994**, *94*, 567; f) K. H. Theopold, *Top. Organomet. Chem.* **2007**, *22*, 17; g) J. Piera, J.-E. Bäckvall, *Angew. Chem.* **2008**, *120*, 3558; *Angew. Chem. Int. Ed.* **2008**, *47*, 3506.

[3] a) L. Que, Y. Dong, *Acc. Chem. Res.* **1996**, *29*, 190; b) W. B. Tolman, *Acc. Chem. Res.* **1997**, *30*, 227; c) L. Que, *J. Chem. Soc. Dalton Trans.* **1997**, 3933; d) A. M. Valentine, S. L. Lippard, *J. Chem. Soc. Dalton Trans.* **1997**, 3925; e) C. Biancini, R. W. Zoellner, *Adv. Inorg. Chem.* **1996**, *44*, 263; f) E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kemsley, S.-K. Lee, N. Lehnert, F. Neese, A. J. Sukulan, Y.-S. Yang, J. Zhou, *Chem. Rev.* **2000**, *100*, 235; g) X. Dai, P. Kapoor, T. H. Warren, *J. Am. Chem. Soc.* **2004**, *126*, 4798.

[4] a) J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, H. Kojer, *Angew. Chem.* **1959**, *71*, 176; Reviews: b) A. Heumann, K. L. Jens, M. Réglier, *Prog. Inorg. Chem.* **1994**, *42*, 483; c) S. S. Stahl, *Angew. Chem.* **2004**, *116*, 3480; *Angew. Chem. Int. Ed.* **2004**, *43*, 3400, and references therein; see also reference [2e].

[5] a) D. Chen, A. E. Martell, *J. Am. Chem. Soc.* **1990**, *112*, 9411; b) C. C. Cheng, J. Gulia, S. E. Rokita, C. J. Burrows, *J. Mol. Catal. A* **1996**, *113*, 379.

[6] a) S. Hikichi, M. Yoshizawa, Y. Sasakura, M. Akita, Y. Moro-oka, *J. Am. Chem. Soc.* **1998**, *120*, 10567; b) K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Watanabe, Y. Moro-oka, *J. Am. Chem. Soc.* **2000**, *122*, 254; c) J. Cho, H. Furutachi, S. Fujinami, M. A. Suzuki, *Angew. Chem.* **2004**, *116*, 3362; *Angew. Chem. Int. Ed.* **2004**, *43*, 3300; d) E. J. Brown, E. A.-K. Duhme-Klair, M. I. Elliott, J. E. Thomas-Oates, P. L. Timmins, P. H. Walton, *Angew. Chem.* **2005**, *117*, 1416; *Angew. Chem. Int. Ed.* **2005**, *44*, 1392.

[7] a) S. Takahashi, K. Sonogashira, N. Hagihara, *J. Chem. Soc. Jpn.* **1966**, *87*, 610; b) G. Wilke, H. Schott, P. Heimbach, *Angew. Chem.* **1967**, *79*, 62; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 92; c) S. Otsuka, A. Nakamura, Y. Tatsuno, *J. Am. Chem. Soc.* **1969**, *91*, 6994.

[8] a) K. Fujita, R. Schenker, W. Gu, T. C. Brunold, S. P. Cramer, C. G. Riordan, *Inorg. Chem.* **2004**, *43*, 3324; b) M. T. Kieber-Emmons, C. G. Riordan, *Acc. Chem. Res.* **2007**, *40*, 618.

[9] M. T. Kieber-Emmons, J. Annaraj, M.-S. Seo, K. M. VanHeuvelen, T. Tosha, T. Kitagawa, T. C. Brunold, W. Nam, C. G. Riordan, *J. Am. Chem. Soc.* **2006**, *128*, 14230; see also [8b].

[10] a) G. Bai, P. Wei, D. W. Stephan, *Organometallics* **2005**, *24*, 5901; b) A. Panda, M. Stender, R. J. Wright, M. M. Olmstead, P. Klavins, P. P. Power, *Inorg. Chem.* **2002**, *41*, 3909; c) P. L. Holland, T. R. Cundari, L. L. Perez, N. A. Eckert, R. J. Lachicotte, *J. Am. Chem. Soc.* **2002**, *124*, 14416; d) Y. Li, L. Jiang, L. Wang, H. Gao, F. Zhu, Q. Wu, *Appl. Organomet. Chem.* **2006**, *20*, 181.

[11] Experimental and theoretical details as well as X-ray diffraction analyses of **1** and **3** are provided in the Supporting Information.

[12] N. Kitajima, S. Hikichi, M. Tanaka, Y. Moro-oka, *J. Am. Chem. Soc.* **1993**, *115*, 5496; see also [6a].

[13] C. J. Cramer, W. B. Tolman, K. H. Theopold, A. L. Rheingold, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3635.

[14] B. Ramdhanie, J. Telser, A. Caneschi, L. N. Zakharov, A. L. Rheingold, D. P. Goldberg, *J. Am. Chem. Soc.* **2004**, *126*, 2515.

[15] H. Frydendahl, H. Toftlund, J. Becher, J. C. Dutton, K. S. Murray, L. F. Taylor, O. P. Anderson, E. R. T. Tiekink, *Inorg. Chem.* **1995**, *34*, 4467.

[16] a) J. C. Schöneboom, H. Lin, N. Reuter, W. Thiel, S. Cohen, F. Ogliaro, S. Shaik, *J. Am. Chem. Soc.* **2002**, *124*, 8142; b) S. Sinnecker, N. Svensen, E. W. Barr, S. Ye, J. M. Bollinger, Jr., F. Neese, C. Krebs, *J. Am. Chem. Soc.* **2007**, *129*, 6168.

[17] E. Kogut, H. L. Wienko, L. Zhang, D. E. Cordeau, T. H. Warren, *J. Am. Chem. Soc.* **2005**, *127*, 11248.