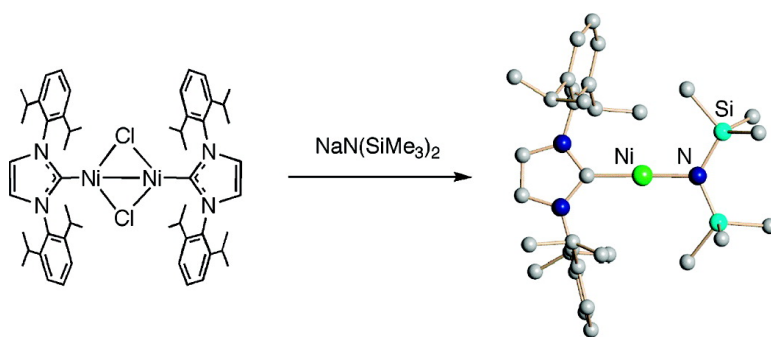


Two-Coordinate d Complexes. Synthesis and Oxidation of NHC Nickel(I) Amides

Carl A. Laskowski, and Gregory L. Hillhouse

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Two-Coordinate d^9 Complexes. Synthesis and Oxidation of NHC Nickel(I) Amides

Carl A. Laskowski and Gregory L. Hillhouse*

Gordon Center for Integrative Science, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Received July 24, 2008; E-mail: g-hillhouse@uchicago.edu

Divalent, square-planar group 10 complexes with π -donor ligands are precluded from forming π -bonds since the empty $d_{x^2-y^2}$ orbital is $M-L \sigma^*$ in nature and does not have the proper symmetry for π -overlap. Trigonal planar geometry, however, affords a metal fragment having an empty in-plane orbital that can participate in π -bonding, exemplified by the low-spin, d^8 nickel complex-cations [(dtbpe)Ni=NHAr⁺] and [(dtbpe)Ni=P^tBu₂⁺] (dtbpe = 1,2-bis(*tert*-butylphosphino)ethane; Ar = 2,6-di-isopropylphenyl).^{1,2} The synthetic strategy to these molecules involved preparing unusual d^9 L_2NiX complexes and subsequent 1- e^- oxidation to the d^8 cations. Due in part to their low coordination number and cationic charge, these complexes exhibit interesting reactivities.¹⁻³ We were intrigued about the possible consequences for reactivity of lowering the coordination number of Ni to two. Power and Arduengo have described examples of neutral, two-coordinate nickel in high spin, d^8 Ni(NMesBMes₂)₂ and the d^{10} N-heterocyclic carbene (NHC) complex Ni(IMes)₂.^{4,5} Herein we report unique two-coordinate, 13-electron d^9 nickel amides of the type (NHC)Ni(NR₂) and their oxidations to afford interesting and surprising low-spin d^8 products.

Reaction of Sigman's d^9-d^9 dimer [(IPr)Ni(μ -Cl)]₂ (**1**; IPr = 1,3-di(2,6-di-isopropylphenyl)imidazolin-2-ylidene)⁶ with NaN(SiMe₃)₂ in a 1:2 stoichiometry yields the monomeric d^9 amide (IPr)Ni[N(SiMe₃)₂] (**2**) as an analytically pure, yellow crystalline compound in 72% isolated yield (Scheme 1). The solution magnetic moment of **2** ($\mu_{\text{eff}} = 1.9 \mu_B$) is characteristic of a 1- e^- paramagnet. The molecular structure of **2** is shown in Figure 1 and features a linear, two-coordinate geometry about nickel with Ni-N(3) =

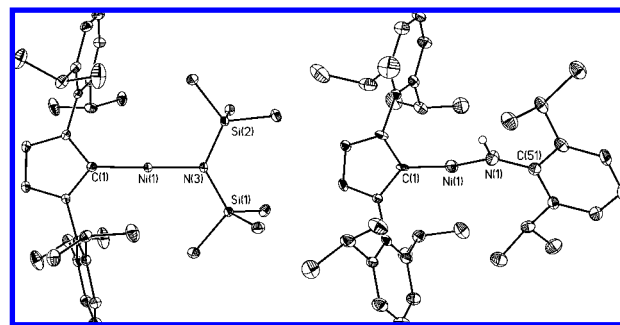


Figure 1. X-ray structures of **2** (l) and **3** (r) with H-atoms (except on N) omitted for clarity. Ellipsoids shown at 50% probability. Selected metrical parameters for **2**: Ni(1)–N(3) = 1.865(2), Ni(1)–C(1) = 1.879(2), N(3)–Si(1) = 1.712(2), N(3)–Si(2) = 1.708(2) Å; C(1)–Ni(1)–N(3) = 178.7(8)°. For **3**: Ni(1)–N(3) = 1.831(4), 1.806(4), Ni(1)–C(1) = 1.878(5), 1.860(5) Å; C(1)–Ni(1)–N(3) = 163.2(2)°, 167.4(2)°.

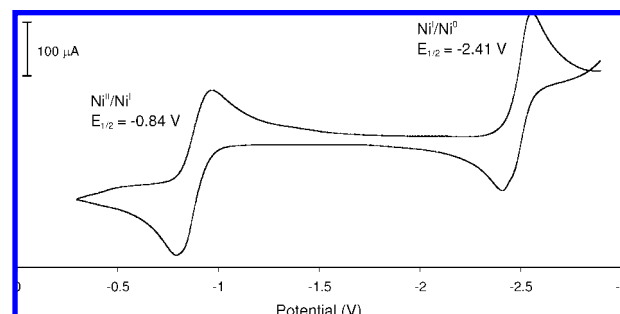
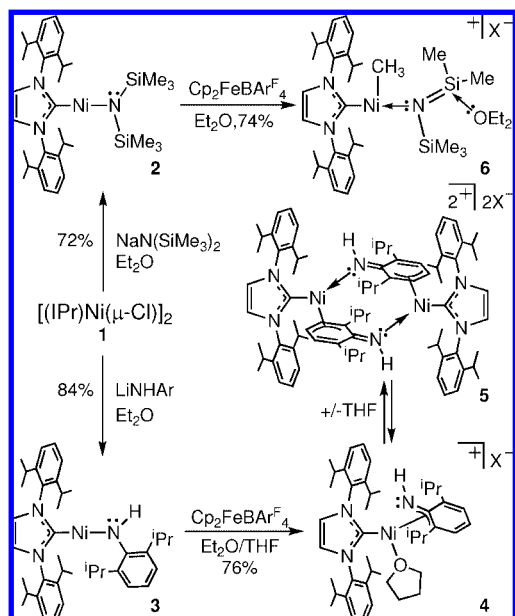


Figure 2. Cyclic voltammogram of **3** (THF/TBAH, 100 mV/s, Cp₂Fe/Cp₂Fe⁺ corrected).



1.865(2) Å and C(1)–Ni–N(3) = 178.7(8)°. There are no short inter- or intramolecular nonbonded contacts. Although not crystallographically required, Si(1), Si(2), Ni, C(1), and three N atoms are essentially coplanar. The Ni–N(3) distance is similar to that found in the three-coordinate Ni(I) amides (PPh₃)₂Ni{N(SiMe₃)₂} (1.88(1) Å)⁷ and (dtbpe)Ni(NHAr) (1.881(2) Å).¹ In an analogous fashion, bright-purple (IPr)Ni(NHAr) (**3**) can be prepared from **1** and LiNHAr in 84% yield (Scheme 1). The solution magnetic moment of **3** at 2.3 μ_B is higher than that expected for a spin-only ion and suggests contributions from low-lying paramagnetic excited states. The solid-state structure of **3** (see Figure 1) reveals two independent molecules in the unit cell with Ni–N distances of 1.831(4) and 1.806(4) Å. Although the C(1)–Ni–N(3) bond angle in **3** (163.2(2)°, 167.4(2)°) deviates from linearity, there are no short nonbonding contacts between Ni and either the IPr or amide ligands.

A cyclic voltammogram of a solution of **3** (THF/TBAH) shows two quasi-reversible waves at $E_{1/2} = -0.84$ and -2.41 V (vs Cp₂Fe/Cp₂Fe⁺) for the Ni(II)/Ni(I) and Ni(I)/Ni(0) couples, respectively

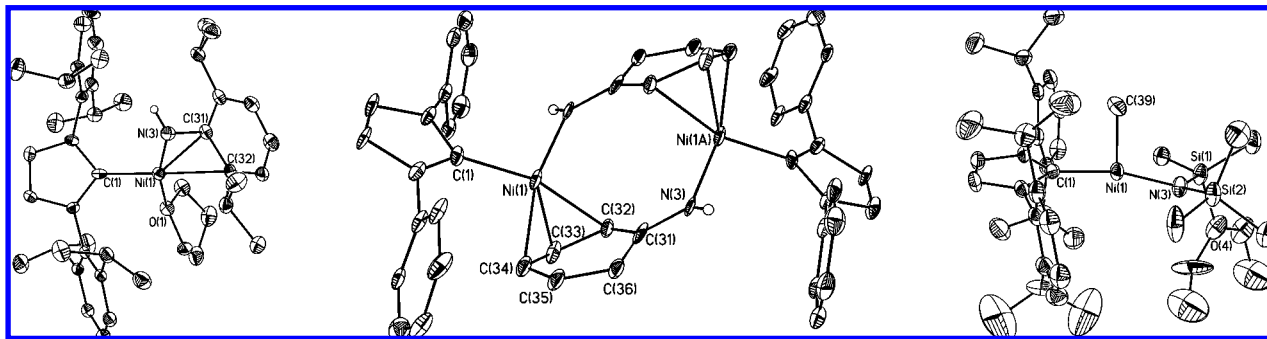


Figure 3. Molecular structures of the complex cations of **4**, **5**, and **6** (l to r). BARF_4^- anions, H-atoms (except on N), and isopropyl groups in **5** have been omitted for clarity. Selected metrical parameters for **4**: Ni(1)–N(3) = 1.871(5), Ni(1)–C(31) = 2.054(6), Ni(1)–C(32) = 2.326(6), Ni(1)–O(1) = 1.947(4), Ni(1)–C(1) = 1.907(6) Å. **5**: Ni(1A)–N(3) = 1.939(6), Ni(1)–C(34) = 2.008(7), Ni(1)–C(33) = 2.044(8), Ni(1)–C(32) = 2.211(6), N(3)–C(31) = 1.322(11), C(31)–C(36) = 1.462(13), C(31)–C(32) = 1.490(11), C(32)–C(33) = 1.401(11), C(33)–C(34) = 1.416(12), C(34)–C(35) = 1.438(12), C(35)–C(36) = 1.364(12) Å. **6**: Ni(1)–N(3) = 1.881(5), Ni(1)–C(1) = 1.868(6), Ni(1)–C(39) = 1.907(7), N(3)–Si(1) = 1.661(5), N(3)–Si(2) = 1.740(5), O(4)–Si(1) = 1.829(5) Å; C(1)–Ni(1)–C(39) = 89.9(3)°, C(39)–Ni(1)–N(3) = 104.1(3)°, C(1)–Ni(1)–N(3) = 166.0(2)°.

(Figure 2). While we have not yet been able to cleanly access the reduction product of **3**, $\text{d}^{10}[(\text{IPr})\text{Ni}(\text{NHAr})^-]$, we note that Gunnoe has reported the isoelectronic Cu(I) complex, $(\text{IPr})\text{Cu}(\text{NHAr})$.⁸ On the other hand, chemical oxidation of ether solutions of **3** with $[\text{Cp}_2\text{Fe}][\text{BARF}_4^-]$ ($\text{BARF}_4^- = \text{B}[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4$) followed by recrystallization of the blue-green product from THF/pentane affords a new diamagnetic Ni(II) species, **4**, in 76% yield (Scheme 1). The ^1H NMR spectrum (THF- d_8 , 289 K) of **4** indicates fluxional amide isopropyl groups and is consistent with the general formulation $[(\text{IPr})\text{Ni}(\text{NHAr})][\text{BARF}_4^-]$, but such a two-coordinate, d^8 Ni complex would almost certainly be high-spin. The diamagnetism of **4** suggested a higher coordination number, and a single-crystal X-ray study revealed that the amide group adopts an η^3 -heterobenzylic coordination mode involving N, the *ipso*- and an *ortho*-C atom, with concurrent ligation of THF (Figure 3). **4** is thus properly formulated as the 16- e^- complex $[(\text{IPr})\text{Ni}(\eta^3\text{-NHAr})\text{-}(\text{THF})][\text{BARF}_4^-]$. VT ^1H NMR data show inequivalent amide ^iPr groups at 198 K (500 MHz), consistent with the solid-state structure, with an ~ 12 kcal/mol barrier to ring-hopping.

The THF ligand of **4** is labile, and recrystallization from CH_2Cl_2 gives a solvent-free (but still diamagnetic) 16- e^- dimer, $[(\text{IPr})\text{Ni}(\text{N},\eta^3\text{-NH}=\text{C}_6\text{Pr}_2\text{H}_3)]_2[\text{BARF}_4^-]_2$ (**5**; Scheme 1). The crystal structure of **5** (Figure 3) revealed unusual bridging NHAr groups with a long Ni–N(1) bond (1.939(6) Å cf. 1.871(5) Å in **4**), an ~ 0.1 Å reduction in the *ipso*-C–N bond compared with **4**, and a disruption of aromaticity in the aryl ring that allows its coordination to a second Ni in a π -allylic manner. In THF solution, **5** rapidly reverts to **4**.

Unlike **3**, the CV of **2** acquired under identical conditions exhibits an irreversible oxidation at $E_0 \sim -0.21$ V. Surprisingly, 1- e^- oxidation of diethyl ether solutions of **2** with $[\text{Cp}_2\text{Fe}][\text{BARF}_4^-]$ gives brilliant-blue, diamagnetic $[(\text{IPr})\text{Ni}(\text{CH}_3)\{\kappa^1\text{-N}(\text{SiMe}_3)=\text{SiMe}_2\cdot\text{Et}_2\text{O}\}][\text{BARF}_4^-]$ (**6**, 74% yield), an iminosilane complex arising from β -Me elimination from the expected d^8 cation $[(\text{IPr})\text{Ni}\{\text{N}(\text{SiMe}_3)_2\}^+]$ (Scheme 1; Figure 3).⁹ The Ni center in **6** adopts a distorted T-shaped geometry with the NHC ligand trans to a κ^1 -iminosilane bound as a simple N-donor (C(1)–Ni–C(39) = 89.9(3)°, C(1)–Ni–N(3) = 166.0(2)°).¹⁰ Free iminosilanes with

bulky substituents are known,¹¹ and early metal η^2 -iminosilane complexes have been reported.¹² The Ni–CH₃ bond length (1.907(7) Å) is comparable to that found in $[(\text{dtbpe})\text{Ni}(\text{CH}_2\text{CMe}_2\text{Ph})^+]$ (1.954(3) Å), where the neophyl ligand also sports an *ipso*-Ph interaction with Ni.¹³ The lack of a stabilizing secondary interaction of the methyl ligand (or solvent) with the metal makes **6** a unique example of a truly three-coordinate, 14- e^- Ni(II) alkyl cation.

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Supporting Information Available: Experimental, spectroscopic, and analytical details (PDF); complete crystallographic details for **2**, **3**, **4**, **5**, and **6** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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