JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Formation of N_2O from a Nickel Nitrosyl: Isolation of the *cis*-$[N_2O_2]^{2-}$ Intermediate

Ashley M. Wright, Guang Wu, and Trevor W. Hayton*

Department of Chemistry and Biochemistry, University of California—Santa Barbara, Santa Barbara, California 93106, United States

Supporting Information

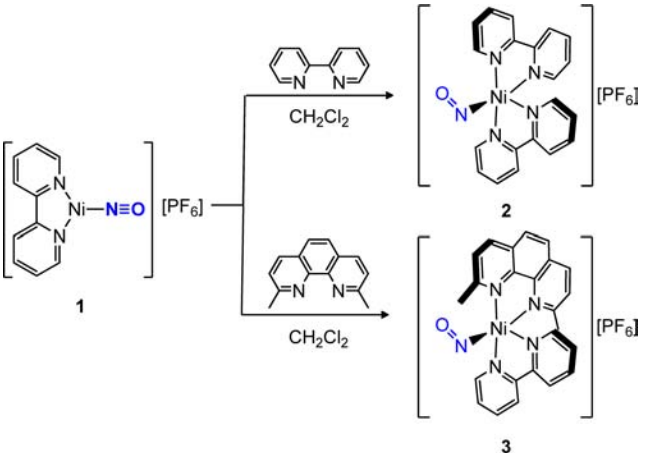
ABSTRACT: Addition of 2,2′-bipyridine (bipy) to [Ni(NO)(bipy)][PF_6] (**1**) results in formation of a rare five-coordinate nickel nitrosyl [Ni(NO)$(bipy)_2$][PF_6] (**2**). This complex exhibits a bent NO^- ligand in the solid state. On standing in acetonitrile, **2** furnishes the NO coupled product, [Ni(κ^2-O_2N_2)(bipy)] (**8**) in moderate yield. Subsequent addition of 2 equiv of acetylacetone (H(acac)) to **8** results in formation of [Ni$(acac)_2$(bipy)], N_2O, and H_2O. Preliminary mechanistic studies suggest that the N−N bond is formed via a bimetallic coupling reaction of two NO^- ligands.

The abatement of NO_x in industrial and automotive exhaust has immense environmental and societal relevance.[1−5] The current catalysts for transportation applications consist of nanoparticulate Pt and Rh on a ceramic support,[3] and there has been an intense effort to understand how NO reduction occurs in these systems.[6−11] There is also interest in replacing the expensive noble metals currently in use with more sustainable, earth abundant elements.[3,6,12] Additionally, there is concern that current technologies will not be able to meet future NO_x emission standards,[3] providing further justification for fundamental research on NO reduction. During catalysis in these systems, it is thought that the first step in NO reduction occurs through an initial NO(g) dissociation step,[3,10,11] but more recent studies point to the possible role of a hyponitrite-like $(NO)_2$ dimer in the catalytic cycle.[6,8,13,14]

A number of homogeneous systems that can reduce NO have also been studied.[1,15−20] Hyponitrite is a postulated intermediate in many of these reactions, but its direct detection has often eluded researchers because of its reactive nature.[21−26] For example, Trogler and co-workers studied a Pd^{2+} catalyst that reduces NO to N_2O in acidic media.[27,28] During the catalytic cycle, $[PdCl_3(NO)]^{2-}$ is proposed to undergo electrophilic attack by $NO^\bullet$ in the critical N−N bond forming step. However, the $[N_2O_2]^{2-}$ intermediate could not be detected.[27,28] More recently, Onishi and co-workers developed a Ru bimetallic complex that effects NO reduction.[22,29] In this example, the hyponitrite intermediate was isolated and structurally characterized, making it one of only a few well-defined hyponitrite complexes.[25,26,30−35] Herein, we report the isolation of a nickel nitrosyl, [Ni(NO)$(bipy)_2$][PF_6], which forms N_2O on standing via a *cis*-$[N_2O_2]^{2-}$ intermediate. To our knowledge, this is the first well-defined example of an Ni-mediated NO reduction.[36−38]

Treatment of [Ni(NO)$(CH_3NO_2)_3$][PF_6][37] with 0.95 equiv of 2,2-bipyridine (bipy) in CH_2Cl_2 results in formation of the three-coordinate nickel nitrosyl [Ni(NO)(bipy)][PF_6] (**1**) in good yield. Complex **1** exhibits a ν_{NO} value of 1869 cm^{-1} in CH_2Cl_2. For comparison, the related cationic three-coordinate nickel nitrosyl, [(dtbpe)Ni(NO)][BAr^F_4], exhibits a much lower ν_{NO} value of 1836 cm^{-1} (solid state).[39] The connectivity of **1** was confirmed by X-ray crystallography (Figure S1). The nickel center in **1** is ligated by a single bipy ligand and one NO ligand in a trigonal planar geometry. The metrical parameters of the Ni−N−O moiety [Ni1−N1 = 1.617(3) Å, N1−O1 =1.152(4) Å, Ni1−N1−O1 = 176.2(3)°] are consistent with previously characterized three-coordinate $\{NiNO\}^{10}$ species.[39,40]

Scheme 1



Further reaction of **1** with 1 equiv of bipy in CH_2Cl_2 affords a deep red solution (Scheme 1). Storage at −25 °C results in precipitation of the five-coordinate nickel nitrosyl complex, [Ni(NO)$(bipy)_2$][PF_6] (**2**), in 93% yield. Alternatively, treatment of **1** with 2,9-dimethylphenanthroline (Me_2phen) furnishes [Ni(NO)(bipy)(Me_2phen)][PF_6] (**3**) in 77% yield. Both complexes have been fully characterized (see the Supporting Information).

As revealed by X-ray crystallography, both **2** and **3** consist of a cationic nickel center coordinated by two dipyridyl ligands and one NO ligand (Figure 1). The metrical parameters of the Ni−N−O moiety in **2** and **3** are similar; however, they contrast

Received: May 1, 2012
Published: June 7, 2012

dx.doi.org/10.1021/ja304204q | *J. Am. Chem. Soc.* 2012, 134, 9930−9933

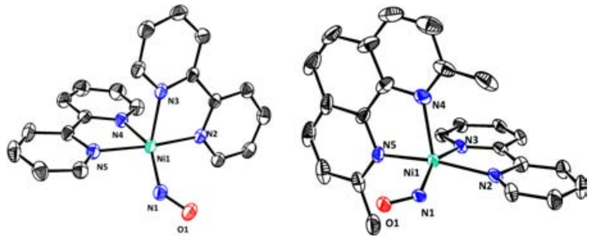


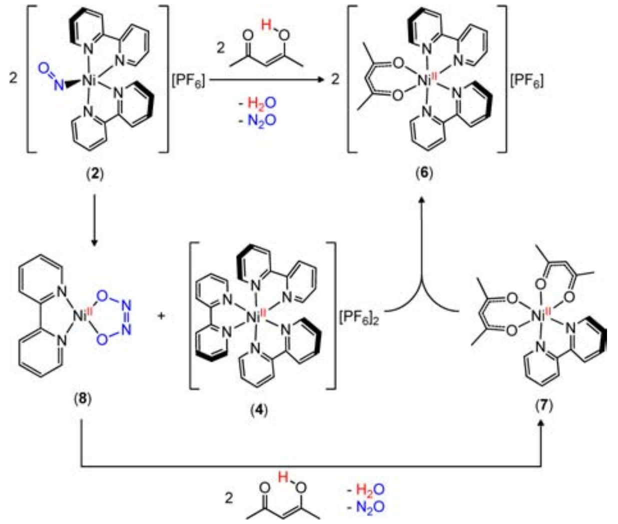
Figure 1. ORTEP drawing of the cationic portion of [Ni(NO)(bipy)$_2$][PF$_6$] (**2**·1.5CH$_2$Cl$_2$) (left) and [Ni(NO)(bipy)(Me$_2$phen)][PF$_6$] (**3**·CH$_2$Cl$_2$) (right), shown with 50% thermal ellipsoids. Hydrogen atoms, PF$_6$ anions, and CH$_2$Cl$_2$ solvate molecules have been omitted for clarity.

significantly with those of **1**. For example, the Ni1−N1 [**2**, 1.762(3) Å; **3**, 1.766(6) Å] and N1−O1 [**2**, 1.207(3) Å; **3**, 1.196(9) Å] bond lengths are both elongated in comparison to those seen in **1**. The Ni1−N1−O1 angle is also small in both **2** and **3** [**2**, 129.5(2)°; **3**, 128.2(5)°]. The changes in metrical parameters upon addition of a second dipyridyl ligand are consistent with a reduction of the nitrosyl moiety to NO$^-$.[40] This is also evidenced by the significantly lower ν_{NO} value of **2** [1567 cm^{-1}] and **3** [1585 cm^{-1}], in comparison to **1**.[40,41] Notably, the coordination environment around the Ni center changes subtly between **2** and **3**. The geometry of **2** is intermediate between trigonal bipyramidal and square pyramidal (τ_5 = 0.49), while **3** is closer to square pyramidal (τ_5 = 0.18) where N4 of the Me$_2$phen ligand forms the apex of the square pyramid.[42] In addition, one of the methyl groups of the Me$_2$phen ligand partially blocks the open coordination site of the Ni center in **3**. There are only a few Ni nitrosyls that feature a bent NO ligand.[16,43,44] For example, (Cp)Ni(NHC)(NO) (NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) exhibits similar Ni−NO metrical parameters to those seen in **2** and **3**,[40] while [Bse$^{\mathrm{Me}}$]Ni(PPh$_3$)(NO) (Bse$^{\mathrm{Me}}$ = bis(mercaptoimidazolyl)borate) features a larger Ni−N−O angle of 149.6(1)°.[43,44]

Complex **2** is unstable in CH$_2$Cl$_2$ solutions at room temperature under an N$_2$ atmosphere. Monitoring this decomposition by IR spectroscopy over 40 min reveals growth of an IR stretch assignable to N$_2$O [2228 cm^{-1}].[45] Its presence is also supported by analysis of the head space by gas chromatography (see the Supporting Information (SI)). Monitoring the transformation of **2** for 24 h by ^{1}H NMR spectroscopy in CD$_2$Cl$_2$ reveals the formation of several new products, including free bipy, [Ni(bipy)$_3$][PF$_6$]$_2$ (**4**),[46] and [(bipy)Ni(NO)(Cl)] (**5**). The identities of **4** and **5** were corroborated by comparison against the authentic materials (see the SI). In contrast to the instability of **2**, complex **3** is stable under the same conditions over 40 min by IR spectroscopy. Moreover, only minor amounts of decomposition are observed by ^{1}H NMR spectroscopy after 15 h in CD$_2$Cl$_2$.

The formation of complex **5**, likely formed by chloride abstraction from CD$_2$Cl$_2$, can be circumvented by addition of a proton source to the reaction mixture. Thus, addition of 1 equiv of H(acac) to **2** in CH$_2$Cl$_2$ results in the formation of N$_2$O, H$_2$O and [Ni(acac)(bipy)$_2$][PF$_6$] (**6**) (Scheme 2). Complex **6** can be isolated from CH$_2$Cl$_2$/hexanes in 74% yield. The generation of N$_2$O in the reaction was confirmed by solution IR spectroscopy and gas chromatography (56% yield when the reaction is performed in pyridine). H$_2$O is also generated, as detected by ^{1}H NMR spectroscopy [δ = 1.54 ppm, 86% yield].[47] Interestingly, monitoring the addition of H(acac) to **2** in CD$_3$CN by ^{1}H NMR spectroscopy reveals the formation of [Ni(bipy)$_3$][PF$_6$]$_2$ (**4**) and [Ni(acac)$_2$(bipy)][48] (**7**) at short reaction times (1 h). On standing, the resonances associated with these two complexes disappear and those associated with complex **6** grow in intensity, suggesting there is ligand redistribution between **4** and **7** to form **6**. This was confirmed by reaction of independently prepared samples (see the SI).

Scheme 2



The formation of N$_2$O from NO can occur by either HNO disproportionation or hyponitrite formation,[2,4] and we endeavored to determine which pathway was operative. Fortuitously, dissolution of **2** in acetonitrile results in precipitation of the NO-coupled product, [Ni(κ^2-*O*$_2$N$_2$)(bipy)] (**8**), after standing for 1 h, suggesting that N$_2$O formation from **2** proceeds via a hyponitrite intermediate. Complex **8** can be isolated as a diamagnetic, orange crystalline solid in moderate but consistent yields (30−50%). Its solid-state IR spectrum (Nujol mull) contains stretches at 937 and 1265 cm^{-1}, consistent with presence of a [N$_2$O$_2$]$^{2-}$ ligand.[25,49] In the solid-state, complex **8** exhibits a square planar Ni center coordinated by one bipy ligand and one *cis*-[N$_2$O$_2$]$^{2-}$ ligand (Figure 2). The *cis*-[N$_2$O$_2$]$^{2-}$ ligand is symmetrically coordinated to the Ni center through two oxygen atoms [Ni1−O1 = 1.800(1) Å, Ni1−O2 = 1.800(1) Å].[25] The O1−N1 and O2−N2 bond distances are 1.384(3) and 1.391(3) Å, respectively, while the N1−N2 bond length [1.240(3) Å] is consistent with a double bond. Overall, these parameters support the presence of a dianionic hyponitrite ligand, [N$_2$O$_2$]$^{2-}$, in **8**.[31,50] For

Figure 2. ORTEP drawing of [Ni(κ^2-*O*$_2$N$_2$)(bipy)] (**8**) shown with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

comparison, $(PPh_3)_2Pt(cis\text{-}O_2N_2)$ exhibits similar O−N [1.39(5) and 1.32(3) Å] and N═N [1.21(5) Å] bond lengths.[34] Similarly, (dppf)Ni(cis-O_2N_2) (dppf =1,1′-bis(diphenylphosphanyl)ferrocene) exhibits O−N bond lengths of 1.400(6) and 1.385(5) Å, and an N═N bond length of 1.236(6) Å.[25,33] In contrast, $(TpRu)_2(\mu\text{-}Cl)(\mu\text{-}pz)\{\mu\text{-}\kappa^2\text{-}N,N\text{-}N_2O_2\}$, which features a neutral N_2O_2 ligand, exhibits a much longer N−N bond length [1.861(3) Å] and shorter N−O bond distances [1.197(3) and 1.193(3) Å].[22]

Complex **8** is very sparingly soluble in CH_2Cl_2, MeCN, and DMF. Once in solution it slowly decomposes, forming an intractable mixture over the course of several days. In contrast, **8** rapidly reacts with 2 equiv of H(acac) in CD_2Cl_2 to cleanly generate **7** and N_2O (Scheme 2), demonstrating its intermediacy in the formation of N_2O from **2**.

Thus, an overall picture of N_2O formation emerges in which two molecules of complex **2** rearrange to generate **8** and **4**. Complex **8** then rapidly reacts with H(acac) to induces N−O bond cleavage with concomitant N_2O generation. Finally, ligand rearrangement occurs between $[Ni(bipy)_3][PF_6]_2$ (**4**) and $[Ni(acac)_2(bipy)]$ (**7**), generating complex **6** as the final product (Scheme 2).

Several questions remain concerning the critical N−N bond forming step that results in hyponitrite formation. This step likely follows one of three pathways: (**A**) coupling of two NO^- ligands via a bimetallic intermediate;[19] (**B**) coupling of a NO^- ligand with NO gas (in this mechanism, rupture of the Ni−NO bond in **2** or **3** generates the required $NO^\bullet$);[34,51] or (**C**) generation of HNO by protonation of the nitrosyl ligand in **2**. HNO then disproportionates via a metal-free dimerization.[52] We can rule out pathway **C**, as addition of H(acac) to **3** does not result in any reaction. We also disfavor pathway **B**. For this mechanism to be operative, $NO^\bullet$ has to be generated in situ by homolytic cleavage of a Ni−NO bond. Spontaneous NO dissociation from an $\{MNO\}^{10}$ complex is extremely rare.[17] Additionally, we expect that Ni−NO bond cleavage would also occur in **3**, given the similarity of the electronic structures of **2** and **3**, according to IR and UV−vis spectroscopies; yet **3** is stable in solution. Nonetheless, to test the plausibility of this mechanism, we monitored the reactions of **2** and **3** with added $NO^\bullet$ directly. When $NO^\bullet$ gas is added to CH_2Cl_2 solutions of **2**, a rapid reaction does occur. N_2O is detected by solution IR spectroscopy, and both complexes **4** and **5** are observed by ^1H NMR spectroscopy. However, several new, as-yet-unidentified products are also formed in the reaction. Similar results are observed when NO is added to **3**. Given this, we suspect that we are generating the products of NO disproportionation (e.g., N_2O and NO_2),[45,53−55] and not NO reduction. Thus, while we cannot completely rule out pathway **B**, we prefer pathway **A**, as this pathway best explains the differing reactivities of complexes **2** and **3**. Accordingly, the stability of **3** is a consequence of the increased steric profile of the Me_2phen ligand, which extends a methyl group into the open coordination site (Figure 3), thereby preventing the close approach of two NO^- ligands. In contrast, the less-bulky bipy ligand in **2** cannot prevent dimerization and NO^- coupling.

In summary, we have discovered a five-coordinate nickel nitrosyl that produces N_2O via intermolecular coupling of two NO^- ligands. This work provides further confirmation that *cis*-hyponitrite, $[N_2O_2]^{2-}$, should be considered a viable intermediate in NO reduction mediated by heterogeneous catalysts, and also the enzyme *NO reductase*.[26,56−59] Future work will focus on the role of Lewis acids in the release of N_2O from $[N_2O_2]^{2-}$. Previously, Bohle and co-workers predicted that N_2O evolution occurs spontaneously with concomitant formation of a Lewis basic "M═O" intermediate.[24,33] In contrast, Cenini and co-workers reported that N_2O release occurs upon acidification of $(PPh_3)_2Pt(O_2N_2)$.[35] Other systems also require protonation of $[N_2O_2]^{2-}$ to induce N_2O release.[22,29,31,35] Ultimately, understanding the chemical behavior of the $[N_2O_2]^{2-}$ ligand will allow more accurate predictions of the mechanisms of both heterogeneous and enzymatic systems.

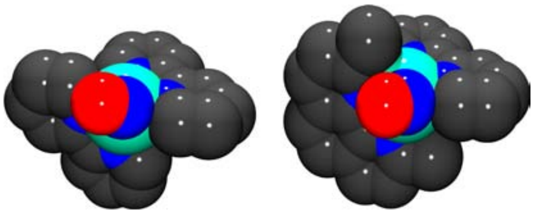


Figure 3. Space filling diagrams of the cationic part of complexes **2** (left) and **3** (right) rendered using Pov-ray.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, crystallographic details (as CIF files) and spectral data for **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

hayton@chem.ucsb.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the University of California, Santa Barbara, for financial support of this work. We also thank Prof. Peter Ford, Dr. Julie Heinecke, and Agustin Pierri for help with gas chromatography measurements.

■ REFERENCES

(1) Lee, D.-H.; Mondal, B.; Karlin, K. D. *Activation of Small Molecules: Organometallic and Bioinorganic Perspectives*; Wiley-VCH: New York, 2006.

(2) Schopfer, M. P.; Wang, J.; Karlin, K. D. *Inorg. Chem.* **2010**, *49*, 6267−6282.

(3) Granger, P.; Parvulescu, V. I. *Chem. Rev.* **2011**, *111*, 3155−3207.

(4) Wasser, I. M.; de Vries, S.; Moenne-Loccoz, P.; Schroder, I.; Karlin, K. D. *Chem. Rev.* **2002**, *102*, 1201−1234.

(5) Ravishankara, A. R. *Chem. Rev.* **2003**, *103*, 4505−4508.

(6) Liu, Z.-P.; Jenkins, S. J.; King, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 7336−7340.

(7) Paredis, K.; Ono, L. K.; Behafarid, F.; Zhang, Z.; Yang, J. C.; Frenkel, A. I.; Cuenya, B. R. *J. Am. Chem. Soc.* **2011**, *133*, 13455−13464.

(8) Brown, W. A.; King, D. A. *J. Phys. Chem. B* **2000**, *104*, 2578−2595.

(9) Rosca, V.; Duca, M.; de Groot, M. T.; Koper, M. T. M. *Chem. Rev.* **2009**, *109*, 2209−2244.

(10) Hu, Y. H.; Griffiths, K.; Norton, P. R. *Surf. Sci.* **2009**, *603*, 1740−1750.

(11) Roy, S.; Hegde, M. S.; Madras, G. *Appl. Energy* **2009**, *86*, 2283−2297.

(12) *Catalysis without Precious Metals*; Bullock, R. M., Ed.; Wiley-VCH: Weinheim, Germany, 2010.

(13) Shiotari, A.; Kitaguchi, Y.; Okuyama, H.; Hatta, S.; Aruga, T. *Phys. Rev. Lett.* **2011**, *106*, 156104.
(14) Beniya, A.; Koitaya, T.; Kondoh, H.; Mukai, K.; Yoshimoto, S.; Yoshinobu, J. *J. Chem. Phys.* **2009**, *131*, 084704.
(15) Bottomley, F. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1989; Vol. 2.
(16) Hayton, T. W.; Sharp, W. B.; Legzdins, P. *Chem. Rev.* **2002**, *102*, 935−992.
(17) Legzdins, P.; Richter-Addo, G. B. *Metal Nitrosyls*; Oxford University Press: New York, 1992.
(18) Ruggiero, C. E.; Carrier, S. M.; Tolman, W. B. *Angew. Chem., Int. Ed.* **1994**, *33*, 895−897.
(19) Paul, P. P.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 6331−6332.
(20) Mahapatra, S.; Halfen, J. A.; Tolman, W. B. *J. Chem. Soc., Chem. Commun.* **1994**, 1625−1626.
(21) Bhaduri, S.; Johnson, B. F. G.; Savory, C. J.; Segal, J. A.; Walter, R. H. *J. Chem. Soc., Chem. Commun.* **1974**, 809−810.
(22) Arikawa, Y.; Asayama, T.; Moriguchi, Y.; Agari, S.; Onishi, M. *J. Am. Chem. Soc.* **2007**, *129*, 14160−14161.
(23) Feltham, R. D.; Carriel, J. T. *Inorg. Chem.* **1964**, *3*, 121−123.
(24) McNeill, K.; Bergman, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 8260−8269.
(25) Arulsamy, N.; Bohle, D. S.; Imonigie, J. A.; Moore, R. C. *Polyhedron* **2007**, *26*, 4737−4745.
(26) Varotsis, C.; Ohta, T.; Kitagawa, T.; Soulimane, T.; Pinakoulaki, E. *Angew. Chem., Int. Ed.* **2007**, *46*, 2210−2214.
(27) MacNeil, J. H.; Gantzel, P. K.; Trogler, W. C. *Inorg. Chim. Acta* **1995**, *240*, 299−304.
(28) MacNeil, J. H.; Berseth, P. A.; Bruner, E. L.; Perkins, T. L.; Wadia, Y.; Westwood, G.; Trogler, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1668−1675.
(29) Arikawa, Y.; Matsumoto, N.; Asayama, T.; Umakoshi, K.; Onishi, M. *Dalton Trans.* **2011**, *40*, 2148−2150.
(30) Bottcher, H.-C.; Graf, M.; Mereiter, K.; Kirchner, K. *Organometallics* **2004**, *23*, 1269−1273.
(31) Xu, N.; Campbell, A. L. O.; Powell, D. R.; Khandogin, J.; Richter-Addo, G. B. *J. Am. Chem. Soc.* **2009**, *131*, 2460−2461.
(32) Xu, N.; Yi, J.; Richter-Addo, G. B. *Inorg. Chem.* **2010**, *49*, 6253−6266.
(33) Arulsamy, N.; Bohle, D. S.; Imonigie, J. A.; Levine, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2371−2373.
(34) Bhaduri, S.; Johnson, B. F. G.; Pickard, A.; Raithby, P. R.; Sheldrick, G. M.; Zuccaro, C. I. *J. Chem. Soc., Chem. Commun.* **1977**, 354−355.
(35) Cenini, S.; Ugo, R.; La Monica, G.; Robinson, S. D. *Inorg. Chim. Acta* **1972**, *6*, 182−184.
(36) Hieber, W.; Nast, R. Z. *Anorg. Allg. Chem.* **1940**, *244*, 23−47.
(37) Wright, A. M.; Wu, G.; Hayton, T. W. *Inorg. Chem.* **2011**, *50*, 11746−11753.
(38) Feltham, R. D. *Inorg. Chem.* **1964**, *3*, 119−121.
(39) Iluc, V. M.; Miller, A. J. M.; Hillhouse, G. L. *Chem. Commun.* **2005**, 5091−5093.
(40) Varonka, M. S.; Warren, T. H. *Organometallics* **2010**, *29*, 717−720.
(41) Enemark, J. H.; Feltham, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 3534−3536.
(42) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.
(43) Maffett, L. S.; Gunter, K. L.; Kreisel, K. A.; Yap, G. P. A.; Rabinovich, D. *Polyhedron* **2007**, *26*, 4758−4764.
(44) Landry, V. K.; Parkin, G. *Polyhedron* **2007**, *26*, 4751−4757.
(45) Franz, K. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 10504−10512.
(46) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864−878.
(47) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176−2179.
(48) Hashagen, J. T.; Fackler, J. P. *J. Am. Chem. Soc.* **1965**, *87*, 2821−2824.
(49) Andrews, L.; Liang, B. *J. Am. Chem. Soc.* **2001**, *123*, 1997−2002.
(50) Feldmann, C.; Jansen, M. *Angew. Chem., Int. Ed.* **1996**, *35*, 1728−1730.
(51) Jackson, M. A.; Tiedje, J. M.; Averill, B. A. *FEBS Lett.* **1991**, *291*, 41−44.
(52) Fehling, C.; Friedrichs, G. *J. Am. Chem. Soc.* **2011**, *133*, 17912−17922.
(53) Fullmer, B. C.; Pink, M.; Fan, H.; Yang, X.; Baik, M.-H.; Caulton, K. G. *Inorg. Chem.* **2008**, *47*, 3888−3892.
(54) Schneider, J. L.; Carrier, S. M.; Ruggiero, C. E.; Young, V. G.; Tolman, W. B. *J. Am. Chem. Soc.* **1998**, *120*, 11408−11418.
(55) Franz, K. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 9034−9040.
(56) Moenne-Loccoz, P. *Nat. Prod. Rep.* **2007**, *24*, 610−620.
(57) Wang, J.; Schopfer, M. P.; Sarjeant, A. A. N.; Karlin, K. D. *J. Am. Chem. Soc.* **2009**, *131*, 450−451.
(58) Collman, J. P.; Dey, A.; Yang, Y.; Decreau, R. A.; Ohta, T.; Solomon, E. I. *J. Am. Chem. Soc.* **2008**, *130*, 16498−16499.
(59) Collman, J. P.; Yang, Y.; Dey, A.; Decreau, R. A.; Ghosh, S.; Ohta, T.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 15660−15665.