

Reactivity of a Nickel Sulfide with Carbon Monoxide and Nitric Oxide

Nathaniel J. Hartmann, Guang Wu, and Trevor W. Hayton*

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

S Supporting Information

ABSTRACT: The reactivity of the “masked” terminal nickel sulfide complex, $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ ($\text{L}^{\text{tBu}} = \{(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(t\text{Bu})_2\text{CH}\}$), with the biologically important small molecules CO and NO, was surveyed. $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ reacts with carbon monoxide (CO) via addition across the Ni–S bond to give a carbonyl sulfide complex, $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S},\text{C}:\eta^2\text{-COS})]$ (**1**). Additionally, $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ reacts with nitric oxide (NO) to yield a nickel nitrosyl, $[(\text{L}^{\text{tBu}})\text{Ni}(\text{NO})]$ (**2**), and a perthionitrite anion, $[K(18\text{-crown-6})][\text{SSNO}]$ (**3**). The isolation of **3** from this reaction confirms, for the first time, that transition metal sulfides can react with NO to form the biologically important $[\text{SSNO}]^-$ anion.

There is a widespread interest in understanding the fundamental reactivity of late metal sulfides with small molecules, such as NO and CO, which are notable for their roles in biological signaling and the carbon cycle, respectively.^{1–3} For example, the reactions of NO with the sulfide ligands in metallo-proteins can not only affect its bioavailability but may also play an important regulatory role (e.g., NO/H₂S “cross talk”).⁴ In this regard, NO is known to react with iron sulfur clusters.^{5,6} The sulfur-containing products from these reactions are S⁰, S²⁻, or H₂S. Other sulfur containing products, such as $[\text{SNO}]^-$, $[\text{SSNO}]^-$, and $[\text{ONN}(\text{O})\text{SO}_3]^{2-}$ have not yet been observed from these reactions; however, these compounds have come under increasing scrutiny because they could function as both NO and sulfur reservoirs *in vivo*.^{4,7,8} Similarly, CO is postulated to react with the sulfide ligands within metallo-enzymes. In particular, the first step of CO oxidation by MoCu CODH is thought to involve CO insertion into a Cu–S bond.⁹

Recently, we reported the synthesis of the “masked” terminal Ni(II) sulfides, $[K(\text{L})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ ($\text{L}^{\text{tBu}} = \{(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(t\text{Bu})_2\text{CH}\}$, L = 18-crown-6, 2,2,2-cryptand). These complexes have proven to react with a variety of small molecules, including CS₂ and N₂O.^{10,11} Given its potent reactivity, we hypothesized that $[K(\text{L})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ would be a good model for exploring the interactions of late metal sulfides with the biologically important small molecules, CO and NO. This survey is especially important because late metal (Ni and Cu) sulfides are found in a variety of metalloenzyme active sites, including the NiFe and MoCu CO dehydrogenases (CODH),^{9,12} the “orange protein complex”,¹³ and N₂O reductase (N₂OR),^{14–16} where they are known to play both catalytic⁹ and structural roles,^{14,17} yet our understanding of late metal sulfide (and thiolate) reactivity is still relatively

limited.^{18–21} Herein, we describe the reactivity of $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ with CO and NO in an effort to understand better the fundamental chemistry of these small molecules with metal sulfides.

Exposure of a toluene solution of $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ to excess carbon monoxide (CO) results in a rapid color change from dark brown to yellow. Workup of the reaction mixture by crystallization from toluene/isooctane provides $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}(\text{S},\text{C}:\eta^2\text{-COS})]$ (**1**) as a orange crystalline solid in 88% yield (eq 1). The solid state

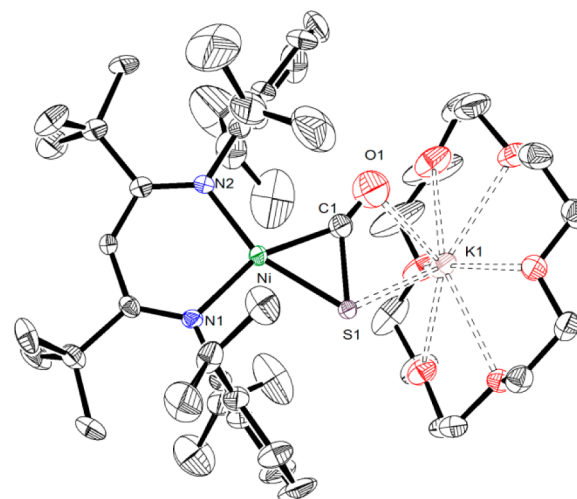
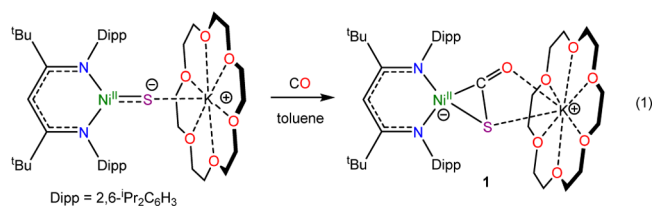


Figure 1. ORTEP drawing of $[K(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S},\text{C}:\eta^2\text{-SCO})]$ (**1**, 2C₆H₆) shown with 50% thermal ellipsoids. Hydrogen atoms, one orientation of the disordered COS moiety, and C₆H₆ solvate molecules have been omitted for clarity. Selected metrical parameters: Ni1–N1 1.929(4) Å, Ni1–N2 1.903(4) Å, Ni1–S1 2.193(2) Å, Ni1–C1 1.871(8) Å, S1–C1 1.791(8) Å, C1–O1 1.07(1) Å, S1–K1 3.250(4) Å, O1–K1 2.841(7) Å, N1–Ni1–N2 97.3(2)°, N1–Ni1–S1 104.7(1)°, N2–Ni1–C1 106.4(3)°, S1–C1–O1 136.6(7)°.

Received: August 3, 2016

Published: September 8, 2016

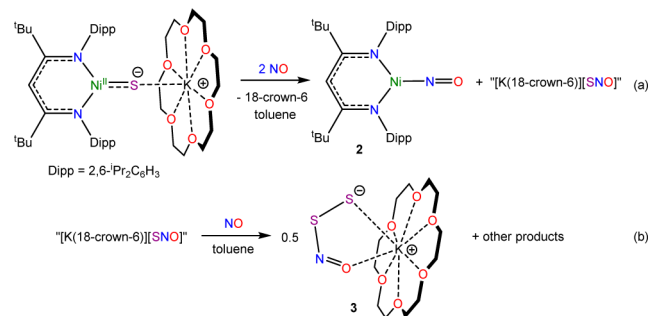
molecular structure of **1** is shown in Figure 1. Complex **1** features a rare carbonyl sulfide ($[\text{COS}]^{2-}$) ligand, formed by the activation of CO by the S^{2-} ligand. The $[\text{COS}]^{2-}$ ligand features a $\mu:\eta^2,\kappa^2$ binding mode, wherein the carbon and sulfur atoms are coordinated to the Ni center, whereas the sulfur and oxygen atoms are coordinated to the K^+ center. The COS ligand is disordered over two positions, which are related by a C_2 rotation axis. This disorder could not be adequately resolved; consequently, the C–O bond length (1.07(1) Å) is anomalously short. A similar problem was observed in the only other structurally characterized COS complex, $[(\text{MeCp})_2\text{Nb}(\text{S},\text{C}:\eta^2\text{-COS})(\text{CH}_2\text{SiMe}_3)]$.²² The Ni–S and Ni–C distances in **1** are 2.193(2) Å and 1.871(8) Å, whereas the K–S distance (3.250(4) Å) is longer than that found in the starting material, $[\text{K}(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$, and is indicative of a rather weak dative interaction. The K–O (2.841(7) Å) distance is similarly long.^{23,24} Finally, the Ni–N distances in **1** are comparable to those found in the starting material.¹⁰

The ^1H NMR spectrum of **1** is consistent with its formulation as a C_s symmetric, diamagnetic, square planar Ni^{II} complex. For example, the ^1H NMR spectrum of **1** in C_6D_6 features two *tert*-butyl resonances at 1.43 and 1.41 ppm and a single γ -CH resonance at 5.48 ppm. Additionally, the ^{13}C NMR spectrum of **1** features a resonance at 214.72 ppm that we have assigned to the $[\text{COS}]^{2-}$ moiety. For comparison, this chemical shift is an exact average of the ^{13}C NMR chemical shifts observed for the CE_2 ligands in $[(\text{dtbpe})\text{Ni}(\eta^2\text{-CO}_2)]$ (*dtbpe* = $^t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{P}^t\text{Bu}_2$) and $[(\text{dtbpe})\text{Ni}(\eta^2\text{-CS}_2)]$, which are found at 164.28 and 264.20 ppm, respectively.²⁵ The IR spectrum (KBr mull) of **1** shows a strong ν_{CO} mode at 1676 cm^{-1} , which is consistent with that expected for $[\text{SCO}]^{2-}$.²²

The formation of **1** represents a rare example of attack of a S^{2-} ligand by CO, and highlights the potent nucleophilicity of the S^{2-} moiety in $[\text{K}(\text{L})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$. Other examples of this transformation include the reaction of $[(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})_2]$ with CO to make COS and $[(\text{Ph}_3\text{P})_4\text{Pt}_2(\mu\text{-S})]$, and the reaction of $[\text{Cp}^*\text{Mo}(\mu\text{-S})\{\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})\}]_2$ with CO and S_8 to make COS and $[\text{Cp}^*\text{Mo}(\text{CO})(\eta^2\text{-S}_2)\{\text{N}(\text{iPr})\text{C}(\text{Ph})\text{N}(\text{iPr})\}]$.^{26,27} For further comparison, the previously mentioned COS complex, $[(\text{MeCp})_2\text{Nb}(\eta^2\text{-SCO})(\text{CH}_2\text{SiMe}_3)]$, was formed by reaction of $[(\text{MeCp})_2\text{Nb}(\text{CO})(\text{CH}_2\text{SiMe}_3)]$ with elemental sulfur.^{22,28,29} Perhaps more importantly, the formation of **1** provides support for the first step in the proposed mechanism of MoCu CODH,⁹ which is thought to involve insertion of CO into a Cu–S bond and formation of a thiocarbonate ligand, $[\text{CO}_2\text{S}]^{2-}$. Additionally, a metal-COS adduct may be a proposed intermediate in the catalytic cycle of thiocyanate hydrolase, which catalyzes the conversion of thiocyanate (SCN^-) to carbonyl sulfide.^{30–32}

Exposure of a toluene solution of $[\text{K}(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ to an excess of nitric oxide (NO) results in a rapid color change from brown to brown-green. Workup of the reaction mixture results in isolation of a nitrosyl complex, $[(\text{L}^{\text{tBu}})\text{Ni}(\text{NO})]$ (**2**), along with a perthionitrite salt, $[\text{K}(18\text{-crown-6})][\text{SSNO}]$ (**3**) (Scheme 1).

Complex **2** was isolated in an 80% yield and has been fully characterized by elemental analysis, X-ray crystallography, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy. Its structural and spectroscopic parameters are consistent with those previously reported for the related β -diketiminate nickel nitrosyl complex, $[(\text{L}^{\text{Me}})\text{Ni}(\text{NO})]$ ($\text{L}^{\text{Me}} = \{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})\}_2\text{CH}$), which was isolated from the reaction of $[(\text{L}^{\text{Me}})\text{Ni}^{\text{I}}(2,4\text{-lutidine})]$ and NO.³³ Complex **3** was isolated

Scheme 1. Synthesis of Complexes **2** and **3**

in 86% yield as orange plates (based on sulfur). Its formulation was confirmed through X-ray crystallography, IR spectroscopy, and UV–vis spectroscopy. Complex **3** crystallizes from $\text{CH}_2\text{Cl}_2/\text{pentane}$ as a CH_2Cl_2 adduct ($\text{K1–Cl1} = 3.2674(8)$ Å) and features a perthionitrite $[\text{SSNO}]^-$ ligand coordinated to a $[\text{K}(18\text{-crown-6})]^+$ cation in a κ^2 fashion (Figure 2). The

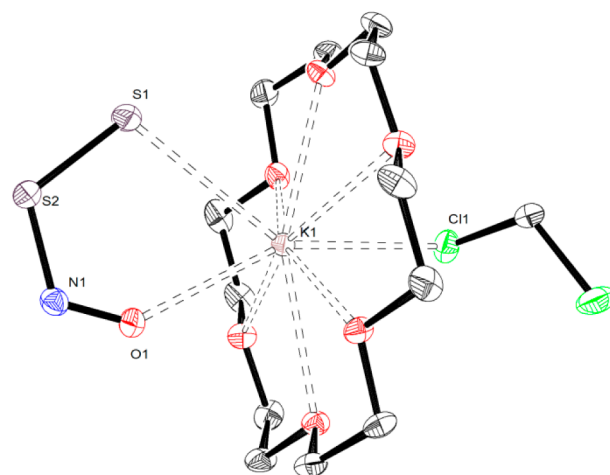
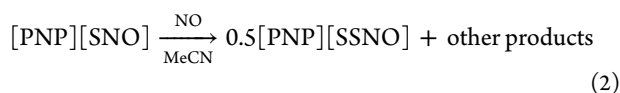


Figure 2. ORTEP drawing of $[\text{K}(18\text{-crown-6})][\text{SSNO}]\cdot\text{CH}_2\text{Cl}_2$ (**3**· CH_2Cl_2) shown with 50% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected metrical parameters: O1–N1 1.247(2) Å, N1–S2 1.669(2) Å, S2–S1 1.9526(9) Å, S1–K1 3.2013(8) Å, O1–K1 2.770(2) Å, Cl1–K1 3.2674(8) Å, O1–N1–S2 119.6(1)°, N1–S2–S1 113.27(7)°.

$[\text{SSNO}]^-$ moiety in complex **3** possesses O–N, N–S, and S–S bond lengths of 1.247(2), 1.669(2), and 1.9526(9) Å, respectively, which agree well with those reported previously for $[\text{PNP}][\text{SSNO}]$ ($\text{PNP} = \text{Ph}_3\text{PNPPH}_3$).³⁴ In addition, the K–S (3.2013(8) Å) and K–O (2.770(2) Å) bond lengths are comparable to those observed in **1**. The UV–vis spectrum of **3** in acetonitrile features an absorbance at 443 nm. For comparison, $[\text{PNP}][\text{SSNO}]$ exhibits an absorbance of 448 nm in acetone.³⁴ The IR spectrum (KBr mull) of complex **3** reveals a ν_{NO} mode at 1313 cm^{-1} , which is somewhat lower than those observed for other $[\text{SSNO}]^-$ salts.^{34,35} This lower value may be a consequence of the $\text{K}\cdots\text{O}$ dative interaction observed in the solid state molecular structure of **3**. Complex **3** is soluble in aromatic solvents, acetonitrile, and dichloromethane, and appears to be indefinitely stable when stored at -25 °C as a solid under inert atmosphere.

The isolation of **3** from the reaction of $[\text{K}(18\text{-crown-6})][(\text{L}^{\text{tBu}})\text{Ni}^{\text{II}}(\text{S})]$ with NO demonstrates for the first time that a transition metal sulfide can react with NO to form $[\text{SSNO}]^-$,

an observation that may have implications for our understanding of the reactions between NO and sulfur-containing metallo-proteins *in vivo*.^{5,6} To account for the formation of **3**, we hypothesize that the first step of the transformation involves sulfur abstraction by NO, forming “[K(18-crown-6)][SNO]” and “[L^{tBu})Ni^I]”. Subsequent reaction of “[L^{tBu})Ni^I]” with NO yields complex **2** (Scheme 1a), a transformation that has been observed previously.³³ Separately, reaction of “[K(18-crown-6)][SNO]” with NO results in formation of complex **3** (Scheme 1b). Alternatively, it is possible that the first step of the reaction yields a nickel-SNO adduct, e.g., [K(18-crown-6)][(L^{tBu})Ni(SNO)], which subsequently reacts with NO to yield the final products. To test this hypothesis, we monitored the reaction of [K(18-crown-6)][(L^{tBu})Ni^{II}(S)] with only 1 equiv of NO, which resulted in only partial consumption of [K(18-crown-6)][(L^{tBu})Ni^{II}(S)], and formation of complex **2** as the only identifiable Ni-containing product (Figures S6 and S7). These two complexes are present in an approximately 1:2 ratio, respectively. The observation of unconsumed [K(18-crown-6)][(L^{tBu})Ni^{II}(S)] in the reaction mixture is consistent with the proposed mechanism, assuming that the sulfide abstraction step is rate determining. In addition, we monitored the reaction of independently prepared [PNP][SNO]³⁴ with nitric oxide by UV–vis spectroscopy (eq 2). Thus, exposure of an MeCN solution of [PNP][SNO] to excess NO resulted in complete consumption of [PNP][SNO], as revealed by the loss of the absorption band at 334 nm, and the generation of [PNP][SSNO], as revealed by the appearance of a new band at 445 nm (Figure S14). The other products generated in the transformation remain unidentified; however, we can rule out formation of N₂O as it could not be detected in the reaction mixture by either gas chromatography or IR spectroscopy. Although conversion of [SSNO][−] to [SNO][−] was previously reported,³⁴ this is the first demonstration that [SNO][−] can be converted into [SSNO][−] upon oxidation.



In summary, the “masked” terminal nickel sulfide complex, [K(18-crown-6)][(L^{tBu})Ni^{II}(S)], readily activates CO to give a carbonyl sulfide complex, [K(18-crown-6)][(L^{tBu})Ni^{II}(S,C;η²-SCO)] (**1**), via CO addition across the Ni–S bond. This result further highlights the high nucleophilicity of the sulfide ligand in [K(18-crown-6)][(L^{tBu})Ni^{II}(S)], despite the K⁺ capping moiety that is present in both solution and the solid-state. Moreover, complex **1** represents a well-defined example of a late metal [COS]^{2−} adduct.^{9,30–32} The sulfide ligand in [K(18-crown-6)][(L^{tBu})Ni^{II}(S)] also activates NO to generate a nickel nitrosyl, [(L^{tBu})Ni(NO)] (**2**), and a perthionitrite salt, [K(18-crown-6)][SSNO] (**3**). This result represents the first confirmed generation of [SSNO][−] from reaction of a transition metal sulfide with NO. This observation is significant because it offers further support for the hypothesis that metal sulfides can play a regulatory role *in vivo* with respect to NO availability.^{4,36,37} We have also discovered that oxidation of [SNO][−] with NO results in formation of [SSNO][−]. This represents a new route to [SSNO][−], and provides us with a better understanding of the fundamental chemistry of this important, but poorly understood, ion.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08084.

Crystallographic details (CIF)

Experimental procedures and spectral data for complexes 1–3 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*hayton@chem.ucsb.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (CHE 1361654) for financial support of this work. This research made use of the 400 MHz NMR Spectrometer of the Chemistry Department, an NIH SIG (1S10OD012077-01A1).

■ REFERENCES

- (1) Mustafa, A. K.; Gadalla, M. M.; Snyder, S. H. *Sci. Signaling* **2009**, 2, re2.
- (2) Wang, R. *Trends Biochem. Sci.* **2014**, 39, 227.
- (3) Chapin, F. S.; Woodwell, G. M.; Randerson, J. T.; Rastetter, E. B.; Lovett, G. M.; Baldocchi, D. D.; Clark, D. A.; Harmon, M. E.; Schimel, D. S.; Valentini, R.; Wirth, C.; Aber, J. D.; Cole, J. J.; Goulden, M. L.; Harden, J. W.; Heimann, M.; Howarth, R. W.; Matson, P. A.; McGuire, A. D.; Melillo, J. M.; Mooney, H. A.; Neff, J. C.; Houghton, R. A.; Pace, M. L.; Ryan, M. G.; Running, S. W.; Sala, O. E.; Schlesinger, W. H.; Schulze, E.-D. *Ecosystems* **2006**, 9, 1041.
- (4) Cortese-Krott, M. M.; Kuhnle, G. G. C.; Dyson, A.; Fernandez, B. O.; Grman, M.; DuMond, J. F.; Barrow, M. P.; McLeod, G.; Nakagawa, H.; Ondrias, K.; Nagy, P.; King, S. B.; Saavedra, J. E.; Keefer, L. K.; Singer, M.; Kelm, M.; Butler, A. R.; Feelisch, M. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, 112, E4651.
- (5) Fitzpatrick, J.; Kim, E. *Acc. Chem. Res.* **2015**, 48, 2453.
- (6) Tran, C. T.; Williard, P. G.; Kim, E. *J. Am. Chem. Soc.* **2014**, 136, 11874.
- (7) Cortese-Krott, M. M.; Fernandez, B. O.; Santos, J. L. T.; Mergia, E.; Grman, M.; Nagy, P.; Kelm, M.; Butler, A.; Feelisch, M. *Redox Biol.* **2014**, 2, 234.
- (8) Wedmann, R.; Zahl, A.; Shubina, T. E.; Dürr, M.; Heinemann, F. W.; Bugenhagen, B. E. C.; Burger, P.; Ivanovic-Burmazovic, I.; Filipovic, M. R. *Inorg. Chem.* **2015**, 54, 9367.
- (9) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, 99, 15971.
- (10) Hartmann, N. J.; Wu, G.; Hayton, T. W. *Angew. Chem., Int. Ed.* **2015**, 54, 14956.
- (11) Hartmann, N. J.; Wu, G.; Hayton, T. W. *Dalton Trans.* **2016**, Advance Article. DOI: 10.1039/C6DT00885B.
- (12) Can, M.; Armstrong, F. A.; Ragsdale, S. W. *Chem. Rev.* **2014**, 114, 4149.
- (13) George, G. N.; Pickering, I. J.; Yu, E. Y.; Prince, R. C.; Bursakov, S. A.; Gavel, O. Y.; Moura, I.; Moura, J. J. G. *J. Am. Chem. Soc.* **2000**, 122, 8321.
- (14) Pomowski, A.; Zumft, W. G.; Kroneck, P. M. H.; Einsle, O. *Nature* **2011**, 477, 234.
- (15) Brown, K.; Djinovic-Carugo, K.; Haltia, T.; Cabrito, I.; Saraste, M.; Moura, J. G.; Moura, I.; Tegoni, M.; Cambillau, C. *J. Biol. Chem.* **2000**, 275, 41133.
- (16) Brown, K.; Tegoni, M.; Prudencio, M.; Pereira, A. S.; Besson, S.; Moura, J. J.; Moura, I.; Cambillau, C. *Nat. Struct. Biol.* **2000**, 7, 191.
- (17) Dobbek, H.; Svetlitchnyi, V.; Gremer, L.; Huber, R.; Meyer, O. *Science* **2001**, 293, 1281.

- (18) Johnson, B. J.; Lindeman, S. V.; Mankad, N. P. *Inorg. Chem.* **2014**, *53*, 10611.
- (19) Zhai, J.; Hopkins, M. D.; Hillhouse, G. L. *Organometallics* **2015**, *34*, 4637.
- (20) Zhang, S.; Melzer, M. M.; Sen, S. N.; Çelebi-Ölçüm, N.; Warren, T. H. *Nat. Chem.* **2016**, *8*, 663.
- (21) Olechnowicz, F.; Hillhouse, G. L.; Jordan, R. F. *Inorg. Chem.* **2015**, *54*, 2705.
- (22) Fu, P. F.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1993**, *12*, 3790.
- (23) Smiles, D. E.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2014**, *136*, 96.
- (24) Smiles, D. E.; Wu, G.; Kaltsoyannis, N.; Hayton, T. W. *Chem. Sci.* **2015**, *6*, 3891.
- (25) Anderson, J. S.; Iluc, V. M.; Hillhouse, G. L. *Inorg. Chem.* **2010**, *49*, 10203.
- (26) Choon Hong, C.; Hor, T. S. A. *J. Organomet. Chem.* **1996**, *509*, 101.
- (27) Farrell, W. S.; Zavalij, P. Y.; Sita, L. R. *Angew. Chem., Int. Ed.* **2015**, *54*, 4269.
- (28) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.
- (29) Winkler, U.; Khan, M. A.; Nicholas, K. M. *Inorg. Chem. Commun.* **1998**, *1*, 317.
- (30) Katayama, Y.; Narahara, Y.; Inoue, Y.; Amano, F.; Kanagawa, T.; Kuraishi, H. *J. Biol. Chem.* **1992**, *267*, 9170.
- (31) Katayama, Y.; Matsushita, Y.; Kaneko, M.; Kondo, M.; Mizuno, T.; Nyunoya, H. *J. Bacteriol.* **1998**, *180*, 2583.
- (32) Bezsudnova, E. Y.; Sorokin, D. Y.; Tikhonova, T. V.; Popov, V. O. *Biochim. Biophys. Acta, Proteins Proteomics* **2007**, *1774*, 1563.
- (33) Puiiu, S. C.; Warren, T. H. *Organometallics* **2003**, *22*, 3974.
- (34) Seel, F.; Kuhn, R. G.; Simon, G.; Wagner, M. Z. *Naturforsch., B: J. Chem. Sci.* **1985**, *40*, 1607.
- (35) Gao, Y.; Toubaei, A.; Kong, X.; Wu, G. *Chem. - Eur. J.* **2015**, *21*, 17172.
- (36) Cortese-Krott, M. M.; Butler, A. R.; Woollins, J. D.; Feelisch, M. *Dalton Trans.* **2016**, *45*, 5908.
- (37) Nava, M.; Martin-Drumel, M.-A.; Lopez, C. A.; Crabtree, K. N.; Womack, C. C.; Nguyen, T. L.; Thorwirth, S.; Cummins, C. C.; Stanton, J. F.; McCarthy, M. C. *J. Am. Chem. Soc.* **2016**, ASAP Article. DOI: [10.1021/jacs.6b05886](https://doi.org/10.1021/jacs.6b05886).