

Synthesis and Characterization of Linear and Square-Planar Nickel Complexes with Primary Amido Ligands

Jianfeng Li, Haibin Song, Chunming Cui,* and Jin-Pei Cheng

State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received February 14, 2008

The synthesis and characterization of the two homoleptic mononuclear nickel complexes $(2,6\text{-Dipp}_2\text{C}_6\text{H}_3\text{NH})_2\text{Ni}$ (**1**) and $[2\text{-C(H)-NDippC}_6\text{H}_4\text{NH}]_2\text{Ni}$ (**2**) (Dipp = $2,6\text{-Pr}_2\text{C}_6\text{H}_3$) are described. **1** is formally two-coordinate and adopts a strictly linear geometry, while **2** features a slightly distorted square-planar geometry. Electrochemistry of **1** and **2** shows that they can be reduced to the corresponding nickel(I) species and oxidized to the corresponding nickel(III) species reversibly or quasi-reversibly. A solid-state magnetic measurement ($\mu_{\text{eff}} = 2.79 \mu_{\text{B}}$) for paramagnetic **1** indicates the presence of two unpaired electrons on the nickel center.

Late-transition-metal amido complexes have been proposed as important intermediates in many catalytic and organic reactions because of their relatively labile M–N bonds.¹ In order to understand the factors that control the nature of M–N bonds, a number of monomeric nickel complexes with amido functionalities have been synthesized and structurally authenticated.^{2–6} These nickel amides are mostly stabilized by employing either a soft donor such as

phosphines or chelating π -type ligands. In contrast, homoleptic mononuclear nickel amido complexes remain extremely rare. The paucity may be related to the incompatibility of “hard” amido groups bonded to “soft” late transition metals⁷ and the propensity for amido groups to form intermetallic bridges.⁸ Nonetheless, the use of multiple dentate and bulky amido ligands has allowed the isolation and structural characterization of several homoleptic mononuclear amido species.⁹ In particular, Power and co-workers have shown that two-coordinate, homoleptic nickel amides can be obtained by employing arylamido ligands with an electronically unsaturated boryl substituent to accept the lone pair of electrons on the nitrogen and prevent nitrogen bridging.¹⁰

Given the unique reactivity of nickel imides,¹¹ we are interested in the investigation of nickel complexes with primary amido ligands as imido precursors via oxidation followed by abstraction of the hydrogen atom from the amido moieties.³ Several nickel primary amido complexes supported by phosphine and β -diketiminato ligands and the Cp family of ligands are known.^{3–6,11} However, to the best of our

* To whom correspondence should be addressed. E-mail: cmcui@nankai.edu.cn (C.C.).

- (1) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (b) Power, P. P. *Comments Inorg. Chem.* **1989**, *8*, 177. (c) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (d) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1. (e) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239. (f) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (g) Wolfe, J. P.; Wagaw, S.; Marcoux, J. F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (h) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (i) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44.
- (2) (a) For examples, see: Bradley, D. C.; Hursthouse, M. B.; Smallwood, R. J.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 872. (b) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592. (c) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918. (d) Matsunaga, P. T.; Hess, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **1994**, *116*, 3665. (e) Koo, K.; Hillhouse, G. L. *Organometallics* **1995**, *14*, 4421. (f) Eckert, N. A.; Bones, E. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2003**, *42*, 1720. (g) Cámpora, J.; Matas, I.; Palma, P.; Graiff, C.; Tiripicchio, A. *Organometallics* **2005**, *24*, 2827.
- (3) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623.
- (4) (a) Cámpora, J.; Palma, P.; del Río, D.; Conejo, M. M.; Alvarez, E. *Organometallics* **2004**, *23*, 5653. (b) Cámpora, J.; Matas, I.; Palma, P.; Alvarez, E.; Graiff, C.; Tiripicchio, A. *Organometallics* **2007**, *26*, 3840.

- (5) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319.
- (6) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12800.
- (7) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115.
- (8) Hope, H.; Olmstead, M. M.; Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 712.
- (9) (a) la Cour, A.; Findeisen, M.; Hansen, K.; Hazell, R.; Hennig, L.; Olsen, C. E.; Pedersen, L.; Simonsen, O. *J. Chem. Soc., Dalton Trans.* **1997**, 2045. (b) Lee, H. K.; Peng, Y.; Kui, S. C. F.; Zhang, Z.-Y.; Zhou, Z.-Y.; Mak, T. C. W. *Eur. J. Inorg. Chem.* **2000**, 2159. (c) Wang, H.-Y.; Meng, X.; Jin, G.-X. *Dalton Trans.* **2006**, 2579. (d) Li, J.; Tian, D.; Song, H.; Wang, C.; Zhu, X.; Cui, C.; Cheng, J.-P. *Organometallics*, ASAP. (e) Ansell, C. W. G.; McPartlin, M.; Tasker, P. A.; Cooper, M. K.; Duckworth, P. A. *Inorg. Chim. Acta* **1983**, *76*, L135. (f) Hicks, F. A.; Jenkins, J. C.; Brookhart, M. *Organometallics* **2003**, *22*, 3533. (g) Liao, C.-Y.; Chan, K.-T.; Chang, Y.-C.; Chen, C.-Y.; Tu, C.-Y.; Hu, C.-H.; Lee, H. M. *Organometallics* **2007**, *26*, 5826.
- (10) (a) Bartlett, R. A.; Chen, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 316. (b) Chen, H.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1990**, *112*, 1048.
- (11) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248.

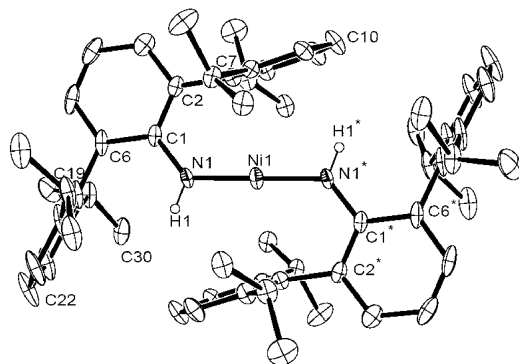


Figure 1. ORTEP representation of the X-ray structure of **1**. Hydrogen atoms and the disordered C30' and C30* have been omitted for clarity (only the hydrogen atoms on N1 and N1* are shown). Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ni1–N1 1.818(3), Ni1–C7 2.680, C1–N1 1.392(5), C2–C7 1.510(5), C6–C19 1.481(7), N1–Ni1–N1* 180.0(3), C1–N1–Ni1 128.2(3).

knowledge, homoleptic, quasi-two-coordinate nickel primary amides have not been reported. Herein we report the synthesis and characterization of the homoleptic nickel amides with the bulky terphenyl primary amido (2,6-Dipp₂C₆H₃NH)[−] and the imine amido [2-C(H)NDippC₆H₄NH][−] ligands.

The reaction of NiBr₂(DME) with 2 equiv of 2,6-Dipp₂C₆H₃NHLi and 2-C(H)NDippC₆H₄NHLi in tetrahydrofuran (THF) at room temperature afforded the air- and moisture-sensitive blue crystals (2,6-Dipp₂C₆H₃NH)₂Ni (**1**) and red crystals [2-C(H)NDippC₆H₄NH]₂Ni (**2**), respectively. Compounds **1** and **2** are thermally robust and have been characterized by NMR and IR spectroscopy, elemental analysis, and X-ray single-crystal analysis.

The molecular structure of **1** is shown in Figure 1 with relevant bond parameters.¹² Its structure has crystallographically required *C*_{2h} symmetry. The C1–N1–Ni1–N1*–C1* fragment is exactly coplanar, and notably the N–Ni–N moiety is strictly linear (N1–Ni1–N1* = 180°). There are only a handful of structurally characterized linear, homoleptic, two-coordinate open-shell (d¹–d⁹) transition-metal complexes, namely, M[C(SiMe₃)₃]₂ (M = Mn, Fe)^{13,14} and (2,6-Ar₂C₆H₃S)₂M (M = Cr, Mn and Ar = 2,4,6-Pr^{*i*}₃C₆H₂; M = Fe and Ar = 2,6-Me₂C₆H₃).¹⁵ To our knowledge, complex **1** is the first example of two-coordinate nickel(II) complexes with an exactly linear geometry.^{10,15a} The Ni–N bond length of 1.818(3) Å in **1** is shorter than those in Ni[N(Ph)BMes₂]₂ [1.885(4) Å (av)] and Ni[N(Mes)BMes₂]₂ [1.866(2) Å (av)] (Mes = 2,4,6-Me₃C₆H₂)¹⁰ and represents

the relatively short distance among nickel amides.^{2–6,8–11} However, it is longer by ca. 0.11 Å than that observed in the terminal imidonickel(II) complex (PBU'₂CH₂CH₂PBU'₂)-NiNDipp [1.702(2) Å].³ The C1–N1 bond length of 1.392(5) Å indicates little electron delocalization from the aryl group to the C–N single bond. The relatively close Ni1⋯C7 (2.680 Å) distance as compared to the van der Waals contact (3.4 Å for Ni⋯C)¹⁶ indicates the existence of the Ni–arene interaction^{10,15,17,18} between the metal center and the ipso carbon of one of the flanking Dipp rings on the ligand, resulting in a slight lengthening of the C2–C7 bond by 0.029 Å compared to the C6–C19 bond. Because of the Ni⋯C(ipso) interaction, a distortion of 9.4° from the coplanar geometry is observed between the C2–C7 bond and the plane of the interacted Dipp ring. The weak interaction may be attributed to the bulkiness of the flanking Dipp rings.

Compound **1** is paramagnetic, as indicated by its abnormal NMR shifts. A solid-state magnetic measurement for **1** at 290 K gave the μ_{eff} value of 2.79 μ_{B} , indicating that **1** features a high-spin configuration with two unpaired electrons, which is likely caused by the relatively weak ligand field considering the quasi-two-coordinate geometry of **1**.¹⁰ The value for the magnetic moment is close to the spin-only value, suggesting the possibility that the Ni⋯C(ipso) interactions in the linear complex **1** are sufficient to essentially quench the orbital contribution to the magnetic moment.

Single crystals of **2** were obtained from toluene. The structure is shown in Figure 2.¹⁹ Compound **2** has a crystallographically required *C*₂ symmetry and adopts a slightly distorted square-planar geometry (dihedral angles of N1–Ni1–N2 and N1*–Ni1–N2* = 8.3°). The primary amido groups reside trans to each other, and the N1–Ni1–N1* angle in **2** is close to linear [176.23(12)°]. This geometry is in sharp contrast to the known bis(amidoimine)nickel complexes, which adopt a tetrahedral geometry around the metal center probably because of the steric demand of the N-substituted group on the aniline fragment.^{9c,d} Compared to the Ni–N(amido) [1.9141(19)–2.001(2) Å] and Ni–N(imine) [1.960(2)–2.049(4) Å] bonds in previously reported bis(amidoimine)nickel complexes,^{9c,d} complex **2** shows the shorter bonds of 1.857(2) and 1.926(2) Å, respectively. Consistent with the high coordination number of **2**, the Ni–N(amido) bond length is longer than that in **1**.

A solution of complexes **1** and **2** in toluene shows significant absorptions in the UV–vis region. The highest energy bands may be attributed to ligand-to-metal charge-

- (12) Crystallographic data: **1**·2C₇H₈, C₇₄H₉₂N₂Ni, *M_w* = 1068.21, triclinic, space group *P* $\bar{1}$, *a* = 10.9100(10) Å, *b* = 11.7540(10) Å, *c* = 13.3740(14) Å, α = 76.560(8)°, β = 76.320(8)°, γ = 70.590(8)°, *V* = 1549.4(3) Å³, *Z* = 1, *d*_{calc} = 1.145 Mg m^{−3}, *T* = 113(2) K. Final *R* = 0.0769 (GOF = 1.103) for 11 736 observed reflections with *I* > 2σ(*I*), *R_w* = 0.0208 for 5350 reflections, all unique data.
- (13) Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1380.
- (14) (a) Viefhaus, T.; Schwarz, W.; Hübler, K.; Locke, K.; Weidlein, J. Z. *Anorg. Allg. Chem.* **2001**, 627, 715. (b) LaPointe, A. M. *Inorg. Chim. Acta* **2003**, 345, 359.
- (15) (a) Nguyen, T.; Panda, A.; Olmstead, M. M.; Richards, A. F.; Stender, M.; Brynda, M.; Power, P. P. *J. Am. Chem. Soc.* **2005**, 127, 8545. (b) Ohta, S.; Ohki, Y.; Ikagawa, Y.; Suizu, R.; Tatsumi, K. *J. Organomet. Chem.* **2007**, 692, 4792.

- (16) Bondi, A. J. *Phys. Chem.* **1964**, 68, 441.
- (17) (a) Campora, J.; Lopez, J. A.; Palma, P.; Valerga, P.; Spillner, E.; Carmona, E. *Angew. Chem., Int. Ed.* **1999**, 38, 147. (b) Campora, J.; Gutierrez-Puebla, E.; Lopez, J. A.; Monge, A.; Palma, P.; del Rio, D.; Carmona, E. *Angew. Chem., Int. Ed.* **2001**, 40, 3641. (c) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreno, E.; Pregosin, P. S. *J. Am. Chem. Soc.* **2002**, 124, 4336.
- (18) (a) Stepien, M.; Latos-Grazynski, L.; Szterenberg, L.; Panek, J.; Latajka, Z. *J. Am. Chem. Soc.* **2004**, 126, 4566. (b) Kitiachvili, K. D.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2004**, 126, 10554.
- (19) Crystallographic data: **2**·2C₇H₈, C₅₂H₆₂N₄Ni, *M_w* = 801.77, monoclinic, space group *C*2/c, *a* = 19.802(11) Å, *b* = 10.739(6) Å, *c* = 21.224(12) Å, α = 90°, β = 95.663(8)°, γ = 90°, *V* = 4492(4) Å³, *Z* = 4, *d*_{calc} = 1.186 Mg m^{−3}, *T* = 113(2) K. Final *R* = 0.0591 (GOF = 1.124) for 24 012 observed reflections with *I* > 2σ(*I*), *R_w* = 0.1438 for 5381 reflections, all unique data.

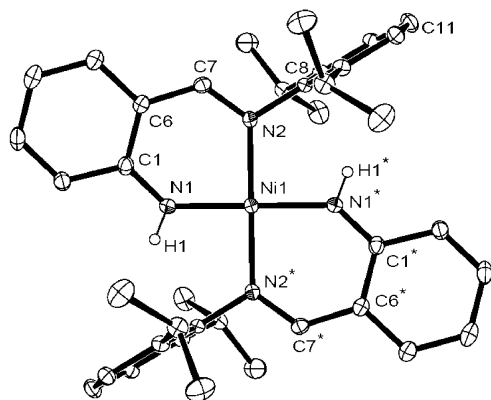


Figure 2. ORTEP representation of the X-ray structure of **2**. Hydrogen atoms have been omitted for clarity (only the hydrogen atoms on N1 and N1* are shown). Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ni1–N1 1.857(2), Ni1–N2 1.926(2), N1–Ni1–N2 89.70(9), N1–Ni1–N1* 176.23(12), N1–Ni1–N2* 90.55(9), C1–N1–Ni1 131.62(17).

Table 1. Redox Potentials (vs Fc/Fc⁺) and Reversibility Data of **1** and **2** from Cyclic Voltammetry^{a,b}

complex	Ni ^{II} /Ni ^{III}			Ni ^I /Ni ^{II}		
	E^{ox} (V)	ΔE_{p} (mV)	$i_{\text{pc}}/i_{\text{pa}}$	E^{red} (V)	ΔE_{p} (mV)	$i_{\text{pc}}/i_{\text{pa}}$
1	0.176 ^c	59	0.54	-1.718	73	1.03
2	-0.027	78	0.95	-2.465	80	1.15

^a In solutions of THF using *n*-Bu₄NPF₆ (0.1 M) as the supporting electrolyte and a scan rate of 100 mV s⁻¹. ^b For reversible one-electron processes, the potentials were taken as the half-wave potentials. ^c For a quasi-reversible wave, the anodic peak potential is given.

transfer phenomena owing to their high absorption coefficients. The well-defined internal transitions within the Ni d orbitals in **1** and **2** with medium absorption coefficients are observed as characteristic broad bands at 778.5 and 495 nm, respectively.^{10,15a,20}

The electrochemistry of complexes **1** and **2** in THF has been studied by cyclic voltammetry, and the electrochemical data are summarized in Table 1. These two nickel complexes featured two important electrochemical processes: a one-electron reduction attributed to the Ni^I/Ni^{II} redox couple and a one-electron oxidation attributed to the Ni^{II}/Ni^{III} redox couple,²¹ which are fully reversible for **2**, and the second process of (2,6-Dipp₂C₆H₃NH)₂Ni^{II} to [(2,6-Dipp₂C₆H₃-NH)₂Ni^{III}]⁺ is quasi-reversible for **1** ($\Delta E_p = 59$ mV, $i_{pc}/i_{pa} = 0.54$; Figure 3). When the electrochemistry of **1** was measured at low temperature (−20 °C) or with different scan rates (20–1000 mV s^{−1}), the quasi-reversible one-electron-oxidation wave was still maintained. Compared to the Ni^I/Ni^{II} and Ni^{II}/Ni^{III} redox potentials of **1**, **2** has more negative redox potentials, indicating that the stronger donation ligand, [2-C(H)NDippC₆H₄NH][−], makes the resulting metal complex more electron-rich. In contrast, the square-planar nickel(II)

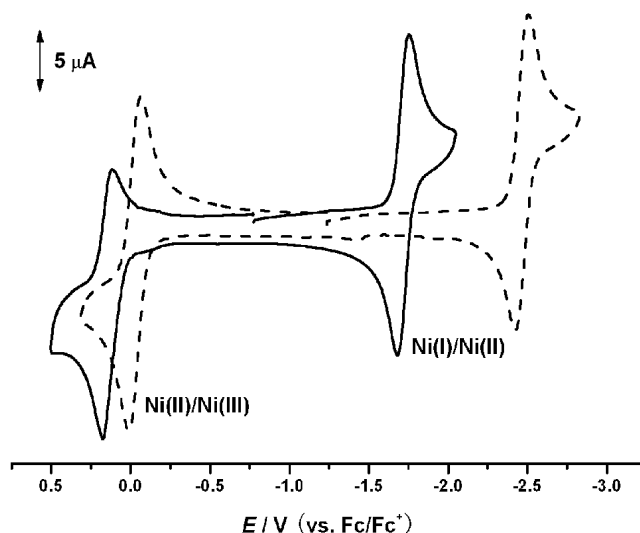


Figure 3. Cyclic voltammograms at 25 °C of 1 mM solutions of **1** (solid line) and **2** (dashed line) in THF containing 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte at a scan rate of 100 mV s⁻¹.

complex [2-C(H)NHC₆H₄NH]₂Ni has different electrochemical behavior, which shows two well-defined oxidation waves and a irreversible reduction wave at +0.28, +1.10, and -1.14 V (vs saturated calomel electrode in *N,N*-dimethylformamide), respectively.²² The known square-planar nickel(II) complexes bearing a dianionic amide-based tetradentate ligand display a reversible or a quasi-reversible one-electron oxidation attributed to the Ni^{II}/Ni^{III} couple; in some cases at least one more positive irreversible oxidation wave attributed to the irreversible ligand oxidation, and no reduction waves were observed in the studied range of potential.^{23–25}

In summary, the first formally two-coordinate nickel amide with an exact linear geometry has been synthesized and structurally characterized. This compound, along with **2**, has a reversible or a quasi-reversible redox potential. Chemical reduction and oxidation of the two compounds are currently under investigation.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 20421202 and 20725205), the Key Project of Chinese Ministry of Education, the Research Fund for the Doctoral Program of Higher Education, and the 111 Plan.

Supporting Information Available: Synthetic procedures, spectroscopic data, and CIF files for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC800288X

- (20) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1980.
- (21) The free ligands 2,6-Dipp₂C₆H₃NH₂ and 2-C(H)NDippC₆H₄NH₂ showed no electrochemical activity when they were studied by cyclic voltammetry in THF under experiment conditions similar to those used for **1** and **2**.

- (22) Higson, B. M.; McKenzie, E. D. J. *Chem. Soc., Dalton Trans.* **1972**, 269. The authors have not drawn any firm conclusions about the nature of the electrode processes.
- (23) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, 96, 3109.
- (24) Sharma, S. K.; Upreti, S.; Gupta, R. *Eur. J. Inorg. Chem.* **2007**, 3247.
- (25) Nivorozhkin, A. L.; Toftlund, H.; Jørgensen, P. L.; Nivorozhkin, L. E. *J. Chem. Soc., Dalton Trans.* **1996**, 1215.