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

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Summary: The nickel(I) β-diketiminates [Me_2NN]Ni(2,4-lutidine) and [2,4,6-Me_3NN]Ni(2,4-lutidine) react with NO to form diamagnetic, three-coordinate Ni−NO complexes, and [Me_2NN]Ni(NO) undergoes insertion with a nitrosobenzene to form the N-aryl-N-nitrosohydroxylaminato species [Me_2NN]Ni(η^2-O_2N_2Ar). Addition of 2 equiv of NO to the Ni(II)−monoalkyl species [Me_2NN]Ni(Et)(2,4-lutidine) at room temperature provides an alternate route to [Me_2NN]Ni(NO), while NO addition at −78 °C favors the formation of [Me_2NN]Ni(η^2-O_2N_2-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 heme[5] 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 [(pz)Ni(NO)]$_2$ and [(pz)$_2$Ni(NO)]$_2$Ni (pz = 3,5-$Me_2N_2C_3H$)[8] as well as the dinuclear iridium complex [Ir(NO)(PPh_3)]$_2$O.[9] While most nickel nitrosyls are tetrahedral {MNO}[10] complexes (following the classification of Enemark and Feltham)[10] of the types [Ni(NO)L_3]$^+$ [7,11,12] and [Ni(NO)XL_2][12,13] (L = neutral donor; X = halogen or pseudo-halogen) that contain a linear nitrosyl ligand, the cylopentadienyl complexes Cp′Ni(NO)[14−16] are probably the best studied Ni−NO species. Both CpNi(NO)[14] and Cp*Ni(NO)[16] have been shown to have a linear Ni−NO ground state, and a side-bound η^2-NO photoexcited state has been characterized by X-ray crystallography for Cp*Ni(NO).[16] Our recent synthesis of the d^9, three-coordinate *β*-diketiminato Ni(I) complexes [Me_2NN]Ni(2,4-lutidine) (**1**) and [2,4,6-Me_3NN]Ni(2,4-lutidine) (**2**) by dihydrogen reduction[17] of the corresponding Ni(II)−ethyl complexes [Me_2NN]Ni(Et)(2,4-lutidine)[18] (**3**) and [2,4,6-Me_3NN]Ni(Et)(2,4-lutidine)[17] (**4**) sparked our interest to prepare related nickel nitrosyl complexes.[19] For instance, addition of NO to the Ni(I) dimer {($^tBu_2PCH_2CH_2PBu^t{}_2$)Ni(μ-Cl)}$_2$ results in the mononuclear ($^tBu_2PCH_2CH_2PBu^t{}_2$)Ni(NO)Cl.[13b]

Addition of NO gas (1.1 equiv) to the Ni(I) *β*-diketiminates **1** and **2** in ether provides [Me_2NN]Ni(NO) (**5**) and [2,4,6-Me_3NN]Ni(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

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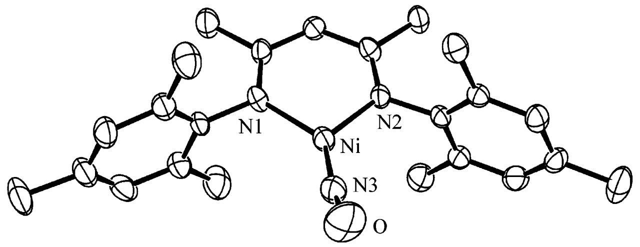
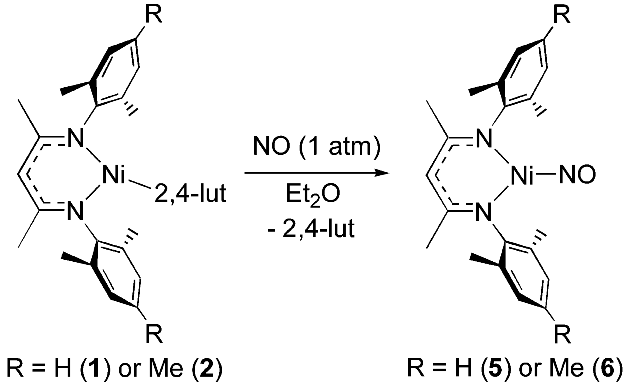


Figure 1. ORTEP diagram of one of the two independent molecules of $[2,4,6\text{-}Me_3NN]Ni(NO)$ found in the solid-state structure of **6**. Selected bond distances (Å) and angles (deg): Ni(1)−N(1) = 1.883(2), Ni(1)−N(2) = 1.885(2), Ni(1)−N(3) = 1.610(3), N(3)−O(1) = 1.170(3); N(1)−Ni(1)−N(2) = 95.79(10), Ni(1)−N(3)−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 (Ni1−N3−O1 = 171.0(3)° and Ni2−N6−O2 = 174.3(3)°). The Ni−NO distances (Ni1−N3 = 1.610(3) Å and Ni2−N6 = 1.616(3) Å) are similar to that found in the pyrazolate-bridged nickel complex $[(pz)Ni(NO)]_2$ (1.616(4) Å),[8] and **6** possesses an N−O bond (N3−O1 = 1.170(3) Å and 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 $[Me_2NN]Ni(Et)(2,4\text{-lutidine})$ (**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-diketiminato backbone-C*H* 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 $[(pz)Ni(NO)]_2$ and $[(pz)_2Ni(NO)]_2Ni$.[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 $[2,4,6\text{-}Me_3NN]^-$ ligand as compared to $[Me_2NN]^-$.

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 from a monoalkyl complex. Treating an ether solution of $[Me_2NN]Ni(Et)(2,4\text{-lutidine})$ (**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 $[Me_2NN]Ni(\eta^2\text{-}O_2N_2Et)$ (**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 $[2,4,6\text{-}Me_3NN]Ni(Et)(2,4\text{-lutidine})$ (**4**) with 2 equiv of NO at −78 °C in ether similarly results in the isolation of $[2,4,6\text{-}Me_3NN]Ni(\eta^2\text{-}O_2N_2Et)$ (**8**) in 57% yield. Such double NO insertion behavior is typical for early-transition-metal alkyl or aryl complexes such as $Cp_2Zr(CH_2Ph)_2$, $CpW(NO)(CH_2SiMe_3)_2$, and WMe_6, which react with NO to form $Cp_2Zr(CH_2Ph)(\eta^2\text{-}O_2N_2CH_2Ph)$,[21] $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}O_2N_2CH_2SiMe_3)$,[22] and $WMe_4(\eta^2\text{-}O_2N_2Me)_2$,[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 $\eta^2\text{-}O_2N_2Et$ moiety, a common feature for *N*-organo-*N*-nitrosohydroxylaminato ligands.[24−26]

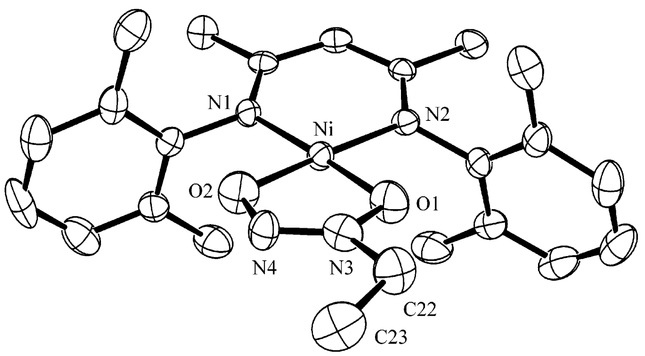
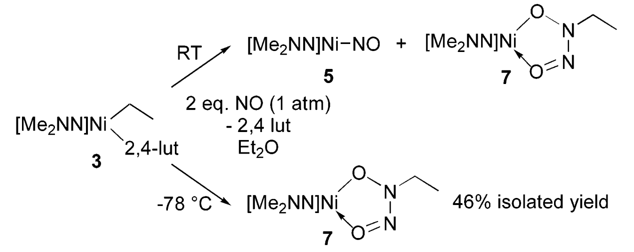


Figure 2. ORTEP diagram of the solid-state structure of **7**. Selected bond distances (Å) and angles (deg): Ni−N(1) = 1.866(3), Ni−N(2) = 1.873(3), Ni−O(1) = 1.863(3), Ni−O(2) = 1.867(3), O(1)−N(3) = 1.340(5), O(2)−N(4) = 1.320(5), N(3)−N(4) = 1.237(5); N(1)−Ni−N(2) = 94.43(15), O(1)−Ni−O(2) = 82.00(14).

Scheme 2. Reaction of 3 with 2 Equiv of NO



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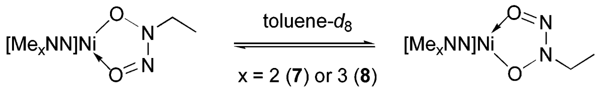
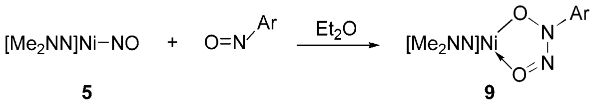
Scheme 3. Rapid Interconversion between Conformers in 7 or 8



The most notable feature in room-temperature ^{1}H 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 [β-diketiminato]Ni fragment (Scheme 3). Low-temperature ^{1}H 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[27] η^2-O_2N_2Et or a trigonal η^1-O_2N_2Et intermediate, it is intramolecular. The ^{1}H 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 $[O_2N_2Et]^-$ anion in **7** and **8**, respectively.

In the reaction of NO with [Me$_2$NN]Ni(Et)(2,4-lutidine) (**3**), 1 equiv of (bound) EtN═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 [Me$_2$NN]Ni(NO) (**5**) with a nonvolatile organonitroso compound[31] to obtain additional insight into the formation of the *N*-ethyl-*N*-nitrosohydroxylaminato complexes **7** and **8**. Addition of the nitrosobenzene derivative ArN═O (Ar = 3,5-Me$_2$C$_6$H$_3$) to a benzene solution of **5** results in the immediate formation of [Me$_2$NN]Ni(η^2-O$_2$N$_2$Ar) (**9**), which may be isolated as yellow crystals from pentane in ca. 70% yield (Scheme 4). The ^{1}H 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 $[O_2N_2X]^-$ (X = R$_2$N, Ph; R = alkyl) serve as a source of NO under a wide variety of conditions[24] and have been employed as nitrosylating reagents in the synthesis of nitrosylmetalloporphyrins,[25,32] reaction of **7** or **9** with Lewis acids[25] such as BF$_3$·OEt$_2$ did not result in RNO loss to form **5**.

Scheme 4. Reaction of 5 with ArN═O (Ar = 3,5-(CH$_3$)$_2$C$_6$H$_3$)



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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(28) CO inserts into the Ni−Et bond of **3** to give the corresponding Ni−acyl species [Me$_2$NN]Ni(C(O)Et)(2,4-lutidine): Wiencko, H. L.; Warren, T. H. Manuscript in preparation.

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