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A Terminal Ni(III)−Imide with Diverse Reactivity Pathways

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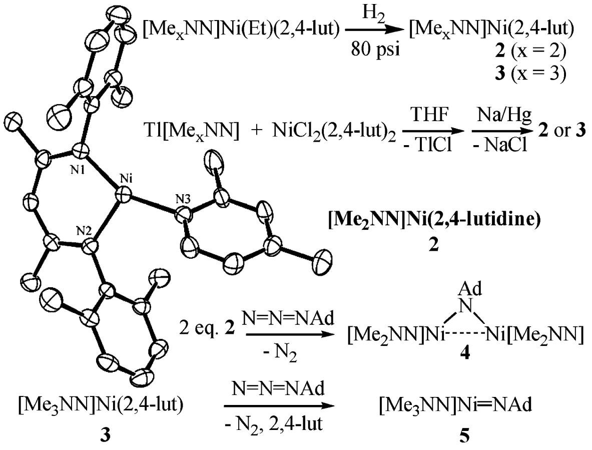
Terminal imido species of the later transition metals have been suggested as key intermediates in catalytic alkene aziridination.[1,2] While iridium and ruthenium imides, such as Cp*Ir≡N^{t}Bu[3] and (η^6-benzene)Ru═NAr[4] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), remained for some time as isolated examples of late metal terminal imides, the anticipated lower metal−ligand bond strengths of first row analogues identify them as attractive synthetic targets to explore the chemistry of the imido functionality. Hillhouse and Mindiola prepared (^{t}Bu$_2$PCH$_2$CH$_2$PBu$^t_2$)Ni═NAr by deprotonation of the corresponding cationic Ni(II)−anilide,[5] which undergoes facile imide group transfer to CO and benzyl isocyanide[6] as well as with ethylene under prolonged heating.[7] Peters,[8] Theopold,[9] and Meyer[10] have explored trigonal Co(I) and Fe(I) platforms with organoazides to give trivalent imido complexes. We have recently shown that the 18-electron Co(I) β-diketiminate [Me$_2$NN]Co(η^6-toluene) reacts with organoazides to give the doubly bridged imide {[Me$_2$NN]Co}$_2$(μ-NAr′)$_2$ (Ar′ = 3,5-Me$_2$C$_6$H$_3$) or a three-coordinate terminal species [Me$_2$NN]Co≡NAd (**1**) (Ad = 1-adamantyl).[11] Herein, we describe the synthesis of related three-coordinate d^9 Ni(I) adducts, which react with AdN$_3$ to form nickel−imido species, including a terminal Ni(III)−imide with diverse modes of reactivity.

Treatment of the square planar Ni(II)−alkyl [Me$_2$NN]Ni(CH$_2$CH$_3$)(2,4-lutidine)[12] with 80 psi H$_2$ in ether results in the rapid formation of the monovalent [Me$_2$NN]Ni(2,4-lutidine)[13] (**2**) that may be isolated as red crystals in 64% yield. More conveniently, addition of Tl[Me$_2$NN] to NiCl$_2$(2,4-lutidine)$_2$ in THF followed by reduction with 0.5% Na/Hg after filtration of initially formed TlCl provides **2** in 81% isolated yield. At room temperature and in the presence of excess lutidine, this complex exhibits a magnetic moment of 1.8 μ_B in benzene-d_6 (Evans method) consistent with the presence of one unpaired electron, and glass EPR spectra at 77 K in toluene indicate a rhombic environment (g_1 = 2.435, g_2 = 2.133, g_3 = 2.068). The X-ray structure of **2** (Scheme 1) shows it to be "bent" trigonal planar as the N1−Ni−N3 angle of 153.58(9)° is considerably more obtuse than the N2−Ni−N3 angle of 108.78(9)°, similar in structure to the d^{10} [Me$_2$NN]Cu(2,4-lutidine).[14]

Reaction of **2** with 1 or 0.5 equiv of N$_3$Ad results in the formation of the paramagnetic, singly bridged dinickel imide {[Me$_2$NN]Ni}$_2$(μ-NAd) (**4**), which may be isolated in 34% yield (Scheme 1). The X-ray structure of **4** (Figure 2) shows the [Me$_2$NN]Ni fragments to be roughly orthogonal (87.9° twist angle). This singly bridged species exhibits considerably shortened Ni−N(imido) bond distances (1.732(4) and 1.752(4) Å) as well as a contracted Ni−Ni distance (2.506(1) Å) relative to corresponding distances in the doubly bridged {[Me$_2$NN]Co}$_2$(μ-NAr′)$_2$.[11] The low solution magnetic moment of **4** (μ_{eff} = 0.95 μ_B in benzene-d_6 at RT) is corroborated by solid-state SQUID measurements which suggest the possibility of weak antiferromagnetic coupling.

Scheme 1. Synthesis and Reactivity of [Me$_x$NN]Ni(2,4-lutidine)



A slight peripheral steric modification to the β-diketiminate ligand allows the isolation of a terminal d^7 imide.[15] Reaction of N$_3$Ad with [Me$_3$NN]Ni(2,4-lutidine) (**3**) that possesses an additional methyl group in the 4-position of each *N*-aryl ring affords the three-coordinate [Me$_3$NN]Ni═NAd (**5**) in 52% yield (Scheme 1). The X-ray structure of **5** (Figure 2) is very similar to that of [Me$_2$NN]Co≡NAd (**1**) with a slightly longer Ni−N(imido) distance of 1.662(2) Å (1.624(4) Å in **1**)[11] and a Ni−N−C angle of 164.5(2)°. The glass EPR spectrum of **5** in toluene at 77 K indicates a rhombic environment (g_1 = 2.162, g_2 = 2.038, g_3 = 1.937). Significantly, the signal at g = 2.038 is a 1:1:1 triplet with A = 22 G, suggesting substantial involvement of the imido nitrogen (^{14}N; I = 1) in the singly occupied molecular orbital of this low-spin species. This orbital picture is corroborated by DFT calculations, which indicate significant spin density on the imido N atom (57%) as a result of the two-center, three-electron interaction involving the Ni d$_{xy}$ and imido N p$_x$ orbitals (Figure 1).[16]

Initial reactivity studies of the terminal imide **5** demonstrate complete imido group transfer to select electrophiles (Scheme 2). Reaction of **5** with CO and CNBu^t results in the rapid formation of AdNCO and AdNCNBu^t in 76 and 84% yields (GC). In the reaction with CO, the [Me$_3$NN]Ni fragment is trapped as the diamagnetic {[Me$_3$NN]Ni}$_2$(μ-CO)$_2$ (**6**) isolated in 85% yield. In light of this apparent nucleophilic behavior for **5**, we were surprised to see that complete group transfer to PMe$_3$ readily occurs to give Me$_3$P═NAd in 91% yield (^{31}P NMR).

A separate manifold of one-electron reactivity results from the radical character at the imido N atom. As cobaltocene is well-known to add to organic radicals R$^\bullet$ to give (η^4-C$_5$H$_5$R)Co^{I}Cp,[17] the reaction

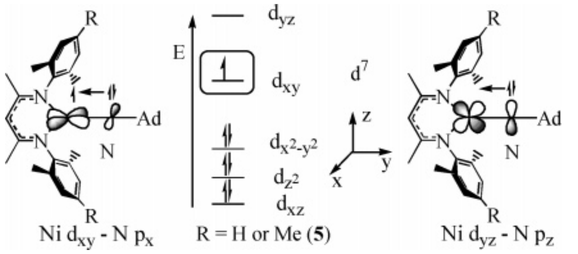


Figure 1. Orbital interactions in β-diketiminato terminal imides.

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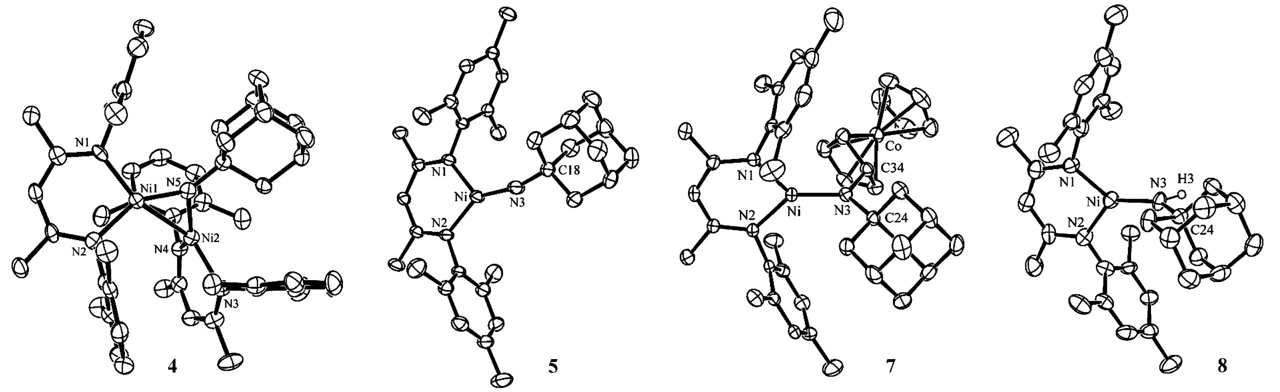
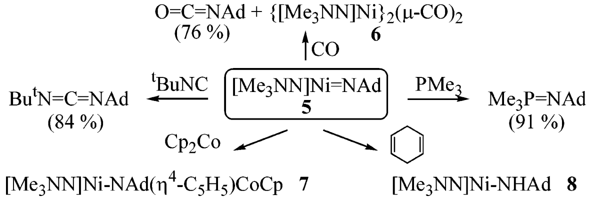


Figure 2. X-ray structures of $\{[Me_2NN]Ni\}_2(\mu\text{-NAd})$ (**4**), $[Me_3NN]Ni{=}NAd$ (**5**), $[Me_3NN]Ni{-}NAd(\eta^4\text{-}C_5H_5)CoCp$ (**7**), and $[Me_3NN]Ni{-}NHAd$ (**8**).

Scheme 2. Reactivity of $[Me_3NN]Ni{=}NAd$ (**5**)



of **5** with Cp_2Co affords the Ni(II)−amide $[Me_3NN]Ni{-}NAd(\eta^4\text{-}C_5H_5)CoCp$ (**7**) isolated in 65% yield. $[Me_3NN]Ni{=}NAd$ also rapidly reacts with H atom donors, such as 1,4-cyclohexadiene, to cleanly give the primary amide $[Me_3NN]Ni{-}NHAd$ (**8**) and benzene. Compared to **5**, X-ray structures of trigonal planar **7** and **8** show lengthened Ni−N distances of 1.812(3) and 1.742(4) Å as well as narrower Ni−N−Ad angles of 123.9(2) and 132.2(3)°, respectively. While **7** is diamagnetic, **8** possesses a mildly temperature-dependent solution and solid-state magnetic moment near 1.0 μ_B at RT. Such behavior contrasts with that of the high-spin Ni(II) β-diketiminates $[NN]Ni{-}NTMS_2$ reported by Power and Holland.[18]

Both **2** and **3** serve as synthons to the 13-electron β-diketiminato Ni(I) fragment $[Me_xNN]Ni$ that reacts with N_3Ad to give dinickel and terminal imido complexes **4** and **5**. The profound structural effect of a minor change in the β-diketiminate ligand is reminiscent of that observed in the related dicopper and monocopper carbenes $\{[Me_2NN]Cu\}_2(\mu\text{-CPh}_2)$ and $[Me_3NN]Cu{=}CPh_2$.[19] The terminal imide $[Me_3NN]Ni{=}NAd$ (**5**) displays reactivity with electrophiles, nucleophiles, and one-electron reagents. In the later regard, **5** may be considered a Ni(II)-stabilized imidyl ($RN^{\bullet -}$) radical anion, which complements the recent report of a tethered aminyl ($R_2N^{\bullet}$) radical coordinated to a d^8 Rh(I) center.[20]

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Supporting Information Available: Detailed experimental and DFT calculation procedures with spectroscopic and analytical data (PDF); crystallographic details for **2**−**5**, **7**, and **8** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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