

Three-Coordinate β -Diketiminato Nickel Nitrosyl Complexes from Nickel(I)–Lutidine and Nickel(II)–Alkyl Precursors

Simona C. Puiu and Timothy H. Warren*

Georgetown University, Department of Chemistry, Box 571227, Washington, D.C. 20057-1227

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Summary: The nickel(I) β -diketiminates $[\text{Me}_2\text{NN}]\text{Ni}(2,4\text{-lutidine})$ and $[\text{2,4,6-Me}_3\text{NN}]\text{Ni}(2,4\text{-lutidine})$ react with NO to form diamagnetic, three-coordinate Ni–NO complexes, and $[\text{Me}_2\text{NN}]\text{Ni}(\text{NO})$ undergoes insertion with a nitrosobenzene to form the N-aryl-N-nitrosohydroxylaminato species $[\text{Me}_2\text{NN}]\text{Ni}(\eta^2\text{-O}_2\text{N}_2\text{Ar})$. Addition of 2 equiv of NO to the Ni(II)–monoalkyl species $[\text{Me}_2\text{NN}]\text{Ni}(\text{Et})(2,4\text{-lutidine})$ at room temperature provides an alternate route to $[\text{Me}_2\text{NN}]\text{Ni}(\text{NO})$, while NO addition at -78°C favors the formation of $[\text{Me}_2\text{NN}]\text{Ni}(\eta^2\text{-O}_2\text{N}_2\text{-Et})$.

The chemistry of transition-metal nitrosyl complexes has received increased attention in recent years, due to the important role that nitric oxide plays as a signaling molecule in biological systems.¹ For instance, binding of NO to a heme iron is believed to activate the enzyme guanylate cyclase toward formation of cyclic GMP,² which regulates a variety of physiological functions, including neurotransmission, vasodilation, inhibition of platelet aggregation, and cell adhesion.³ NO is also involved in respiration rate regulation via its reversible binding to the heme a_3 active site of the respiratory enzyme cytochrome *c* oxidase.⁴ Many heme⁵ as well as non-heme^{1,2,6,7} nitrosyl complexes of Fe–Cu have been synthesized and provide insight into the active sites of such enzymes.

Transition-metal nitrosyl complexes with a coordination number of 3, however, are rare. Examples characterized by X-ray are the pyrazolate-bridged nickel nitrosyls $[(\text{pz})\text{Ni}(\text{NO})]_2$ and $[(\text{pz})_2\text{Ni}(\text{NO})]_2\text{Ni}$ ($\text{pz} = 3,5\text{-Me}_2\text{N}_2\text{C}_3\text{H}$)⁸ as well as the dinuclear iridium complex

$[\text{Ir}(\text{NO})(\text{PPh}_3)]_2\text{O}$.⁹ While most nickel nitrosyls are tetrahedral $\{\text{MNO}\}$ ¹⁰ complexes (following the classification of Enemark and Feltham)¹⁰ of the types $[\text{Ni}(\text{NO})\text{L}_3]^+$ ^{7,11,12} and $[\text{Ni}(\text{NO})\text{XL}_2]$ ^{12,13} ($\text{L} =$ neutral donor; $\text{X} =$ halogen or pseudo-halogen) that contain a linear nitrosyl ligand, the cyclopentadienyl complexes $\text{Cp}^*\text{Ni}(\text{NO})$ ^{14–16} are probably the best studied Ni–NO species. Both $\text{CpNi}(\text{NO})$ ¹⁴ and $\text{Cp}^*\text{Ni}(\text{NO})$ ¹⁶ have been shown to have a linear Ni–NO ground state, and a side-bound $\eta^2\text{-NO}$ photoexcited state has been characterized by X-ray crystallography for $\text{Cp}^*\text{Ni}(\text{NO})$.¹⁶ Our recent synthesis of the d⁹, three-coordinate β -diketiminato Ni(I) complexes $[\text{Me}_2\text{NN}]\text{Ni}(2,4\text{-lutidine})$ (**1**) and $[\text{2,4,6-Me}_3\text{NN}]\text{Ni}(2,4\text{-lutidine})$ (**2**) by dihydrogen reduction¹⁷ of the corresponding Ni(II)–ethyl complexes $[\text{Me}_2\text{NN}]\text{Ni}(\text{Et})(2,4\text{-lutidine})$ ¹⁸ (**3**) and $[\text{2,4,6-Me}_3\text{NN}]\text{Ni}(\text{Et})(2,4\text{-lutidine})$ ¹⁷ (**4**) sparked our interest to prepare related nickel nitrosyl complexes.¹⁹ For instance, addition of NO to the Ni(I) dimer $\{(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{PBu}_2)\text{Ni}(\mu\text{-Cl})\}_2$ results in the mononuclear $(\text{Bu}_2\text{PCH}_2\text{CH}_2\text{PBu}_2)\text{Ni}(\text{NO})\text{-Cl}$.^{13b}

Addition of NO gas (1.1 equiv) to the Ni(I) β -diketiminates **1** and **2** in ether provides $[\text{Me}_2\text{NN}]\text{Ni}(\text{NO})$ (**5**) and $[\text{2,4,6-Me}_3\text{NN}]\text{Ni}(\text{NO})$ (**6**), which may be isolated as air-stable, green crystals from pentane in 65–75% yield (Scheme 1). The X-ray structure of **6** (Figure 1) contains

* To whom correspondence should be addressed. E-mail: thw@georgetown.edu.

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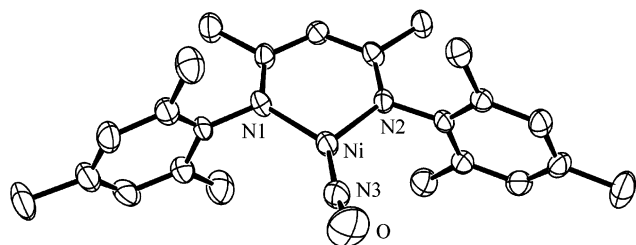
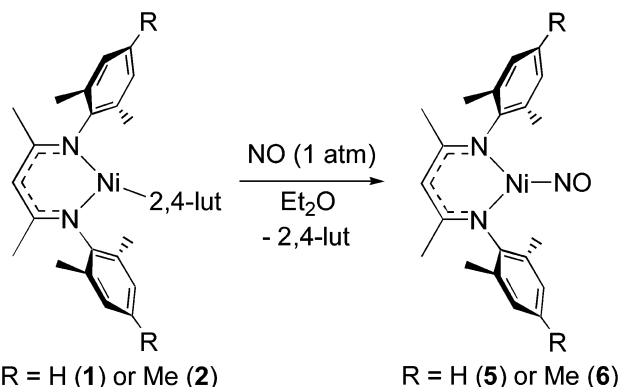


Figure 1. ORTEP diagram of one of the two independent molecules of $[2,4,6\text{-Me}_3\text{NN}]\text{Ni}(\text{NO})$ found in the solid-state structure of **6**. Selected bond distances (Å) and angles (deg): $\text{Ni}(1)\text{--N}(1) = 1.883(2)$, $\text{Ni}(1)\text{--N}(2) = 1.885(2)$, $\text{Ni}(1)\text{--N}(3) = 1.610(3)$, $\text{N}(3)\text{--O}(1) = 1.170(3)$; $\text{N}(1)\text{--Ni}(1)\text{--N}(2) = 95.79(10)$, $\text{Ni}(1)\text{--N}(3)\text{--O} = 171.0(3)$.

Scheme 1. Synthesis of Ni–NO Complexes



two independent molecules in the asymmetric unit with nearly identical metrical parameters and reveals trigonal-planar coordination at nickel as well as a linear nitrosyl ligand ($\text{Ni1--N3--O1} = 171.0(3)^\circ$ and $\text{Ni2--N6--O2} = 174.3(3)^\circ$). The Ni–NO distances ($\text{Ni1--N3} = 1.610(3)$ Å and $\text{Ni2--N6} = 1.616(3)$ Å) are similar to that found in the pyrazolate-bridged nickel complex $[(\text{pz})\text{Ni}(\text{NO})_2]$ (1.616(4) Å),⁸ and **6** possesses an N–O bond ($\text{N3--O1} = 1.170(3)$ Å and $\text{N6--O2} = 1.161(3)$ Å) slightly longer than that of free NO (1.154 Å).²⁰ Consistent with a lower coordination number at nickel, the β -diketiminate Ni–N distances (1.883(2)–1.885(2) Å) in **6** are shorter as compared to those in $[\text{Me}_2\text{NN}]\text{Ni}(\text{Et})(2,4\text{-lutidine})$ (**1**; 1.915(3) and 1.987(3) Å).¹⁸ ^1H NMR spectra of **5** and **6** in benzene- d_6 show significantly upfield shifted β -diketiminate CH resonances (δ 4.351 and 4.398 ppm, respectively) as compared to the corresponding Ni(II)–ethyl complexes **3** and **4** (δ 5.03 and 4.99 ppm, respectively, in toluene- d_8), suggestive of a more electron-rich metal center in the nitrosyl derivatives. Solid-state IR spectra of **5** and **6** display sharp bands at 1792 and 1785 cm^{-1} , respectively, which are at the lower end of the range of ν_{NO} values (1817–1779 cm^{-1}) found in the family of neutral pyrazolato nickel nitrosyls $[(\text{pz})\text{Ni}(\text{NO})_2]$ and $[(\text{pz})_2\text{Ni}(\text{NO})_2]\text{Ni}$.⁸ The somewhat lower value of ν_{NO} for **6** as compared to **5** may be attributed to a slightly more electron-donating character of the $[2,4,6\text{-Me}_3\text{NN}]^-$ ligand as compared to $[\text{Me}_2\text{NN}]^-$.

Since the Ni(I)–lutidine precursors **1** and **2** employed in the synthesis of **5** and **6** are prepared by H_2 reduction of the corresponding Ni(II)–ethyl species **3** and **4**,¹⁷ we explored the synthesis of a nitrosyl derivative directly

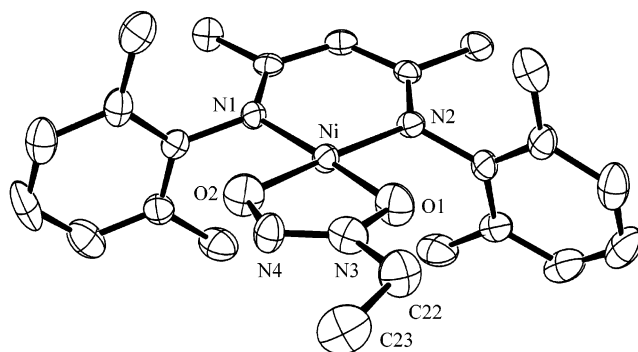
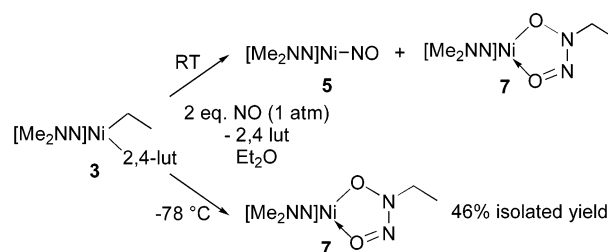


Figure 2. ORTEP diagram of the solid-state structure of **7**. Selected bond distances (Å) and angles (deg): $\text{Ni--N}(1) = 1.866(3)$, $\text{Ni--N}(2) = 1.873(3)$, $\text{Ni--O}(1) = 1.863(3)$, $\text{Ni--O}(2) = 1.867(3)$, $\text{O}(1)\text{--N}(3) = 1.340(5)$, $\text{O}(2)\text{--N}(4) = 1.320(5)$, $\text{N}(3)\text{--N}(4) = 1.237(5)$; $\text{N}(1)\text{--Ni--N}(2) = 94.43(15)$, $\text{O}(1)\text{--Ni--O}(2) = 82.00(14)$.

Scheme 2. Reaction of 3 with 2 Equiv of NO



from a monoalkyl complex. Treating an ether solution of $[\text{Me}_2\text{NN}]\text{Ni}(\text{Et})(2,4\text{-lutidine})$ (**3**) with 2 equiv of NO (1 atm) at room temperature results in the formation of both **5** and the N -alkyl- N -nitrosohydroxylaminato complex $[\text{Me}_2\text{NN}]\text{Ni}(\eta^2\text{-O}_2\text{N}_2\text{Et})$ (**7**) in a 0.6:0.4 ratio (determined by ^1H NMR analysis), from which a sample of **5** (contaminated with ca. 10% of **7**) could be isolated in 40% yield after recrystallization (Scheme 2). Performing the reaction at -78°C , however, allows for the selective formation of **7** and its isolation as light green crystals from pentane in 46% yield (Scheme 2). Reaction of $[2,4,6\text{-Me}_3\text{NN}]\text{Ni}(\text{Et})(2,4\text{-lutidine})$ (**4**) with 2 equiv of NO at -78°C in ether similarly results in the isolation of $[2,4,6\text{-Me}_3\text{NN}]\text{Ni}(\eta^2\text{-O}_2\text{N}_2\text{Et})$ (**8**) in 57% yield. Such double NO insertion behavior is typical for early-transition-metal alkyl or aryl complexes such as $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})_2$, $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$, and WMe_6 , which react with NO to form $\text{Cp}_2\text{Zr}(\text{CH}_2\text{Ph})(\eta^2\text{-O}_2\text{N}_2\text{CH}_2\text{Ph})$,²¹ $\text{CpW}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta^2\text{-O}_2\text{N}_2\text{CH}_2\text{SiMe}_3)$,²² and $\text{WMe}_4(\eta^2\text{-O}_2\text{N}_2\text{Me})_2$,²³ respectively. The X-ray structure of **7** reveals a square-planar Ni(II) center chelated by the N -ethyl- N -nitrosohydroxylaminato ligand with nearly identical Ni–O bond distances of 1.863(3) and 1.867(3) Å (Figure 2). The long N–O distances (1.340(5) and 1.320(5) Å) and the short N(3)–N(4) distance (1.237(5) Å) indicate a high degree of delocalization along the $\eta^2\text{-O}_2\text{N}_2\text{Et}$ moiety, a common feature for N -organo- N -nitrosohydroxylaminato ligands.^{24–26}

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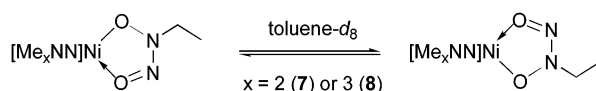
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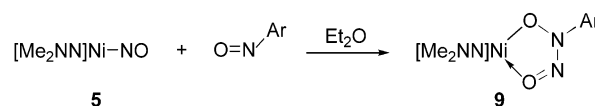
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Scheme 3. Rapid Interconversion between Conformers in 7 or 8


The most notable feature in room-temperature ^1H NMR spectra of **7** and **8** (300 MHz, benzene- d_6) is the presence of single resonances each for the β -diketiminato *N*-aryl and backbone methyl groups, which suggests that conformers of the *N*-ethyl-*N*-nitrosohydroxylaminato group rapidly interconvert within the coordination wedge of the $[\beta$ -diketiminato]Ni fragment (Scheme 3). Low-temperature ^1H NMR spectra of **7** at -75°C (300 MHz, toluene- d_8) also show sharp, single resonances for these methyl groups, indicating that the symmetrization is quite facile. While this process could take place via a tetrahedral $\eta^2\text{-O}_2\text{N}_2\text{Et}$ or a trigonal $\eta^1\text{-O}_2\text{N}_2\text{Et}$ intermediate, it is intramolecular. The ^1H NMR spectrum of a 1:1 mixture of **7** and **8** at room temperature in benzene- d_6 shows sharp, overlapping multiplets at δ 2.616 and 2.621 ppm as well as at δ 0.247 and 0.263 ppm, corresponding to the CH_2 and CH_3 resonances of the $[\text{O}_2\text{N}_2\text{Et}]^-$ anion in **7** and **8**, respectively.

In the reaction of NO with $[\text{Me}_2\text{NN}]\text{Ni}(\text{Et})(2,4\text{-lutidine})$ (**3**), 1 equiv of (bound) $\text{EtN}=\text{O}$ is likely produced either by direct insertion of NO into the Ni–ethyl bond^{28,29} or by reductive nitrosylation (reduction to Ni(I) by NO followed by insertion of NO^+ into the resulting Ni–alkyl bond).³⁰ We explored the reaction of $[\text{Me}_2\text{NN}]\text{Ni}(\text{NO})$ (**5**) with a nonvolatile organonitroso compound³¹ to obtain additional insight into the formation of the

Scheme 4. Reaction of 5 with $\text{ArN}=\text{O}$ (Ar = 3,5-(CH_3) $_2\text{C}_6\text{H}_3$)


N-ethyl-*N*-nitrosohydroxylaminato complexes **7** and **8**. Addition of the nitrosobenzene derivative $\text{ArN}=\text{O}$ (Ar = 3,5- $\text{Me}_2\text{C}_6\text{H}_3$) to a benzene solution of **5** results in the immediate formation of $[\text{Me}_2\text{NN}]\text{Ni}(\eta^2\text{-O}_2\text{N}_2\text{Ar})$ (**9**), which may be isolated as yellow crystals from pentane in ca. 70% yield (Scheme 4). The ^1H NMR spectrum of **9** at room temperature is similar in form to that of **7** and **8**, indicating a related, facile symmetrization process. Although diazeniumdiolates $[\text{O}_2\text{N}_2\text{X}]^-$ (X = R_2N , Ph; R = alkyl) serve as a source of NO under a wide variety of conditions²⁴ and have been employed as nitrosylating reagents in the synthesis of nitrosylmetalloporphyrins,^{25,32} reaction of **7** or **9** with Lewis acids²⁵ such as $\text{BF}_3\cdot\text{OEt}_2$ did not result in RNO loss to form **5**.

In summary, the addition of NO to both Ni(I)–lutidine and Ni(II)–alkyl β -diketiminato precursors results in the formation of three-coordinate Ni–NO complexes, which react with organonitroso compounds to give *N*-organo-*N*-nitrosohydroxylaminato species. Efforts are underway to extend this methodology to the synthesis of other low-coordinate metal nitrosyl complexes.

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Supporting Information Available: Text giving details on the syntheses of **5**–**9** with relevant analytical and spectroscopic data and CIF files giving crystallographic information for **6** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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