JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

A Structurally Rigid Bis(amido) Ligand Framework in Low-Coordinate Ni(I), Ni(II), and Ni(III) Analogues Provides Access to a Ni(III) Methyl Complex via Oxidative Addition

Michael I. Lipschutz,[†] Xinzheng Yang,[‡,§] Ruchira Chatterjee,[∥] and T. Don Tilley*,[†]

[†]Department of Chemistry and [‡]Molecular Graphics and Computation Facility, University of California, Berkeley, Berkeley, California 94720, United States

[§]Institute of Chemistry, Chinese Academy of Sciences, Bejing, 100190, P.R. China

[∥]Physical Biosciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd, Berkeley, California 94720, United States

S *Supporting Information*

ABSTRACT: A structurally persistent bis-amido ligand framework capable of supporting nickel compounds in three different oxidation states has been identified. A highly unusual, isolable Ni(III) alkyl species has been prepared and characterized via a rare example of a two-electron oxidative addition of MeI to Ni(I).

Due to their comparatively low toxicity, minimal cost, and high abundance, catalysts based on first-row transition metals are attracting considerable interest.[1] Many attempts to develop such catalysts are based on well-known mechanisms associated with second- and third-row metals; however, alternative design strategies might leverage the chemical transformations and properties that are unique to the 3d metals. Among the many features that distinguish first-row metals from their heavier congeners is their ability to adopt very low-coordination numbers (e.g., two and three) that are associated with electrophilic metal centers and high reactivity.[2a−g]

Whereas a number of low-coordination number complexes are known, e.g., with Cr, Mn, Fe, Co, and Ni, the reaction chemistry associated with this structural type is relatively unexplored.[2a] Exceptions are found in the research of Hillhouse et al., who have explored a number of novel transformations for low-coordinate, neutral Ni(I) and Ni(0) complexes.[3a−g] Applications of such complexes to catalysis are less well studied, but this laboratory has recently described use of the precatalyst $Fe[N(SiMe_3)_2]_2$ for hydrosilations of carbonyl compounds[4] and $Ni[N(SiMe_3)DIPP]_2$ (**1**, DIPP = 2,6-diisopropylphenyl) as an alkene hydrosilation catalyst.[5] Herein, we describe the redox chemistry of **1** and demonstrate that this nickel bis(amido) framework readily supports low-coordinate complexes in three different oxidations states, Ni(I/II/III), and accommodates a two-electron oxidative addition to anionic $\{Ni[N(SiMe_3)DIPP]_2\}^-$ (**2**) to produce the unusual nickel(III) alkyl complex $(Me)Ni[N(SiMe_3)DIPP]_2$ (**3**).

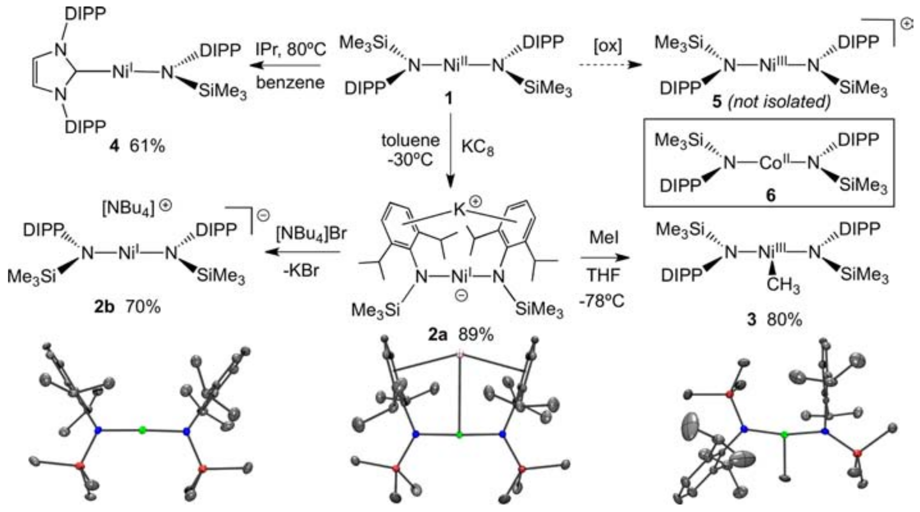
Previous reactivity studies of **1** demonstrated that simple two-electron donors, such as MeCN and 4-(*N*,*N*-dimethylamino)pyridine, add rapidly to form three-coordinate, T-shaped adducts.[5] However, the more sterically demanding N-heterocyclic carbene IPr (*N*,*N*′-1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) reacted with **1** upon heating at 80 °C to form the yellow nickel(I) species $(IPr)Ni[N(SiMe_3)DIPP]$ (**4**) in 61% isolated yield (Scheme 1). This interesting redox process, which formally involves displacement of $\bullet N(SiMe_3)$-DIPP, represents a convenient route to low-coordinate Ni(I) amido complexes, which have been used as precursors to Ni-imido complexes by Hillhouse et al.[3d,f] The unusual redox process associated with this reaction prompted an examination of **1** by cyclic voltammetry (CV), which reveals fully reversible Ni(I/II) and Ni(II/III) couples at −1.28 V ($E_{1/2}$ vs Fc/Fc$^+$, $ip_a/ip_c = 0.98$) and +0.18 V ($E_{1/2}$ vs Fc/Fc$^+$, $ip_a/ip_c = 0.97$; see Supporting Information, SI). The relatively low and reversible reduction potential for **1** suggested that the corresponding anionic Ni(I) complex might be isolable.

The reduction of **1** by 1.1 equiv of KC_8 in toluene occurred over 20 min at −30 °C and workup of the solution provided $K\{Ni[N(SiMe_3)DIPP]_2\}$ (**2a**) as light-yellow crystals in 89% yield (Scheme 1). The X-ray structure of **2a** reveals that the complex maintains a linear geometry about nickel with a N−Ni−N bond angle of 178.05(9)° (Scheme 1) and a Ni−N bond distance of 1.8436(2) Å. The potassium atom in this complex is sandwiched via η^6-coordination to the aryl rings of both amido ligands (Scheme 1). The potassium was exchanged for tetrabutylammonium ($N^nBu_4^+$) by reaction of **2a** with $[N^nBu_4]Br$ in THF to give $N^nBu_4\{Ni[N(SiMe_3)DIPP]_2\}$ (**2b**) as yellow crystals in 70% yield. As shown by the crystal structure (Scheme 1), **2** exists as a rigorously two-coordinate bis(amido) complex with metrical parameters similar to those of **2a** and both of these complexes exhibit an eclipsed conformation of the planar amido substituents. The solution magnetic moments of **2a**,**b**, determined by Evans' method,[6] are 1.66 and 2.03 μ_B, respectively, and are consistent with one unpaired electron as expected for a d^9 configuration.

To better understand the electronic configuration of this eclipsed, bis-amido structural motif, DFT calculations were performed on **1** and **2b**, using both the hybrid functional ωB97XD[7] and the pure functional revTPSS,[8] since these functionals treat open-shell spin states in fundamentally different ways. The optimized structures of **1** and **2b** are in close agreement with their respective crystal structures in

Received: August 6, 2013
Published: September 30, 2013

Scheme 1. Reactions of Ni Bis(amido) Complexes



retaining a linear, eclipsed coordination geometry with bond lengths and angles consistent with experimental values (see SI). In both calculations of **1**, the triplet spin state is favored over the singlet state by a considerable margin (17 and 7 kcal/mol for the ωB97XD and revTPSS calculations, respectively). This is in agreement with the magnetic moment of 2.67 μ_B observed for **1**, consistent with two unpaired electrons.

In addition to the conformational and metrical similarities between neutral **1** and anionic **2b**, the DFT calculations indicate that their electronic structures are closely related. A single qualitative MO diagram can be used to represent the electronic structures of both **1** and **2b** as shown in Figure 1. The HOMO for both complexes is a singly occupied N−Ni−N π-antibonding orbital. This three-centered π system may be viewed as resulting from combinations of Ni d_{yz} and N p_y orbitals to give bonding, nonbonding, and antibonding orbitals populated by a total of five electrons. Single occupancy of the π-antibonding HOMO results in a net bond order of one-half for this π system, for both **1** and **2b**. It is difficult to assess the contribution of this π bonding to the stability of eclipsed structures for **1** and **2a**. However, it is worth noting that the conversion of **1** to **2a** is accompanied by a rotation about the Ni−N bond to place the two aryl groups *cis* to one another. That this occurs at ambient temperatures suggests that the rotational barrier is minimal and thus that the π bonding interaction is weak.

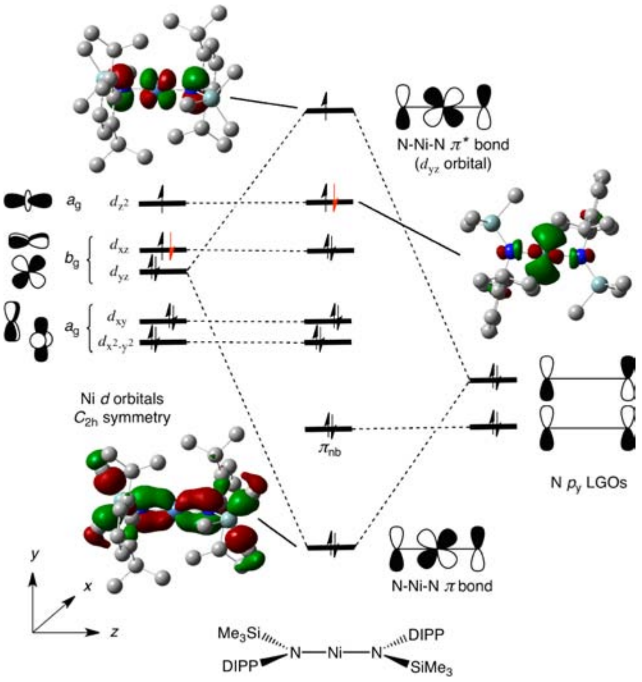


Figure 1. Qualitative MO diagram for Ni bis(amido) ligand framework with selected calculated molecular orbitals. The red electron is present only in Ni(I) d^9 species **2a**,**b**. Calculated MO figures are from the hybrid calculations on compound **1**.

Given the striking similarities between the electronic structures of the two-coordinate Ni(I) and Ni(II) complexes **1** and **2b**, it was of interest to synthetically access the analogous Ni(III) (d^7) cation. The optimized geometry of the Ni(III) cation $\{Ni[N(SiMe_3)DIPP]_2\}^+$ (**5**), calculated by the DFT methods described above,[9] is predicted to feature an eclipsed conformation and a linear coordination geometry. The more electrophilic metal center in this case results in a canting of the aryl groups within the coordination plane to provide close aryl-Ni interactions and a smaller Ni−N−C_{ipso} bond angle (88.15° compared to 106.66(9)° for **1** and 121.62(19)° for **2b**, see SI). The hybrid calculation also predicts that the doublet spin state is favored over the quartet spin state by 14 kcal/mol.

Observation of the reversible oxidation wave for **1** at +0.18 V suggested that the Ni(III) cation might be chemically accessible. However, this wave lies close to an irreversible event at ~0.67 V (E_p vs Fc/Fc$^+$), with an onset potential of ~0.40 V. The close proximity of these two oxidation events places upper and lower bounds on the oxidation potential for the oxidant required to isolate the Ni(III) cation. Attempts to observe the oxidation of **1** with Ag(I) reagents led to an intractable mixture of Ni-containing products ($Ag(Et_2O)[B(C_6F_5)_4]$ and $Ag[CH_6B_{11}Br_6]$) or no reaction at 60 °C (AgOTf, $AgBF_4$, and $AgNTf_2$).

Given these results, the isoelectronic d^7 Co bis(amido) complex $Co[N(SiMe_3)DIPP]_2$ (**6**) was obtained by a procedure analogous to that used for **1** (see SI). This complex was isolated as red crystals with a solution μ_{eff} value of 5.67 μ_B, reflecting a high-spin configuration with strong spin−orbit coupling, as previously observed for related two-coordinate Co(II) bis-amido complexes.[10] Complexes **1** and **6** are isostructural, with an eclipsed conformation of the amido substituents. There are several structural and electronic differences between the calculated properties of **5** and the observed properties of **6**, but this comparison is convoluted by the difference in charge and the strong spin−orbit coupling interactions observed in **6**.

Further analysis of the calculated electronic structures of **1** and **2b** suggested an alternative route to complexes with the Ni(III) oxidation state. The HOMO-1 orbital of both compounds is the σ-antibonding d_{z^2} orbital, in which most of the electron density has been pushed into the torus of the d_{z^2} orbital. Substantial mixing between d_{z^2} and $d_{z^2-y^2}$, expected for the C_{2h} symmetry of **1** and **2b**, results in electron density being distributed along the "in-plane" molecular x-axis instead of in a radially symmetrical fashion (Figure 1). This creates a much more directional orbital, which is more amenable to bond formation. Prior work with **1** has shown that this orbital, depicted in Figure 1 (and derived from d_{z^2}), acts as an acceptor for neutral, two-electron donors.[5] However, in **2b**, this orbital is doubly occupied, suggesting it may instead serve as a reasonable nucleophile toward a small, organic substrate.

The reaction of **2a** with methyl iodide occurred over 35 min starting at −78 °C and warming to room temperature. Workup of the reaction mixture and recrystallization from pentane afforded the unusual Ni(III) alkyl complex (Me)Ni[N(SiMe$_3$)-DIPP]$_2$ (**3**, Scheme 1) as green prisms in 80% yield. Compound **3** is thermally unstable, decomposing in benzene solution at ambient temperature over ~24 h to **1**, accompanied by the formation of ethane (detected by ^{1}H and ^{13}C NMR spectroscopy). However, **3** was found to be sufficiently stable for single crystal X-ray diffraction studies and combustion analysis and exhibited no signs of decomposition after three months as a solid at −30 °C.

Complex **3** is a rare example of a Ni(III) organometallic complex and appears to be only the third structurally characterized Ni(III) alkyl complex.[11a−d] The X-ray structure of **3** reveals two inequivalent molecules, each in a T-shaped coordination geometry, with an average N−Ni−N angle of 167.4(1)° and an average Ni−C_{Me} bond length of 1.923(4) Å. Both molecules display a close contact between the Ni center and the ipso carbon of an adjacent aryl ring, similar to the interactions predicted in the calculated structure of **5**. Although the relevant distances and angles vary by a significant amount between the two molecules (Ni−C_{ipso}: 2.377(2) and 2.541(2) Å, Ni−N−C_{ipso}: 94.01(1) and 102.90(1)°, respectively), this suggests that the predicted structure of **5** is qualitatively reasonable. The Ni−C bond length of 1.923(4) Å is similar to those reported for the two previously known Ni(III) alkyl species (1.994(3) and 2.015(3) Å for −Me and −Et analogs, respectively), although both of these examples are five-coordinate, negatively charged species.[11a] The solution magnetic moment of **3** was determined to be 1.78 μ_B, consistent with one unpaired electron and a low spin, d^7 electronic configuration.

Efforts to better understand the electronic structure of **3** involved EPR spectroscopy and DFT calculations using the same two functionals employed in the analyses of **1** and **2a,b**. Both computations of **3** place the odd electron in a π^* orbital bearing substantial metal character (see SI) supporting the assignment of **3** as Ni(III). The frozen glass EPR spectrum of **3** in toluene reveals an anisotropic signal with g_{xx}, g_{yy}, g_{zz} = (2.32, 2.15, 2.13), indicating that the unpaired spin resides in an orbital with significant metal character (see SI). The signal also displays hyperfine coupling to the two nitrogen atoms, indicating substantial delocalization of the unpaired spin density onto those nitrogen atoms, which is in agreement with the calculated HOMO of **3**. Together, the calculations and EPR data support the characterization of **3** as a Ni(III) complex rather than a Ni(II) complex with an oxidized, ligand-based radical.

While **3** is an unusual compound in and of itself, the oxidative process which gives rise to it is also quite rare. Analysis of **2a,b** and **3** by DFT calculations and EPR spectroscopy supports the oxidation state assignments of Ni(I) (see SI) and Ni(III), respectively (vide supra); thus, the formation of **3** from **2a** is formally a two-electron oxidative addition. Notably, the lack of well-defined, two-electron redox processes for first-row metal complexes is thought to represent a major impediment to the development of catalytic cycles for these metals.[1] While oxidative additions to nickel are known, they are much more commonly observed in Ni(0)/Ni(II) or Ni(II/IV) couples. Well-defined Ni(I)/Ni(III) oxidative additions are rare,[12] but similar, ligand-assisted two-electron oxidative additions are implicated in various nickel-catalyzed cross-coupling reactions and Ni(III) alkyl complexes like **3** are proposed as intermediates in those reactions.[13,14] To the best of our knowledge, no other Ni(I)/Ni(III) oxidative additions leading to an isolable Ni(III) product are known. Remarkably, complex **3** was found to be unreactive toward both powerful electrophiles (Me$_3$SiOTf, triflic acid) and nucleophiles (KO^{t}Bu, KOMe, LiSPh). No reaction was observed with the above reagents in THF at ambient temperature prior to the complete thermal decomposition of **3** (~24 h, via ^{1}H NMR spectroscopy). Similarly, **3** (0.0035 mM in THF) was found to be unreactive toward saturated THF solutions of [N^{n}Bu$_4$]X (X = Cl, 0.022 mM; Br, 0.11 mM; I, 0.0050 mM), indicating that the oxidative addition of methyl iodide is not readily reversible under these conditions.

In summary, a structurally persistent bis-amido ligand framework for nickel compounds in three oxidation states has been identified, and a highly unusual Ni(III) alkyl species has been prepared and characterized. Further exploration of this system should yield important mechanistic information relevant to nickel-catalyzed coupling reactions and multi-electron redox processes for first-row metals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving further experimental and spectroscopic details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

tdtilley@berkeley.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the National Science Foundation under grant no. CHE-1265674. The Molecular Graphics and Computational facility (College of Chemistry, University of California, Berkeley) is supported by the National Science Foundation under grant no. CHE-0840505.

REFERENCES

(1) *Catalysts Without Precious Metals*; Bullock, R. M., Eds.; Wiley-VCH: Weinheim, 2010.

(2) (a) Power, P. P. *Chem. Rev.* **2012**, *112*, 3482. (b) Lei, H.; Fettinger, J. C.; Power, P. P. *Inorg. Chem.* **2012**, *51*, 1821. (c) Dugan, T. R.; Sun, X.; Rybak-Akimova, E. V.; Olatunji-Ojo, O.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 12418. (d) Harrold, N. D.; Hillhouse, G. L. *Chem. Sci.* **2013**, *4*, 4011. (e) Nia, C.; Power, P. P. *Chem. Commun.* **2009**, 5543. (f) Danopoulos, A. A.; Braunstein, P. *Dalton Trans.* **2013**, *42*, 7276. (g) Laskowski, C. A.; Hillhouse, G. L. *Organometallics* **2009**, *28*, 6114.

(3) (a) Laskowski, C. A.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2008**, *130*, 13846. (b) Laskowski, C. A.; Miller, A. J. M.; Hillhouse, G. L.; Cundari, T. R. *J. Am. Chem. Soc.* **2011**, *133*, 771. (c) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 11890. (d) Laskowski, C. A.; Morello, G. R.; Saouma, C. T.; Cundari, T. R.; Hillhouse, G. L. *Chem. Sci.* **2013**, *4*, 170. (e) Iluc, V. M.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2010**, *132*, 15148. (f) Anderson, J. S.; Iluc, V. M.; Hillhouse, G. L. *Inorg. Chem.* **2010**, *49*, 10203. (g) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623.

(4) Yang, J.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2010**, *49*, 10186.

(5) Lipschutz, M. I.; Tilley, T. D. *Chem. Commun.* **2012**, *48*, 7146.

(6) Evans, D. F. *J. Chem. Soc.* **1957**, 2003.

(7) Chai, J. D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615.

(8) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. *Phys. Rev. Lett.* **2011**, *106*, 179902.

(9) Calculations of the Ni(III) cation based on the pure functional would only converge using an unrestricted, quadratically convergent SCF procedure. The optimized geometry derived from this calculation was similar in all relevant aspects to that calculated using the hybrid functional and the doublet spin state was also found to be the lowest energy. Backsay, G. B. *Chem. Phys.* **1988**, *61*, 385.

(10) Bryan, A. M.; Merrill, W. A.; Reiff, W. M.; Fettinger, J. C.; Power, P. P. *Inorg. Chem.* **2012**, *51*, 3366.

(11) (a) Lee, C.-M.; Chen, C.-H.; Liao, F.-X.; Hu, C.-H.; Lee, G.-H. *J. Am. Chem. Soc.* **2010**, *132*, 9256. (b) Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. *J. Am. Chem. Soc.* **1983**, *105*, 1379. (c) Grove, D. M.; van Koten, G.; Mul, W. P.; van der Zeijden, A.; Terheijden, J. *Organometallics* **1985**, *5*, 33. (d) Kelley, D. G.; Marchaj, A.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 7583.

(12) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547.

(13) Hu, X. *Chem. Sci.* **2011**, *2*, 1867.

(14) Jones, G. D.; Martin, J. L.; McFarland, C.; Allen, O. R.; Hall, R. E.; Haley, A. D.; Brandon, R. J.; Konovalova, T.; Desrochers, P. J.; Pulay, P.; Vicic, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 13175.