Title

Synthesis of a “Masked” Terminal Nickel(II) Sulfide by Reductive Deprotection and its Reaction with Nitrous Oxide

Journal

Angewandte Chemie International Edition, 54(49)

ISSN

1433-7851

Authors

Hartmann, Nathaniel J
Wu, Guang
Hayton, Trevor W

Publication Date

2015-12-01

DOI

10.1002/anie.201508232

Peer reviewed

Synthesis of a "Masked" Terminal Nickel(II) Sulfide via Reductive Deprotection and its Reaction with Nitrous Oxide

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

Abstract: Addition of 1 equiv of $KSCPh_3$ to $[L^RNiCl]$ (L^R = {(2,6-$^iPr_2C_6H_3$)NC(R)}$_2$CH, R = Me, ^tBu) in C_6H_6 results in the formation of $[L^RNi(SCPh_3)]$ (**1**, R = Me; **2**, R = ^tBu) in good yields. Subsequent reduction of **1** and **2** with 2 equiv of KC_8, in cold (-25 °C) Et_2O, in the presence of 2 equiv of 18-crown-6, results in the formation of "masked" terminal Ni^{II} sulfides, [K(18-crown-6)][$L^RNi(S)$] (**3**, R = Me; **4**, R = ^tBu), also in good yields. An X-ray crystallographic analysis of these complexes suggests that they feature partial multiple bond character in their Ni-S linkages. Addition of N_2O to a toluene solution of **4** provides [K(18-crown-6)][$L^{tBu}Ni(SN{=}NO)$] (**6**), which features the first example of a thiohyponitrite ($[\kappa^2\text{-SN=NO}]^{2-}$) ligand.

Metal-ligand multiple bonding in the late metals (groups 9, 10, 11) is relatively rare.[1,2] This observation can be rationalized by the "oxo wall" concept,[3] which postulates that a tetragonal complex with a d^5 configuration (or greater) cannot form stable multiple bonds because of occupation of the M=E π^* orbitals. While no exceptions to the "oxo wall" concept are currently known, it can be circumvented by reducing the coordination number at the metal center. For example, two late metal oxos have been reported, namely $[Ir(O)(Mes)_3]$ (Mes = 2,4,6-$Me_3C_6H_2$) and [Pt(O)(PCN)] (PCN = $C_6H_3[CH_2P(tBu)_2](CH_2CH_2NMe_2)$), and both feature four coordinate geometries.[4,5] Two recently isolated Ir nitride complexes also feature four coordinate geometries.[6,7] Similarly, a handful of isolable cobalt, nickel, and copper nitrenes are known, such as $[(Me_2NN)Co(NAd)]$ (Me_2NN = ({2,6-$Me_2C_6H_3$)NC(Me)}$_2$CH), [(dtbpe)Ni(N(2,6-$^iPr_2C_6H_3$)] (dtbpe = $P^tBu_2CH_2CH_2P^tBu_2$), [(IPr*)Ni(N(2,6-$(Mes)_2C_6H_3$)], and $[\{(Me_3NN)Cu\}_2(\mu\text{-NAd})]$ (Me_3NN = {(2,4,6-$Me_3C_6H_2$)NC(Me)}$_2$CH), which also feature low coordination numbers (2-4).[8-11] Also of note are the closely related nickel carbene and phosphinidene complexes, [(dtbpe)Ni(E)] (E = CPh_2, P[2,6-$Mes_2C_6H_3$]), reported by Hillhouse and co-workers.[12,13] This class of materials is highly reactive and is capable of effecting CO oxidation, C-H activation, and [2+2] cycloaddition, demonstrating their utility for small molecule activation.[14-25]

In contrast to the above-mentioned success with C, O, N, and P-donor multiple bonds, attempts to synthesize a stable late metal terminal sulfide have been unsuccessful. For example, Driess and co-workers postulated that reaction of $[L^RNi(\eta^2\text{-}S_2)]$ (L^R = {(2,6-$^iPr_2C_6H_3$)NC(R)}$_2$CH, R = Me) with Ph_3P resulted in transient formation of $[L^RNi(S)]$, but it rapidly dimerizes to form a bridged disulfide complex.[26] Similarly, Jones and co-workers reported the transient formation of [(dippe)Ni(S)], which could be trapped by a variety of nitrones.[27]

Recently, we reported the synthesis of a Th^{IV} sulfide complex, [K(18-crown-6)][$Th(S)(NR_2)_3$] (R = $SiMe_3$), via reductive removal of the trityl protecting group.[28] Building on this work, we next attempted to apply this "reductive deprotection" reaction to the synthesis of an isolable late metal terminal sulfide. Herein, we report the synthesis of a "masked" terminal Ni^{II} sulfide and describe its reactivity with nitrous oxide.

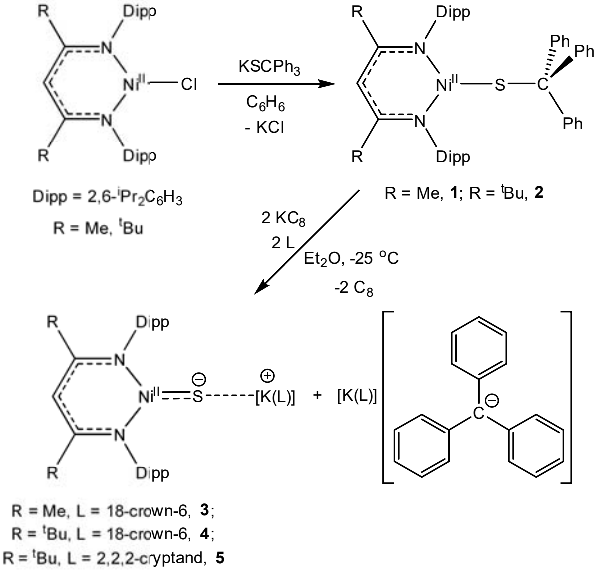
Addition of 1 equiv of $KSCPh_3$ to $[L^RNiCl]$ (R = Me, ^tBu)[29] in C_6H_6 results in the formation of $[L^RNi(SCPh_3)]$ (**1**, R = Me; **2**, R = ^tBu) (Scheme 1). Their formulations were confirmed by elemental analysis and X-ray crystallography (full structural details can be found in the Supporting Information). Moreover, their ^1H NMR spectra are similar to those reported for other Ni^{II} *β*-diketiminate thiolate complexes, such as $[L^{tBu}Ni(SPh)]$ and $[L^{tBu}Ni(SEt)]$.[30,31]

Subsequent reduction of **1** and **2** with 2 equiv of KC_8, in cold (-25 °C) Et_2O, in the presence of 2 equiv of 18-crown-6, results in the formation of [K(18-crown-6)][$L^RNi(S)$] (**3**, R = Me; **4**, R = ^tBu). Complex **3** can be isolated as dark green blocks from hexanes/C_6H_6 in 66% yield, while complex **4** can be isolated as dark brown plates from toluene/isooctane in 88% yield (Scheme 1). Similarly, use of 2,2,2-cryptand in place of 18-crown-6 affords [K(2,2,2-cryptand)][$L^{tBu}Ni(S)$] (**5**), which can be isolated as brown needles in 89% yield after crystallization from hexanes (Scheme 1). The syntheses of **3**, **4**, and **5** also produce one equiv of $[K(L)][CPh_3]$ (L = 18-crown-6, 2,2,2-cryptand), which precipitates from the reaction mixtures as a bright red solid that can be separated from the Ni-containing products via filtration (Scheme 1). Interestingly, C-S bond cleavage has been observed previously in a Ni tritylthiolate complex.[32] For example, Riordan and co-workers reported the formation of $[\{PhB(CH_2S^tBu)_3Ni\}_2(\mu_2\text{-}\eta^2,\eta^2\text{-}S_2)$ and $\cdot CPh_3$ upon thermal decomposition of $[\{PhB(CH_2S^tBu)_3\}Ni(SCPh_3)]$, however, there is no evidence for the generation of a terminal sulfide in this reaction.

---

[*] N. J. Hartmann, Dr. G. Wu, Prof. Dr. T. W. Hayton
Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106
E-mail: hayton@chem.ucsb.edu

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



Scheme 1. Syntheses of complexes **1**-**5**.

The formulations of complexes **3**, **4**, and **5** were confirmed through elemental analysis, ^{1}H NMR spectroscopy, and X-ray crystallography. The solid-state structures of **4** and **5** are shown in Figure 1, while selected metrical parameters can be found in Table 1. Complexes **3**, **4** and **5** feature identical coordination environments about their Ni centers. In the solid state, each exhibits a planar (Σ(L-Ni-L) ~ 360°), Y-shaped geometry. The Ni-S bond lengths in **3**-**5** range from 2.0635(6)-2.0843(1) Å. All three complexes feature long S-K interactions,[28,33] which range from 3.094(2)-3.3795(1) Å. Not surprisingly, complex **5**, which features the strongest K^{+} chelator (2,2,2-cryptand), exhibits the longest S-K interaction. Interestingly, the Ni-S-K angles vary widely, from 153.73(3)° (for **3**) to 177.9(1)° (for **4**), a disparity we ascribe to crystal packing. Also of note, complex **4** exists as a dimer in the solid state; its monomer units are connected via bridging interaction between the [K(18-crown-6)]$^{+}$ cations (Figure 1). Finally, the Ni-N distances in **3**-**5** are typical of those found in other three coordinate Ni^{II} β-diketiminate complexes.[29-31,34]

The Ni-S bond lengths in complexes **3**, **4**, and **5** are amongst the shortest known, and are intermediate between the additive covalent radii projected for nickel-sulfur single (2.13 Å) and double bonds (1.95 Å).[23,24,35] For comparison, [{L^{tBu}Ni}$_2$(μ-S)],[30] [{(IPr)Ni}$_2$(μ-S)$_2$] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[36] and [(PhB{CH$_2$S^{t}Bu}$_3$)Ni]$_2$(μ-S),[32] possess comparable Ni-S bond lengths of 2.0651(7), 2.0972(6), and 2.0714(4) Å, respectively, despite each possessing a bridging S^{2-} ligand. Overall, this suggests similar magnitudes of π-bonding in both classes of materials.

Table 1. Selected Bond Lengths and Angles for the Nickel(II) Sulfide Complexes **3**, **4**, and **5**.

bond (Å) / angle (°)	3	4	5
Ni1-S1	2.0635(6)	2.0643(2)	2.0843(1)
S1-K1	3.1212(7)	3.094(1)	3.3795(1)
Ni-N (av.)	1.94	1.93	1.93
Ni1-S1-K1	153.74(3)	177.95(8)	170.08(5)

The ^{1}H NMR spectra of complexes **3**-**5** in C$_6$D$_6$ are typical of those observed for other three coordinate, high spin Ni^{II} β-diketiminate complexes.[29,34] Notably, the resonances assignable to the [K(18-crown-6)]$^{+}$ cations are broad and shifted to 1.18 and 0.28 ppm for **3** and **4**, respectively. The 2,2,2,-cryptand resonances for **5** are similarly broadened and shifted. These data suggest that the [K(L)]$^{+}$ cations form a contact pair with the [L^{R}Ni(S)]$^{-}$ anions in solution. In the solid state, complexes **3** and **4** exhibit effective magnetic moments of 2.80 B.M. at 300 K (D = 91 cm^{-1}) and 2.98 B.M. at 300 K (D = 94 cm^{-1}), respectively (Figures S22, S23). This behavior is consistent with that anticipated for a Y-shaped Ni^{II} complex with an S = 1 ground state.[37] Overall, the solid state molecular structures and magnetic properties of **3**-**5** confirm our Ni^{II} oxidation state assignments, and exclude the possibility that the sulfur atom is protonated, as this would require nickel to be in the +1 oxidation state. Intriguingly, the related Ni^{II} imido, carbene, and phosphinidene complexes, e.g., [(dtbpe)Ni(E)], are diamagnetic.[9,12,13] This change in spin state may reflect differing amounts of π-bonding between the two classes of molecules.

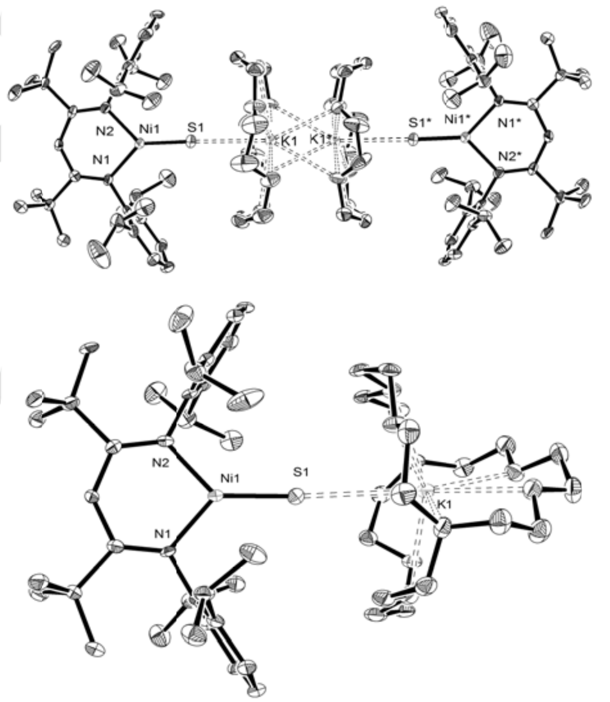
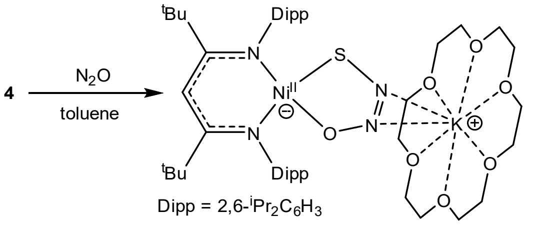


Figure 1. ORTEP drawings of [K(18-crown-6)][L^{tBu}Ni(S)] (**4**·C$_8$H$_{18}$) (top) and [K(2,2,2-cryptand)][L^{tBu}Ni(S)] (**5**) (bottom) shown with 50% thermal ellipsoids. Hydrogen atoms and C$_8$H$_{18}$ solvate molecule have been omitted for clarity.

The combined characterization data for complexes **3**-**5** reveal that the S-K interaction is conserved in both solution and the solid state. However, preliminary reactivity data suggest that the S-K interaction is quite labile, permitting these complexes to behave as “masked” terminal sulfides.[38] For example, exposure of complex **4** to an atmosphere of nitrous oxide (N$_2$O) results in a rapid color change from dark brown to yellow. Isolation of the resulting product via crystallization from toluene/isooctane provides [K(18-crown-6)][L^{tBu}Ni(SN=NO)] (**6**) as an orange crystalline solid in 62% yield (eq 1). Complex **6** crystallizes in the triclinic space group *P-1*, and its solid state molecular structure is shown in Figure 2. Complex **6** features an unprecedented κ^2-thiohyponitrite ($[SN{=}NO]^{2-}$) ligand, formed by [3 + 2] cycloaddition of N_2O across the Ni-S bond. The S-N and O-N distances in the $[SN{=}NO]^{2-}$ moiety are 1.787(6) Å and 1.308(1) Å, respectively, and are suggestive of single bonds, while the N-N bond length of 1.154(9) Å is indicative of a double bond. These parameters are consistent with the presence of a dianionic hyponitrite moiety, which, in combination with the diamagnetism of **6**, as revealed by its ^1H NMR spectrum (see SI), is consistent with the anticipated Ni^{II} oxidation state assignment.



6

(1)

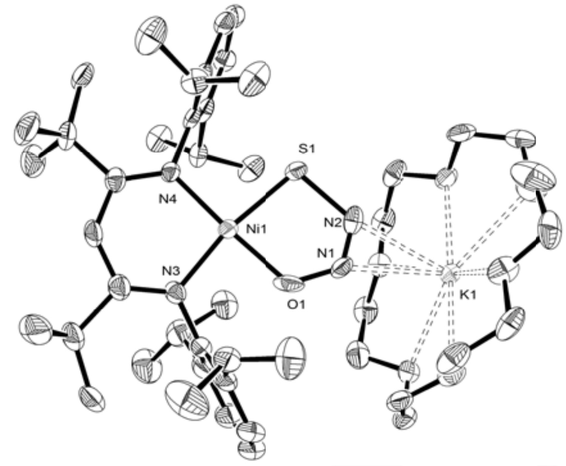


Figure 2. ORTEP drawing of [K(18-crown-6)][L^{tBu}Ni(κ^2-SN=NO)] ($\mathbf{6}\cdot1.5C_7H_8\cdot0.5C_8H_{18}$) shown with 50% thermal ellipsoids. Hydrogen atoms and C_7H_8 and C_8H_{18} solvate molecules have been omitted for clarity.

Complex **6** is a rare example of a structurally characterized transition metal complex containing activated N_2O and features the first example of a thiohyponitrite ($[\kappa^2\text{-}SN{=}NO]^{2-}$) ligand. Its formation is reminiscent of the Frustrated Lewis Pair (FLP) systems, $^tBu_3P/B(C_6F_5)_3$ and $[\{(C_6H_4)_2(O)CMe_2\}(PMes_2)(B(C_6F_5)_2)]$, which react with N_2O to form $[^tBu_3P(N{=}NO)B(C_6F_5)_3]$[39] and $[\{(C_6H_4)_2(O)CMe_2\}(PMes_2)(N{=}NO)(B(C_6F_5)_2)]$[40] respectively, or the reaction of N_2O with Na_2O, which results in formation of *trans*-$[Na_2N_2O_2]$.[41,42] Also relevant is the reaction of IPr with N_2O to form IPr-N_2O.[43] These results support the conclusion that the $[SN{=}NO]^{2-}$ ligand is formed by nucleophilic attack of N_2O by the sulfide ligand in **4**.[39,43,44]

In summary, cleavage of the C-S bond in [L^RNi(SCPh$_3$)] by reductive deprotection allows access to a family of "masked" terminal Ni^{II} sulfides, namely [K(L)][(L^R)Ni(S)]. The Ni-S distances in this class of materials are amongst the shortest observed, suggesting the presence of partial multiple bond character. [K(18-crown-6)][(L^{tBu})Ni(S)] reacts with N_2O to form a novel thio-hyponitrite complex, [K(18-crown-6)][L^{tBu}Ni(SN=NO)], confirming the lability of the S-K interaction. Going forward, we will continue to explore the small molecule reactivity of this class of complexes. In addition, we will target the synthesis of their oxygen congeners.

Acknowledgements

We thank the National Science Foundation (CHE 1361654) for financial support of this work. This research made use of the SQUID Magnetometer of the Materials Research Laboratory, an NSF MRSEC (DMR 1121053), and the 400 MHz NMR Spectrometer of the Chemistry Department, an NIH SIG (1S10OD012077-01A1).

Keywords: Nickel • Nitrogen Oxides • Protecting Group • Sulfide

[1] J. F. Berry, *Comments Inorg. Chem.* **2009**, *30*, 28.
[2] K. Ray, F. Heims, F. F. Pfaff, *Eur. J Inorg. Chem.* **2013**, 3784.
[3] J. Winkler, H. Gray, *Struct. Bond.* **2012**, *142*, 17.
[4] R. S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates, M. B. Hursthouse, *Polyhedron* **1993**, *12*, 2009.
[5] E. Poverenov, I. Efremenko, A. I. Frenkel, Y. Ben-David, L. J. W. Shimon, G. Leitus, L. Konstantinovski, J. M. L. Martin, D. Milstein, *Nature* **2008**, *455*, 1093.
[6] J. Schöffel, A. Y. Rogachev, S. DeBeer George, P. Burger, *Angew. Chem. Int. Ed.* **2009**, *48*, 4734; *Angew. Chem.* **2009**, *121*, 4828.
[7] M. G. Scheibel, B. Askevold, F. W. Heinemann, E. J. Reijerse, B. de Bruin, S. Schneider, *Nat. Chem.* **2012**, *4*, 552.
[8] X. Dai, P. Kapoor, T. H. Warren, *J. Am. Chem. Soc.* **2004**, *126*, 4798.
[9] D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2001**, *123*, 4623.
[10] C. A. Laskowski, A. J. M. Miller, G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2011**, *133*, 771.
[11] Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem. Int. Ed.* **2008**, *47*, 9961; *Angew. Chem.* **2008**, *120*, 10109.
[12] D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2002**, *124*, 9976.
[13] R. Melenkivitz, D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2002**, *124*, 3846.
[14] D. M. Jenkins, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2002**, *124*, 11238.
[15] D. T. Shay, G. P. A. Yap, L. N. Zakharov, A. L. Rheingold, K. H. Theopold, *Angew. Chem. Int. Ed.* **2006**, *45*, 7870; *Angew. Chem.* **2006**, *117*, 1532.
[16] C. Jones, C. Schulten, R. P. Rose, A. Stasch, S. Aldridge, W. D. Woodul, K. S. Murray, B. Moubaraki, M. Brynda, G. La Macchia, L. Gagliardi, *Angew. Chem. Int. Ed.* **2009**, *48*, 7406; *Angew. Chem.* **2009**, *121*, 7542.
[17] E. R. King, G. T. Sazama, T. A. Betley, *J. Am. Chem. Soc.* **2012**, *134*, 17858.
[18] M. P. Mehn, S. D. Brown, D. M. Jenkins, J. C. Peters, L. Que, *Inorg. Chem.* **2006**, *45*, 7417.
[19] D. J. Mindiola, R. Waterman, V. M. Iluc, T. R. Cundari, G. L. Hillhouse, *Inorg. Chem.* **2014**, *53*, 13227.
[20] T. R. Cundari, J. O. C. Jimenez-Halla, G. R. Morello, S. Vaddadi, *J. Am. Chem. Soc.* **2008**, *130*, 13051.
[21] A. W. Pierpont, T. R. Cundari, *Inorg. Chem.* **2010**, *49*, 2038.
[22] V. M. Iluc, G. L. Hillhouse, *J. Am. Chem. Soc.* **2010**, *132*, 15148.
[23] V. M. Iluc, G. L. Hillhouse, *J. Am. Chem. Soc.* **2014**, *136*, 6479.

[24] V. M. Iluc, A. J. M. Miller, J. S. Anderson, M. J. Monreal, M. P. Mehn, G. L. Hillhouse, *J. Am. Chem. Soc.* **2011**, *133*, 13055.

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

[26] S. Yao, C. Milsmann, E. Bill, K. Wieghardt, M. Driess, *J. Am. Chem. Soc.* **2008**, *130*, 13536.

[27] D. A. Vicic, W. D. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 4070.

[28] D. E. Smiles, G. Wu, N. Kaltsoyannis, T. W. Hayton, *Chem. Sci.* **2015**, *6*, 3891.

[29] P. L. Holland, T. R. Cundari, L. L. Perez, N. A. Eckert, R. J. Lachicotte, *J. Am. Chem. Soc.* **2002**, *124*, 14416.

[30] P. Holze, B. Horn, C. Limberg, C. Matlachowski, S. Mebs, *Angew. Chem. Int. Ed.* **2014**, *53*, 2750; *Angew. Chem.* **2014**, *126*, 2788.

[31] B. Horn, C. Limberg, C. Herwig, B. Braun, *Inorg. Chem.* **2014**, *53*, 6867.

[32] J. Cho, K. M. Van Heuvelen, G. P. A. Yap, T. C. Brunold, C. G. Riordan, *Inorg. Chem.* **2008**, *47*, 3931.

[33] D. E. Smiles, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2014**, *136*, 96.

[34] N. A. Eckert, E. M. Bones, R. J. Lachicotte, P. L. Holland, *Inorg. Chem.* **2003**, *42*, 1720.

[35] P. Pyykkö, *J. Phys. Chem. A* **2015**, *119*, 2326.

[36] F. Olechnowicz, G. L. Hillhouse, R. F. Jordan, *Inorg. Chem.* **2015**, *54*, 2705.

[37] C. A. Laskowski, G. R. Morello, C. T. Saouma, T. R. Cundari, G. L. Hillhouse, *Chem. Sci.* **2013**, *4*, 170.

[38] D. J. Mindiola, *Angew. Chem. Int. Ed.* **2008**, *47*, 1557; *Angew. Chem.* **2008**, *120*, 1580.

[39] E. Otten, R. C. Neu, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 9918.

[40] Z. Mo, E. L. Kolychev, A. Rit, J. Campos, H. Niu, S. Aldridge, *J. Am. Chem. Soc.* **2015**, ASAP Article.

[41] C. Feldmann, M. Jansen, *Angew. Chem. Int. Ed.* **1996**, *35*, 1728; *Angew. Chem.* **1996**, *108*, 1807.

[42] A. M. Wright, T. W. Hayton, *Inorg. Chem.* **2015**. ASAP Article.

[43] A. G. Tskhovrebov, E. Solari, M. D. Wodrich, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2012**, *51*, 232; *Angew. Chem.* **2012**, *124*, 236.

[44] H. Yu, G. Jia, Z. Lin, *Organometallics* **2008**, *27*, 3825.

COMMUNICATION

Late metal sulfides: Reductive deprotection of β-diketiminate supported nickel tritylthiolates results in the formation of the first “masked” terminal nickel sulfide complexes. Surprisingly, **4** reacts with nitrous oxide (N_2O) via [3 + 2] cycloaddition across the Ni-S bond to form an unprecedented cis-thiohyponitrite complex (**6**).

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

Page No. – Page No.

Synthesis of a “Masked” Terminal Nickel(II) Sulfide via Reductive Deprotection and its Reaction with Nitrous Oxide