Inorganic Chemistry

Communication

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

The synthesis and characterization of the two homoleptic mononuclear nickel complexes (2,6-Dipp$_2$C$_6$H$_3$NH)$_2$Ni (**1**) and [2-C(H)-NDippC$_6$H$_4$NH]$_2$Ni (**2**) (Dipp = 2,6-Pr$^i_2$C$_6$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 ($\mu_{eff} = 2.79 \mu_B$) 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 metals[7] 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.; Álvarez, 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.

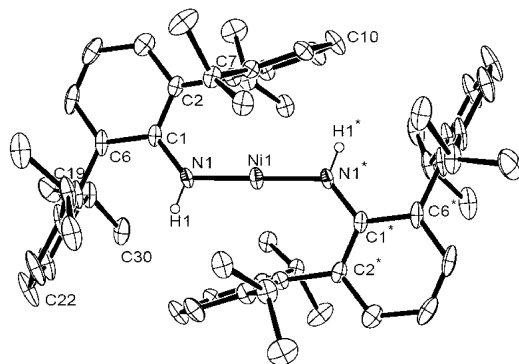(11) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. *J. Am. Chem. Soc.* **2005**, *127*, 11248.

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-$Dipp_2C_6H_3NH)^-$ and the imine amido [2-C(H)NDippC$_6$-H$_4$NH]$^-$ ligands.

The reaction of NiBr$_2$(DME) with 2 equiv of 2,6-Dipp$_2$C$_6$H$_3$NHLi and 2-C(H)NDippC$_6$H$_4$NHLi in tetrahydrofuran (THF) at room temperature afforded the air- and moisture-sensitive blue crystals (2,6-Dipp$_2$C$_6$H$_3$NH)$_2$Ni (**1**) and red crystals [2-C(H)NDippC$_6$H$_4$NH]$_2$Ni (**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 (d^1−d^9) transition-metal complexes, namely, M[C(SiMe$_3$)$_3$]$_2$ (M = Mn, Fe)[13,14] and (2,6-Ar$_2$C$_6$H$_3$S)$_2$M (M = Cr, Mn and Ar = 2,4,6-Pr$^i_3$C$_6$H$_2$; M = Fe and Ar = 2,6-Me$_2$C$_6$H$_3$).[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)BMes$_2$]$_2$ [1.885(4) Å (av)] and Ni[N(Mes)BMes$_2$]$_2$ [1.866(2) Å (av)] (Mes = 2,4,6-Me$_3$C$_6$H$_2$)[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$^t_2$CH$_2$CH$_2$PBu$^t_2$)-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**·2C$_7$H$_8$, C$_{74}$H$_{92}$N$_2$Ni, 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) Å^3, Z = 1, d_{calcd} = 1.145 Mg m^{-3}, T = 113(2) K. Final R = 0.0769 (GOF = 1.103) for 11 736 observed reflections with $I > 2\sigma(I)$, R_w = 0.2028 for 5350 relections, 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**·2C$_7$H$_8$, C$_{52}$H$_{62}$N$_4$ Ni, M_w = 801.77, monoclinic, space group $C2/c$, 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) Å^3, Z = 4, d_{calcd} = 1.186 Mg m^{-3}, T = 113(2) K. Final R = 0.0591 (GOF = 1.124) for 24 012 observed reflections with $I > 2\sigma(I)$, R_w = 0.1438 for 5381 relections, all unique data.
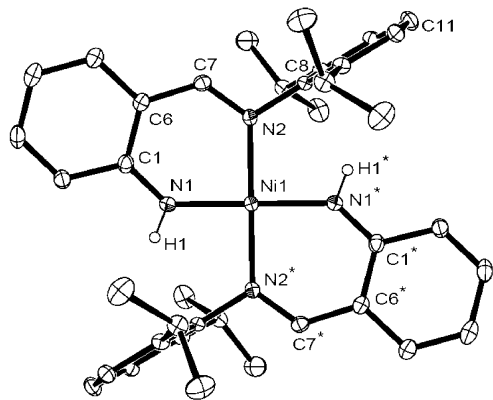
Figure 2. ORTEP representation of the X-ray structure of **2**. Hydrogen atoms have been omitted for clarity (only the hydrogen atoms on N1 and N1* are shown). Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ni1−N1 1.857(2), Ni1−N2 1.926(2), N1−Ni1−N2 89.70(9), 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}

	Ni^{II}/Ni^{III}			Ni^{I}/Ni^{II}		
complex	E^{ox} (V)	ΔE_p (mV)	i_{pc}/i_{pa}	E^{red} (V)	ΔE_p (mV)	i_{pc}/i_{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-Bu$_4$NPF$_6$ (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-Dipp$_2$C$_6$H$_3$NH)$_2$Ni^{II} to [(2,6-Dipp$_2$C$_6$H$_3$-NH)$_2$Ni^{III}]$^+$ is quasi-reversible for **1** (ΔE_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)NDippC$_6$H$_4$NH]$^-$, makes the resulting metal complex more electron-rich. In contrast, the square-planar nickel(II)
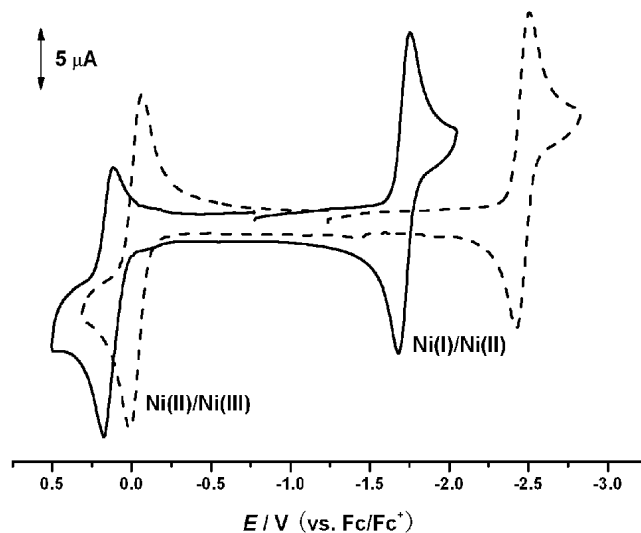

Figure 3. Cyclic voltammograms at 25 °C of 1 mM solutions of **1** (solid line) and **2** (dashed line) in THF containing 0.1 M n-Bu$_4$NPF$_6$ as the supporting electrolyte at a scan rate of 100 mV s^{-1}.

complex [2-C(H)NHC$_6$H$_4$NH]$_2$Ni 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.

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.

(20) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1980.

(21) The free ligands 2,6-Dipp$_2$C$_6$H$_3$NH$_2$ and 2-C(H)NDippC$_6$H$_4$NH$_2$ 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.