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Reductive Cleavage of *O*-, *S*-, and *N*-Organonitroso Compounds by Nickel(I) β-Diketiminates

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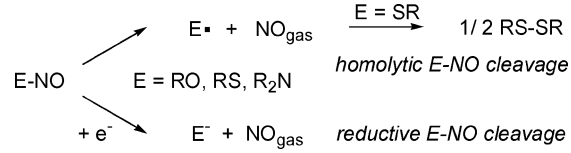
An electron-rich nickel(I) β-diketiminate cleaves the E−NO bond of *O*-, *S*-, and *N*-organonitroso species to give the nickel nitrosyl [Me$_3$NN]NiNO along with dimeric nickel(II) alkoxide or thiolate complexes {[Me$_3$NN]Ni}$_2$(μ-E)$_2$ or the mononuclear nickel(II) amide [Me$_3$NN]NiNPh$_2$. This diamagnetic three-coordinate amide exhibits temperature-dependent NMR spectra due to a low-lying triplet state.

The biochemistry of organic nitroso compounds (E−NO, E = RS, RO, R$_2$N, R) is connected to that of nitric oxide. These organic derivatives can either serve as sources of NO in vivo or produce effects similar to those of NO such as vasodilation. In contrast to free NO, these organic derivatives do not readily react with dioxygen.

Stamler and others recognized *S*-nitrosothiols (RSNOs) in the early 1990s to serve as potent sources of NO in vivo.[1] In contrast to *O*- and *N*-nitroso derivatives, *S*-nitrosothiols can thermally expel NO with concomitant formation of the corresponding disulfide (Scheme 1) because of the relative weakness of the RS−NO bond (31−32 kcal/mol)[2] and the strength of the RS−SR bond (65−66 kcal/mol).[3] This leads to relatively short lifetimes for RSNOs, although they circulate at ca. 0.2 μM in human plasma.[4]

Organic nitrites (RONOs) and *N*-nitrosamines (R$_2$NNOs) are much more thermally stable than *S*-nitrosothiols and typically require a reducing equivalent or photolysis[5] to release NO (Scheme 1). This reflects their higher E−NO homolytic dissociation energies (e.g., ^{t}BuO−NO = 40.9(8) kcal/mol[6] and Ph$_2$N−NO = 87.7 kcal/mol[7]). Because release of NO from many organonitroso compounds requires a reducing equivalent, it suggests a role for metalloenzymes in their metabolism. Each of these three classes of organonitroso substances is known to interact with heme-containing biomolecules,[8−10] and copper ions are implicated in the catalytic decomposition of *S*-nitrosothiols.[11]

Scheme 1. NO Formation from *O*-, *S*-, and *N*-Organonitroso Compounds



While *N*-nitroso compounds typically form intact E−NO adducts with metal complexes, *O*-nitroso and *S*-nitroso compounds commonly undergo E−NO bond cleavage, serving as nitrosating agents in metal−nitrosyl synthesis.[8] For instance, metalloporphyrin adducts of *N*-nitrosamines (porph)M(ONNR$_2$) (M = Fe,[12] Ru,[13] Os[14]) are known, while RONOs and RSNOs react to give a net trans addition to form *trans*-(porph)M(NO)(E) (E = OR or SR) species.[15] Mechanistic studies of NO transfer from the stable *S*-nitrosothiol Ph$_3$CSNO to a cobalt(II) porphyrin suggest that Co−NO bond formation proceeds via concerted homolytic S−NO bond cleavage.[10] In the case of nickel, polymeric [(RS)Ni(NO)]$_x$ species have been obtained upon the reaction of Ni(CO)$_4$ with RSNOs.[16]

Employing the β-diketiminate framework, we have found that related *C*-nitroso compounds such as 3,5-dimethylnitrosoben-

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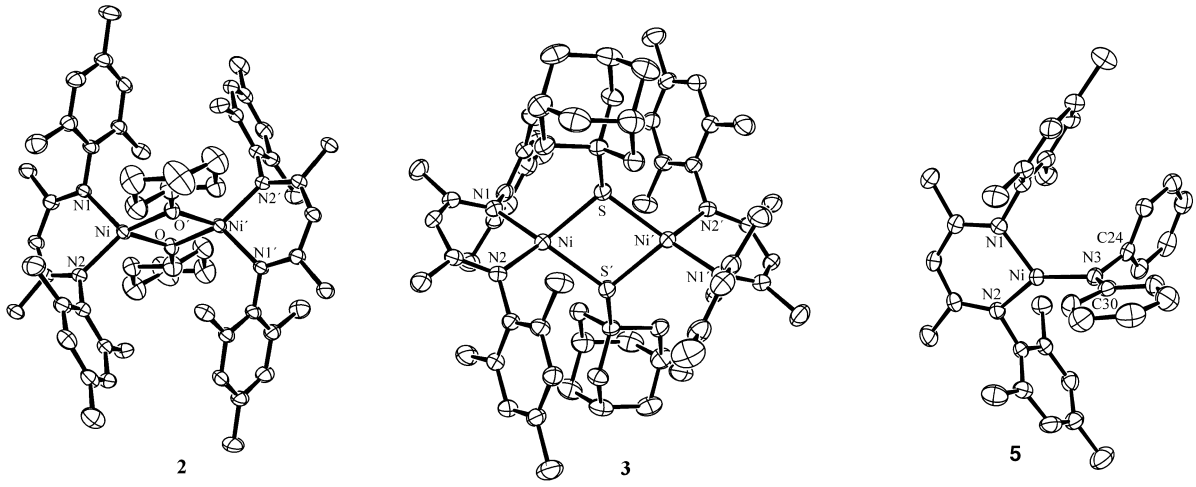
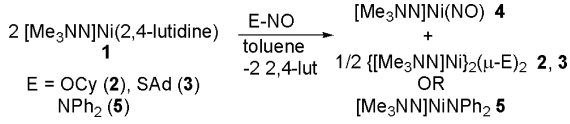


Figure 1. X-ray structures of β-diketiminato Ni^{II} complexes **2**, **3**, and **5** (only one unique molecule of $\{[Me_2NN]Ni\}_2(\mu\text{-}OC_y)_2$ (**2**) is shown).

zene react with 2 equiv of the d^8 $[Me_2NN]Co^{I}(\eta^6\text{-toluene})$ to undergo a four-electron reductive cleavage of the ArN=O bond to give $\{[Me_2NN]Co^{III}\}_2(\mu\text{-NAr})(\mu\text{-O})$.[17] Because the addition of NO_{gas} to related d^9 β-diketiminato Ni^{I} complexes results in the formation of stable [β-diketiminato]Ni(NO) species,[18] we felt that the reducing ability of the β-diketiminato Ni^{I} fragment coupled with its low coordination number could result in clean one-electron reactions with organonitroso compounds.

The careful addition of 1.0 equiv of CyONO or AdSNO to 2.0 equiv of $[Me_3NN]Ni$(2,4-lutidine) (**1**) in toluene at room temperature results in the formation of green solutions. Green crystals also immediately precipitate from the solution with CyONO, whereas purple crystals form after standing at room temperature overnight with AdSNO. X-ray characterization of each solid substance identifies them as $\{[Me_3NN]Ni\}_2(\mu\text{-}OCy)_2$ (**2**; 83% yield) and $\{[Me_3NN]Ni\}_2(\mu\text{-}SAd)_2$ (**3**; 88% yield), respectively (Scheme 2). When these reactions are performed in benzene-d_6, ^{1}H NMR analysis shows that $[Me_3NN]Ni(NO)$[18] (**4**) is formed in ~90% yield based on integration of its characteristic β-diketiminato backbone C−H resonance at δ 4.40 ppm against an internal standard.

Scheme 2. Reaction of 2 equiv of **1** with E–NO



Despite the steric bulk of the cyclohexyl alkoxide and adamantyl thiolate ligands, the X-ray structures of **2** and **3** consist of $[Me_3NN]NiE$ (E = OCy, SAd) dimers related by inversion symmetry (Figure 1). The asymmetric unit in the X-ray structure of **2** consists of two unique monomeric $[Me_3NN]NiOCy$ units. Both **2** and **3** show pseudotetrahedral coordination at nickel (twist angles between N−Ni−N and E−Ni−E planes: 81.1° and 83.0° for **2** and 70.7° for **3**) but have distinct Ni···Ni separations of 3.050(1) and 3.072(1) Å (for **2**) and 3.559(1) Å (for **3**). This is partially a result of the considerably shorter Ni−O bond distances spanning 1.955(2)−1.994(2) Å in **2** relative to the longer Ni−S distances of 2.318(1) and 2.303(8) Å in **3**.

In contrast to reactions with CyONO and AdSNO, which produce very insoluble dimeric products, the reaction between 1.0 equiv of Ph_2NNO and 2.0 equiv of **1** in benzene-d_6 results in a deep-blue-violet, *homogeneous* solution. We anticipated that $[Me_3NN]NiNPh_2$ (**5**) would form along with the nickel nitrosyl **4** (Scheme 2). ^{1}H NMR analysis shows **4** in >90% yield along with broad resonances for 2,4-lutidine. Attempts at crystallization failed to produce X-ray-quality crystals of any new product.

The nickel(II) amide **5** can be synthesized independently by the addition of $LiNPh_2$ to $[Me_3NN]NiI$(2,4-lutidine) (prepared from the addition of NiI_2 and 2,4-lutidine to $[Me_3NN]Tl$) in THF. Crystallization of the product from pentane provided the nickel amide **5** as deep-blue crystals in 59% yield. The X-ray structure of three-coordinate **5** exhibits short $Ni-N_{amido}$ [1.823(1) Å] and $Ni-N_{\beta\text{-dik}}$ [1.826(1) and 1.833(3) Å] distances. The N_{amido} atom is planar [sum of angles about N = 358.1(1)°] with one of the two *N*-aryl rings coplanar with the other twisted out of the Ni−N−C plane by 65.9°.

Following the addition of Ph_2NNO to **1** by UV−vis spectroscopy demonstrates that **5** (λ_{max} = 375 nm, ε = 6770 M^{-1} cm^{-1}; λ = 598 nm, ε = 2210 M^{-1} cm^{-1}) is formed in the presence of 2,4-lutidine (Figure S1 in the Supporting Information and Scheme 2). In addition, **4** is observed at λ_{max} = 445 nm (ε = 2000 M^{-1} cm^{-1}).

5 exhibits rich solution behavior. Despite the diamagnetic nature of benzene-d_6 solutions of **5** (μ_{eff} = 0.0 μ_B at room temperature by the Evans method),[19] ^{1}H NMR spectra of **5** prepared from $[Me_3NN]NiI$(2,4-lutidine) invariably show broad

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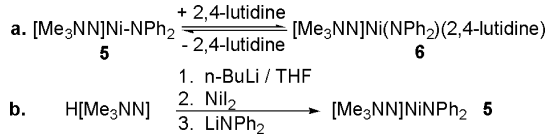
peaks devoid of coupling information (Figure S4 in the Supporting Information). We believe this to be due to trace amounts of 2,4-lutidine present in samples of **5** prepared from [Me_3NN]NiI(2,4-lutidine), which can lead to a rapid equilibrium between **5** and its 2,4-lutidine adduct [Me_3NN]Ni(NPh_2)(2,4-lutidine) (**6**; Scheme 3a).

Scheme 3. (a) Equilibrium between **5** and its 2,4-Lutidine Adduct **6** and (b) Independent Synthesis of **5** under 2,4-Lutidine-Free Conditions



To avoid the possibility of any exchange broadening in NMR spectra of **5** by 2,4-lutidine, we prepared **5** in a one-pot procedure in 53% yield under conditions excluding this Lewis base (Scheme 3b). The addition of incremental amounts of 2,4-lutidine up to 1 equiv per **5** results in increased broadening followed by the complete disappearance of all ^{1}H NMR resonances attributed to **5** (Figure S4 in the Supporting Information). Moreover, the effective magnetic moment of this solution increases to 1.3 μ_B (based on **5**) when a full equivalent of 2,4-lutidine is present. The decrease in the UV−vis band of **5** at $\lambda = 598$ nm in the presence of excess 2,4-lutidine (Figure S5 in the Supporting Information) also supports the formation of a Lewis base adduct. Presumably, this sterically encumbered adduct **6** would be tetrahedral with an expected spin-only magnetic moment of 2.8 μ_B (Scheme 3a).

Room temperature ^{1}H NMR spectra of lutidine-free **5** in toluene-d_8 show sharp signals expected for a diamagnetic species, but many appear at chemical shifts considerably different from those in other related diamagnetic complexes such as **4**. For instance, the backbone C−H resonance in **5** occurs at δ 1.83 ppm, whereas it appears at δ 4.40 ppm in **4**. Moreover, this and many other chemical shifts in **5** such as the *o*- and *p*-NPh_2 resonances are particularly temperature-sensitive (Figure 2). Upon cooling to −70 °C, the backbone C−H resonance migrates to δ 4.39 ppm and the *p*-NPh_2 signal moves from δ 5.67 (room temperature) to 7.03 ppm.

We attribute this behavior to contact shifts from a minute contribution of the high-spin state of [Me_3NN]NiNPh$_2$ (**5-HS**), which increases with increasing temperature. Both low-spin and high-spin three-coordinate β-diketiminato nickel-amides have been isolated such as [Me_3NN]NiN(Cp_2Co)Ad)[20] and LNiN-(TMS)$_2$,[21] respectively. While density functional theory studies on [Me_3NN]NiNPh$_2$ suggest that the low-spin form is favored by 8 kcal/mol, the β-diketiminato central backbone as well as the *o*- and *p*-NPh_2 carbon atoms bear significant electron density in the two "singly occupied" Kohn−Sham molecular orbitals of **5-HS** (Figure 2).

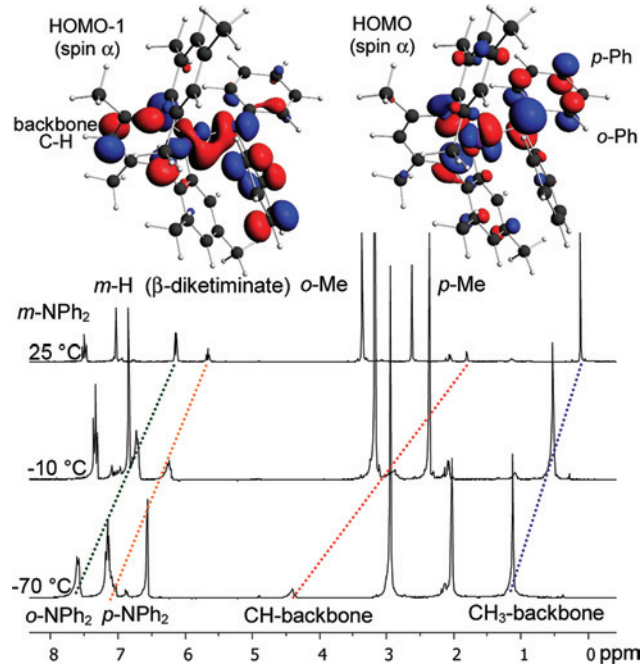


Figure 2. Variable-temperature ^{1}H NMR spectra of **5** (300 MHz, toluene-d_8) and contour plots for frontier Kohn−Sham molecular orbitals of **5-HS**.

In summary, the electron-rich nickel(I) β-diketiminate [Me_3-NN]Ni(2,4-lutidine) reductively cleaves the E−NO bond of *O*-, *S*-, and *N*-organonitroso compounds to give the nickel nitrosyl [Me_3NN]Ni(NO) and corresponding [Me_3NN]NiE species. This behavior contrasts with the reductive nitrosylation[22] observed by Ford involving $Cu^{II}OR$[23] and $Cu^{II}NR_2$[24] species, which react with NO to give the corresponding *O*- and *N*-organonitroso species along with Cu^I complexes. Studies are in progress to explore this reactivity at related β-diketiminato Cu^I complexes.

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Note Added after ASAP Publication. There were several text errors in the version published ASAP October 18, 2008; the corrected version published ASAP October 29, 2008.

Supporting Information Available: Experimental and calculational details (PDF) as well as X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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