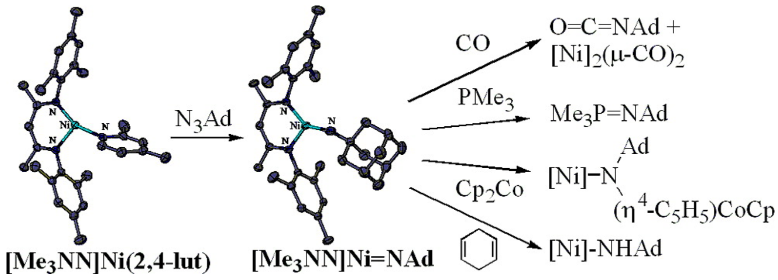
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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

Elzbieta Kogut, Heather L. Wiencko, Libei Zhang, Douglas E. Cordeau, and Timothy H. Warren

J. Am. Chem. Soc., **2005**, 127 (32), 11248-11249• DOI: 10.1021/ja0533186 • Publication Date (Web): 20 July 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

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

Elzbieta Kogut, Heather L. Wiencko, Libei Zhang, Douglas E. Cordeau, and Timothy H. Warren*

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

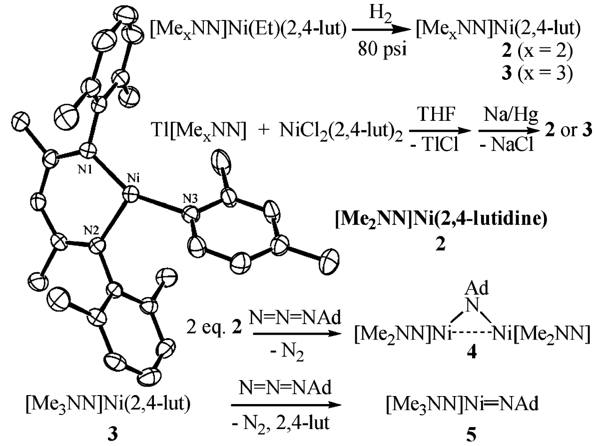
Received May 20, 2005; E-mail: thw@georgetown.edu

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 $\mathrm{Cp^{*}Ir{\equiv}N^{t}Bu}$[3] and ($\eta^6$-benzene)Ru=NAr[4] (Ar = 2,6-$^i\mathrm{Pr_2C_6H_3}$), 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 ($^t\mathrm{Bu_2PCH_2CH_2PBu^t_2}$)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-$\mathrm{Me_2C_6H_3}$) 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** ($\mu_{\mathrm{eff}} = 0.95\ \mu_B$ 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$^{\mathrm{I}}$Cp,[17] the reaction

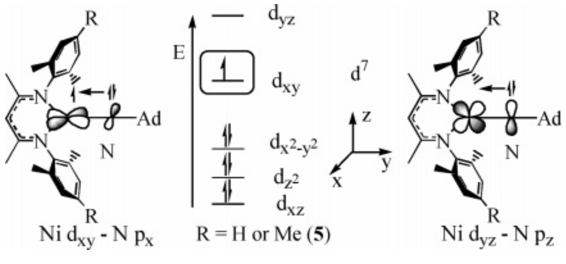


Figure 1. Orbital interactions in β-diketiminato terminal imides.

10.1021/ja0533186 CCC: $30.25 © 2005 American Chemical Society

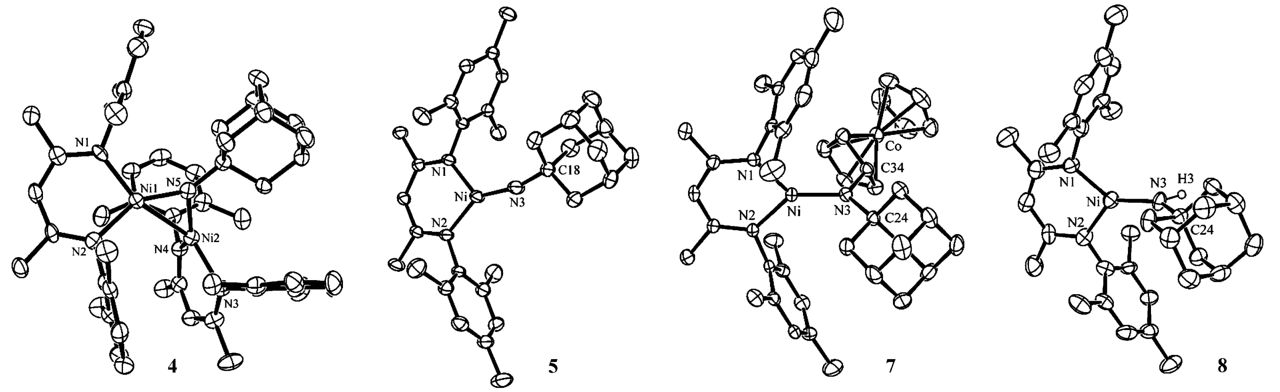
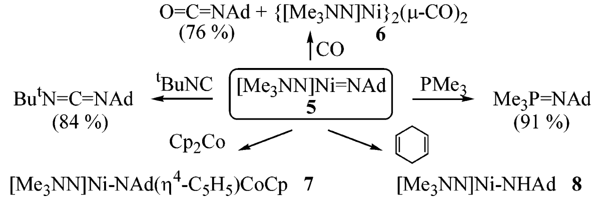


Figure 2. X-ray structures of $\{[Me_2NN]Ni\}_2(\mu\text{-NAd})$ (**4**), $[Me_3NN]Ni{=}NAd$ (**5**), $[Me_3NN]Ni{-}NAd(\eta^4\text{-}C_5H_5)CoCp$ (**7**), and $[Me_3NN]Ni{-}NHAd$ (**8**).

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]

Acknowledgment. T.H.W. thanks Georgetown University, the ACS Petroleum Research Fund (Type-G), and the NSF CAREER program for financial support. We also thank Prof. Jeffrey Petersen for obtaining EPR spectra of **2**, **3**, and **5**, and Prof. Karsten Meyer for obtaining SQUID data for **4** and **8**.

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.

References

(1) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) DuBois, J. L.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364. (c) Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889. (d) Brandt, P.; Södergren, M. J.; Andersson, P. G.; Norrby, P.-O. *J. Am. Chem. Soc.* **2000**, *122*, 8013. (e) Au, S.-M.; Huang, J.-S.; Yu, W.-Y.; Fung, W.-H.; Chi, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120. (f) Mansuy, D.; Battioni, P.; Mahy, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4487.

(2) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(3) (a) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719. (b) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

(4) (a) Burrell, A. K.; Steedman, A. J. *Chem. Commun.* **1995**, 2109. (b) Burrell, A. K.; Steedman, A. J. *Organometallics* **1997**, *16*, 1203.

(5) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623.

(6) Mindiola, D. J.; Hillhouse, G. L. *Chem. Commun.* **2002**, 1840.

(7) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2003**, *125*, 13350.

(8) (a) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238. (b) Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 322. (c) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 10782. (d) Brown, S. D.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 4538. (e) Brown, S. D.; Peters, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 1913.

(9) (a) Thyagarajan, S.; Shay, D. T.; Incarvito, C. D.; Rhengold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2003**, *125*, 4440. (b) Shay, D. T.; Yap, G. P. A.; Zakharov, L. N.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1508.

(10) Hu, X.; Meyer, K. *J. Am. Chem. Soc.* **2004**, *126*, 16322.

(11) Dai, X.; Kapoor, P.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 4798.

(12) (a) Wiencko, H. L.; Kogut, E.; Warren, T. H. *Inorg. Chim. Acta* **2003**, *345*, 199. (b) Kogut, E.; Zeller, A.; Warren, T. H.; Strassner, T. *J. Am. Chem. Soc.* **2004**, *126*, 11984.

(13) Puiu, S. C.; Warren, T. H. *Organometallics* **2003**, *22*, 3974.

(14) Amisial, L. D.; Dai, X.; Kinney, R. A.; Krishnaswamy, A.; Warren, T. H. *Inorg. Chem.* **2004**, *43*, 6537.

(15) A related *p*-substituent effect in terphenyl indium species has been observed: Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538.

(16) See Supporting Information for details.

(17) Herberich, G. E.; Schwarzer, J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 897.

(18) (a) Panda, A.; Stender, M.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909. (b) Eckert, N. A.; Bones, E. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2003**, *42*, 1720.

(19) Dai, X.; Warren, T. H. *J. Am. Chem. Soc.* **2004**, *126*, 10085.

(20) Büttner, T.; Geier, J.; Frison, G.; Harmer, J.; Calle, C.; Schweiger, A.; Schönberg, H.; Grützmacher, H. *Science* **2005**, *307*, 235.

JA0533186