Synthesis and Crystal Structures of Monomeric Diamidonickel(II) Complexes

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The thermally stable nickel(II) diamides $[NiL_2]$ [L = $^{-}N(SiMe_3)(8\text{-}C_9H_6N)$ (**1**), $^{-}N(SitBuMe_2)(8\text{-}C_9H_6N)$ (**2**)] have been synthesized from the reaction of $NiCl_2$ with the appropriate lithium amide. X-ray crystallography revealed that the amido ligands bind in a chelating manner, forming a distorted tetrahedral environment around the nickel center. Complexes **1** and **2** have magnetic moments of 3.05 and 2.74 μ_B, respectively, which indicate a d^8 electronic configuration with two unpaired electrons.

Introduction

The study of late transition metal amides has elicited considerable interest due to their involvement in a number of important reactions, ranging from industrial processes[1] to biological phenomena.[2] Among these reactions, the formation of C−N bonds by insertion of unsaturated compounds into the highly reactive M−N bonds has attracted much attention in the past decade.[3] Although an enormous amount of effort has gone into the synthesis of late transition metal amides, structural data for these complexes are still scarce due to the lability of the M−N bonds. It is generally believed that M−N bonds are relatively weak due to an incompatibility that exists between the "hard" anionic amido ligand and the "soft" low-valent late transition metal center.[4−5] Alternatively, on the basis of orbital arguments, the "reluctance" of the electronically saturated late transition metal center to function as a π-acceptor for the amido nitrogen lone-pair electrons through M−N ($d \leftarrow p$) π-interactions also imposes a destabilizing effect on these complexes.[6]

Examples of fully characterized nickel amide complexes containing $Ni-NR_2$ bonds are rare, in contrast to those of nickel complexes containing Ni−X bonds (X = alkyl, halide, hydrido). An early attempt to prepare nickel(II) diamides by reacting $NiCl_2(PPh_3)_2$ with $LiN(SiMe_3)_2$ was unsuccessful and only the three-coordinate nickel(I) complex $[Ni\{N(SiMe_3)_2\}(PPh_3)_2]$ was obtained.[7] By using a "hybrid" ligand consisting of both a hard amido ligand and soft phosphane donors, Fryzuk et al. have successfully synthesized the nickel(II) amide $[Ni(Cl)\{N(SiMe_2CH_2PPh_2)_2\}]$.[8] Recently, a series of monomeric nickel(II) amides $[Ni(Mes)(L)(PMe_3)_2]$ [Mes = mesityl; L = $^{-}NHPh$, $^{-}N(Ph)C(O)CHPh_2$, $^{-}N(Ph)\{C(O)NHtBu\}$] that contain supporting phosphane ligands have been prepared and structurally characterized by Abboud, Boncella, and coworkers.[3d,9] Delocalization of the lone pair of electrons on the amido nitrogens to the π molecular orbitals of the ligands and/or π-interactions between the lone pair electrons with the nickel center in these complexes have been observed.

In recent years, a number of novel metal amides containing the bulky *N*-functionalized amido ligands $[^{-}N(Ph)(2\text{-}C_5H_4N)]$,[10,11] $[^{-}N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$,[12] $[^{-}N(SiMe_3)(2\text{-}C_5H_3N\text{-}4\text{-}Me)]$,[13] and $[^{-}N(SiMe_3)(8\text{-}C_9H_6N)]$,[12a,12b,12d,14] have been synthesized and structurally characterized. Interestingly, these amido ligands can bind to the metal centers in a number of bonding modes, for example as monodentate amido ligands, bidentate *N*,*N*-chelating ligands or bidentate *N*,*N*-bridging ligands. However, late transition metal amides derived from these ligands are still rare.[13a] Currently, we are interested in the structure and reactivities of metal amides. One of our synthetic strategies involves the use of bulky chelate ligands in order to stabilize those otherwise kinetically labile transition metal amido complexes. Several sterically more demanding *N*-functionalized amido ligands, namely $[^{-}N(SitBuMe_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$, $[^{-}N(SitBuPh_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]$, and $[^{-}N(SitBuMe_2)(8\text{-}C_9H_6N)]$ have been prepared in our laboratory and shown to be capable of stabilizing a number of novel main group and transition metal amides with unusual coordination geometries.[15] In this communication, we report the synthesis and crystal structures of two novel monomeric nickel(II) amido complexes, namely $[Ni\{N(SiMe_3)(8\text{-}C_9H_6N)\}_2]$ (**1**) and $[Ni\{N(SitBuMe_2)(8\text{-}C_9H_6N)\}_2]$ (**2**).

Addition of $[\{Li(OEt_2)(L^1)\}_2]$ [L^1 = $^{-}N(SiMe_3)(8\text{-}C_9H_6N)$][12a] to a slurry of anhydrous $NiCl_2$ in THF at ambient temperature gave the homoleptic nickel(II) amide **1** in satisfactory yield (Scheme 1). Complex **2** was prepared analogously by the reaction of $NiCl_2$ with two molar equivalents of the lithium reagent LiL^2 [L^2 = $^{-}N(SitBuMe_2)(8\text{-}C_9H_6N)$]. The latter was prepared by lithiation of HL^2 [15] with a solution of *n*BuLi in hexane. Compound **2** could also be obtained by the reaction of nickelocene with two molar equivalents of LiL^2 in THF at

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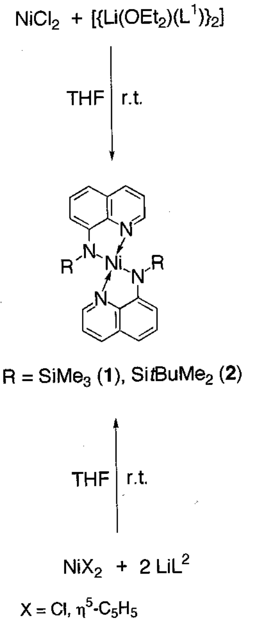
room temperature. Both **1** and **2** were isolated as very air-sensitive, reddish brown crystals. They are thermally stable at room temperature and can be stored indefinitely under an inert atmosphere. They have been characterized by ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis,[16] in addition to single-crystal X-ray diffraction studies. In the solid state, complex **1** consists of two independent molecules of nearly the same structure (Figure 1), which are also analogous to that of **2** (Figure 2). Both complexes are mononuclear and exhibit a distorted tetrahedral coordination geometry around the nickel center, with each pair of amido ligands binding in an *N,N*-chelating manner. The Ni−N$_{quinolyl}$ bond lengths in **1** [1.92−2.06(1) Å] and **2** [2.00−2.03(1) Å], are slightly shorter than the Ni−N$_{pyridyl}$ bond lengths of 2.093 Å (av.) in the trinickel(II) complex of dipyridylamide [$Ni_3(L^3)_4Cl_2$] [L^3 = $^{-}N(2\text{-}C_5H_4N)_2$], in which the amido ligands bind in a *N,N*-bridging manner.[17]



Scheme 1

The nearly trigonal planar geometry around the amido nitrogen centers [sum of bond angles (av.): 359.7° and 360.0° in **1** and 359.3 in **2**] are consistent with sp^2-hybridized nitrogen atoms. The average Si−N bond lengths of 1.710 and 1.716 Å in **1** and 1.739 Å in **2**, are not significantly different from those typical for aminosilanes (ca. 1.73 Å).[4] This suggests the presence of a significant Si−N (*d*←*p*) π-bonding interaction. Delocalization of the lone-pair electrons of the amido nitrogen onto the quinolyl ring is also evidenced by the relatively short N$_{amido}$−C$_{quinolyl}$ distances of 1.361 and 1.365 Å (av.) in **1**, which are similar to the N$_{amido}$−C$_{phenyl}$ distance of 1.354(5) Å in *trans*-[Ni(Mes)(NHPh)(PMe$_3$)$_2$] (**3**).[3d,9a] The observed Ni−N$_{amido}$ distances of 1.92−1.94(1) Å in **1** are relatively short and are similar to the observed Ni−N distances of 1.924(2) Å in [Ni(Cl){N(SiMe$_2$CH$_2$PPh$_2$)$_2$}][8] (**4**) and 1.932(3) Å in **3**,[3d,9a] suggesting that weak π-bonding interactions between the amido nitrogens and the nickel center may be present in **1**. Apparently, ligand L^1 behaves as a weak π-acceptor in this case. The average Ni−N$_{amido}$ distance in **2** [1.94(1) Å] is similar to those in **3** and **4**, but slightly shorter than that of 1.974(3) Å in *trans*-[Ni(Mes){N(Ph)C(O)CHPh$_2$}(PMe$_3$)$_2$] (**5**),[3d,9b] where an Ni−N π-interaction was suggested to be absent in the latter complex. Since the structures of ligands L^1 and L^2 are similar, we surmise that Ni−N π-bonding interaction may also be present in complex **2**.

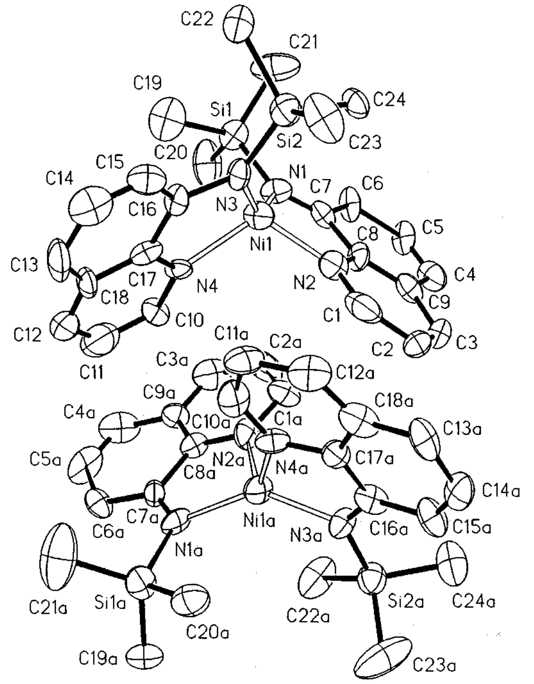


Figure 1. Perspective view of the two independent molecules (30% thermal ellipsoids) in the crystal structure of [Ni{N(SiMe$_3$)(8-C$_9$H$_6$N)}$_2$] (**1**) with the atomic labeling scheme; selected bond lengths [Å] and bond angles [°]: Ni(1)−N(1) 1.94(1), 1.93(1), Ni(1)−N(2) 1.92(1), 2.00(1), Ni(1)−N(3) 1.92(1), 1.93(1), Ni(1)−N(4) 2.06(1), 2.00(1), Si(1)−N(1) 1.73(1), 1.67(1), Si(2)−N(3) 1.69(1), 1.76(1), N(1)−C(7) 1.26(2), 1.34(2), N(3)−C(16) 1.46(1), 1.39(1); N(1)−Ni(1)−N(2) 82.2(7), 84.5(6), N(3)−Ni(1)−N(4) 85.0(6), 82.4 (6), N(1)−Ni(1)−N(3) 138.2(2), 138.9(2), C(7)−N(1)−Si(1), 126(1), 127(1), C(7)−N(1)−Ni(1) 114(1), 113(1), Si(1)−N(1)−Ni(1) 119.6(8), 120.7(7), C(16)−N(3)−Si(2) 127(1), 128(1), C(16)−N(3)−Ni(1) 112(1), 114(1), Si(2)−N(3)−Ni(1) 121.6(7), 117.9(8)

The N$_{amido}$−Ni−N$_{pyridyl}$ bite angles in **1** and **2** are similar, falling within the range 79.6(7)° to 89.1(6)°. The interligand angles N$_{amido}$−Ni−N$_{amido}$ of 158.1(4)° in **2** are much larger than the corresponding angles of 138.2(2)° and 138.9(2)° in **1**. This may be due to the presence of the sterically more demanding Si*t*BuMe$_2$ groups in **2**.

The ^{1}H NMR spectra of **1** and **2** show broad signals with significant isotropic shifts. The resonance signals have been assigned on the basis of their relative intensities and are summarized in Table 1. Both complexes show one set of resonance signals, indicating that each pair of amido ligands in each complex molecule are chemically equivalent. Complex **1** shows one signal due to the SiMe$_3$ groups, whereas two signals are observed for the SiMe$_2$ moiety of

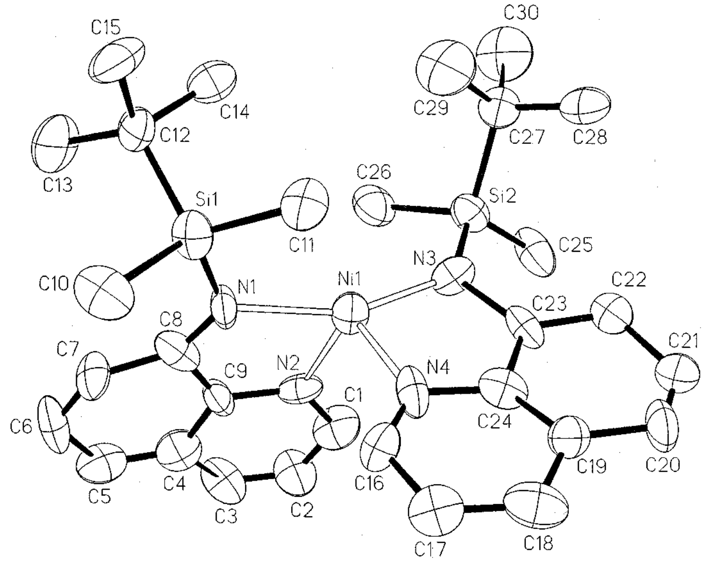


Figure 2. Molecular structure of [Ni{N(Si*t*BuMe$_2$)(8-C$_9$H$_6$N)}$_2$] (**2**) (30% thermal ellipsoids) with the atomic labeling scheme; selected bond lengths [Å] and bond angles [°]: Ni(1)−N(1) 2.03(1), Ni(1)−N(2) 2.00(1), Ni(1)−N(3) 1.85(1), Ni(1)−N(4) 2.03(1), Si(1)−N(1) 1.76(1), Si(2)−N(3) 1.72(1), N(1)−C(8) 1.32(3), N(3)−C(23) 1.49(3); N(1)−Ni(1)−N(2) 79.6(7), N(3)−Ni(1)−N(4) 89.1(6), N(1)−Ni(1)−N(3) 158.1(4), C(8)−N(1)−Si(1) 131(1), C(8)−N(1)−Ni(1) 112(1), Si(1)−N(1)−Ni(1) 116.3(8), C(23)−N(3)−Si(2) 119(1), C(23)−N(3)−Ni(1) 111(1), Si(2)−N(3)−Ni(1) 128.7(9).

Table 1. ^{1}H NMR spectroscopic data of **1** and **2**

Compound	Aryl	*t*Bu	SiMe$_2$	SiMe$_3$
1	−52.8 (br, 1 H), −27.9 (br, 1 H), −18.0 (br, 1 H), 25.8 (br, 1 H), 74.9 (br, 1 H), 179.0 (br, 1 H)	–	–	19.8 (br, 6 H)
2	−46.3 (br, 1 H), −21.6 (br, 1 H), −14.6 (br, 1 H), 23.7 (br, 1 H), 74.1 (br, 1 H), 185.2 (br, 1 H)	6.7 (br, 9 H)	22.6 (br, 3 H), 35.2 (br, 3 H)	–

complex **2**. It is noteworthy that the two Me substituents on the Si*t*BuMe$_2$ group of ligand L^2 are prochiral. The two prochiral Me substituents on the Si*t*BuMe$_2$ groups in complex **2** are nonequivalent due to the presence of the chiral nickel center. A similar case has been observed for the *cis*-dioxo-Mo^{VI} and -W^{VI} amido compounds, [MoO$_2$(L^2)$_2$] and [WO$_2$(L^2)$_2$].[18] Mass spectra of both complexes show the presence of the respective parent ion [M]$^+$. This suggests that both complexes are monomeric in the gas phase, as they are in the solid state. The respective magnetic moments of 3.05 and 2.74 μ_B for **1** and **2**, as measured by the Evans NMR method,[19] are close to the spin-only value of 2.83 μ_B for two unpaired electrons but slightly lower than the expected values for tetrahedral nickel(II) species.[20] One plausible reason for these values may be the presence of a tetrahedral-to-square-planar-type equilibrium for both complexes in solution.[21]

In conclusion, the two homoleptic mononuclear nickel(II) amide complexes [Ni(L^n)$_2$] [L^n = L^1 (**1**), L^2 (**2**)] have been successfully synthesized and structurally characterized. To the best of our knowledge, they are the first example of *homoleptic* mononuclear nickel(II) diamides containing *N*-functionalized amido ligands to be reported. We are currently investigating the reactivities of these two complexes towards carbon−nitrogen bond formation by their reactions with unsaturated electrophilic compounds such as PhNCO and PhCN.

Experimental Section

Synthesis of [Ni(L^1)$_2$] (1): To a stirred suspension of anhydrous NiCl$_2$ (0.09 g, 0.66 mmol) in THF (20 mL) at 0 °C was slowly added a solution of [{Li(OEt$_2$)(L^1)}$_2$] (0.39 g, 0.66 mmol) in THF (20 mL). The resulting solution was stirred at room temperature for 12 h, whereupon a reddish brown solution with a white precipitate was obtained. All volatiles were removed in vacuo and the residue was extracted with hexane. The extract was filtered and concentrated to ca. 10 mL. Upon cooling of the solution to −30 °C, complex **1** was obtained as reddish brown crystals. They were washed with cold pentane and dried under vacuum. Yield: 0.23 g (71%), m.p. 192−194 °C (dec.). − MS (70 eV, EI): *m/z* (%) = 489 (93) [M]$^+$, 474 (91) [M − CH$_3$]$^+$, 459 (23) [M − 2CH$_3$]$^+$. − ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = −52.8 (br, 2 H, qui), −27.9 (br, 2 H, qui), −18.0 (br, 2 H, qui), 19.8 (br, 18 H, SiMe$_3$), 25.8 (br, 2 H, qui), 74.9 (br, 2 H, qui), 179.0 (br, 2 H, qui). − Magnetic moment μ_{eff} = 3.05 BM. − C$_{24}$H$_{30}$N$_4$NiSi$_2$ (489.40): calcd. C 58.90, H 6.18, N 11.44; found C 58.63, H 6.06, N 11.65.

Synthesis of [Ni(L^2)$_2$] (2): This complex was prepared in 66% yield by an analogous procedure as described for **1**, starting from NiCl$_2$ and LiL^2. M.p. 218−219 °C (dec.). − MS (70 eV, EI): *m/z* (%) =

573 (34) $[M]^+$, 558 (4) $[M - CH_3]^+$, 516 (100) $[M - tBu]^+$. − ^{1}H NMR (300 MHz, C_6D_6): δ = −46.3 (br, 2 H, qui), −21.6 (br, 2 H, qui), −14.6 (br, 2 H, qui), 6.7 (br, 18 H, Si*t*Bu), 22.6 (br, 6 H, $SiMe_2$), 23.7 (br, 2H qui), 35.2 (br, 6 H, $SiMe_2$), 74.1 (br, 2 H, qui), 185.2 (br, 2 H, qui). − Magnetic moment $\mu_{eff} = 2.74$ BM. − $C_{30}H_{42}N_4NiSi_2$ (573.56): calcd. C 62.82; H,7.38, N 9.76; found C 61.22, H 7.17, N 9.39.

X-ray Crystallography:[22] The crystallographic data for complexes **1** and **2** are shown in Table 2. All crystals were grown from toluene solutions. Single crystals suitable for X-ray diffraction studies were sealed in capillaries under dinitrogen. X-Ray data were collected on a Rigaku RAXIS-IIC diffractometer at 294 K using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) by taking oscillation photos. The structures were solved by direct-phase determination using the computer program SHELX-97 on a PC 486 computer and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were introduced in their idealized positions and included in structure-factor calculations with assigned isotropic temperature factors.

Table 2. Selected X-ray data collection and structure analysis parameters for **1** and **2**

	1	**2**
Molecular formula	$C_{24}H_{30}N_4NiSi_2$	$C_{30}H_{44}N_4NiSi_2$
Molecular weight	489.41	575.58
Crystal size/mm	0.5 × 0.4 × 0.4	0.38 × 0.20 × 0.18
Crystal system	Monoclinic	Monoclinic
Space group	*Cc*	*Cc*
a/Å	18.536(4)	18.928(4)
b/Å	15.225(3)	8.3706(17)
c/Å	18.433(4)	20.174(4)
β/°	91.35(3)	104.00(3)
Z	8	4
V/Å^3	5200.5(18)	3101.4(11)
Density/g cm^{-3}	1.250	1.233
μ/mm^{-1}	0.856	0.728
Reflections collected	4726	3243
Unique data measured	4726	2095
Observed data with $I \leq 2\sigma(I)$	2642	1732
No. of variables	560	335
Final *R* indices [$I \leq 2\sigma(I)$][a]	$R1 = 0.0410$, $wR2 = 0.0961$	$R1 = 0.0666$, $wR2 = 0.1751$
R indices (all data)[a]	$R1 = 0.1179$, $wR2 = 0.1223$	$R1 = 0.0777$, $wR2 = 0.1896$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

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[22] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138623 (**1**) and CCDC-138624 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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