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Article

Nickel Complexes of a Bulky *β*-Diketiminate Ligand

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Nickel(II) chloride forms a complex with tetrahydrofuran, $NiCl_2(THF)_{1.5}$, that can be used to prepare nickel chloride complexes of a bulky *β*-diketiminate ligand L^{Me}. $[L^{Me}NiCl]_2$ and $L^{Me}NiCl_2LiTHF_2$, which have tetrahedral geometries in the solid state, are in equilibrium with three-coordinate $L^{Me}NiCl$. Thermodynamic parameters for the equilibrium between $[L^{Me}NiCl]_2$ and $L^{Me}NiCl$ are $\Delta H = 51(5)$ kJ/mol and $\Delta S = 116(11)$ J/(mol·K). $L^{Me}NiCl$ forms a tetrahydrofuran complex with a binding constant of 1.2(2) M^{-1} at 21 °C. The chloride complexes were used to generate a three-coordinate nickel(II)–amido complex. This amido complex, $L^{Me}NiN(SiMe_3)_2$, is compared with $L^{Me}MN(SiMe_3)_2$ (M = Mn, Fe, Co) (Panda, A.; Stender, M.; Wright, R. J.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Inorg. Chem.* **2002**, *41*, 3909–3916). Trends in the metrical parameters of the three-coordinate $L^{Me}M^{II}$ amido compounds are similar to the trends in three-coordinate $L^{tBu}M^{II}$ chloride compounds (Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416–14424).

Introduction

β-Diketiminate ligands have experienced a resurgence in inorganic and organometallic chemistry.[1] Compounds with bulky *β*-diketiminate ligands (Figure 1, right) have been synthesized for use in small-molecule activation and catalytic studies and include examples from all of the late first-row and several second- and third-row transition metals.[2] However, nickel compounds with bulky *β*-diketiminate ligands are extremely rare,[1] despite the fact that group 10 metals with bulky bidentate ligands are utilized as catalysts for transformations such as olefin polymerization[3] and alkene and alkyne amination.[4] Because ligand loss from four-coordinate complexes is an initial step in catalytic reactions,
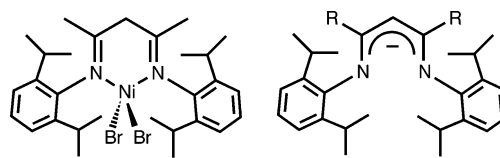
Figure 1. Literature *β*-diketimine compound[7] (left) and the *β*-diketiminate ligands described in this study (right; L^{Me}, R = Me, and L^{tBu}, R = *t*Bu).

a number of groups have studied the structure, spectroscopic properties, and reactivity of three-coordinate Ni(II) compounds.[5] *β*-Diketiminate complexes are a key part of this continuing effort.

Several bis(*β*-diketiminato)nickel complexes have been reported[6] and Feldman et al. synthesized a Ni(II) compound with a neutral *β*-diketimine ligand[7] (Figure 1, left), but no 1:1 nickel/*β*-diketiminate complexes were known until our recent report of three-coordinate $L^{tBu}NiCl$.[8] $L^{tBu}NiCl$ and its

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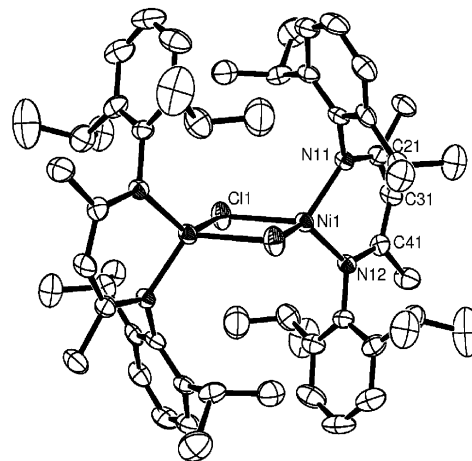
Table 1. Data Collection and Refinement Parameters

	$[L^{Me}NiCl]_2$	$L^{Me}NiCl_2Li(THF)(OEt_2)$	$L^{Me}NiN(SiMe_3)_2$
empirical formula	$C_{58}H_{82}N_4Ni_2Cl_2$	$C_{37}H_{59}N_2O_2NiLiCl$	$C_{35}H_{59}N_3NiSi_2$
fw	1023.59	700.49	636.74
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	14.324(1)	19.708(2)	9.1530(5)
b (Å)	13.516(1)	9.798(1)	20.257(1)
c (Å)	14.797(1)	21.389(2)	20.197(1)
β (deg)	105.411(1)	109.993(2)	90.785(1)
V (Å^3)	2761.7(3)	3881.3(8)	3744.4(3)
Z	4	4	4
ρ (g/cm^3)	1.231	1.181	1.130
μ (mm^{-1})	0.818	0.669	0.608
$R1$, $wR2$ ($I > 2\sigma(I)$)	0.0479, 0.0979	0.0853, 0.2168	0.0643, 0.1244
GOF	0.969	1.047	1.135

three-coordinate analogues $L^{tBu}FeCl$ and $L^{tBu}CoCl$ form a well-characterized series of trigonal planar complexes.[8] While these compounds are interesting in that the third ligand can be substituted while maintaining a three-coordinate geometry, the synthesis of L^{tBu} entails several steps.[8,9] Three-coordinate complexes of the very similar ligand L^{Me} would be preferable because of the easy synthesis of $L^{Me}H$ from 2,4-pentanedione and 2,6-diisopropylaniline.[7,10] The copper(II) chloride complex of L^{Me} is three-coordinate.[11] Here we report that, in an interesting contrast, nickel(II) chloride complexes of L^{Me} are four-coordinate. Despite the higher coordination number in the halide complexes, the $L^{Me}Ni^{II}$ salts are convenient starting materials for three-coordinate nickel(II) compounds.

Results and Discussion

Synthesis of NiCl$_2$THF$_{1.5}$. In recent work, we found FeCl$_2$-THF$_{1.5}$[12] to be a convenient source of iron(II), because it is more soluble than FeCl$_2$.[2e] We desired an analogous nickel starting material, but Kern reported that NiCl$_2$ does not react with THF.[12] In our hands, heating anhydrous NiCl$_2$[13] in boiling THF under N$_2$ did form an adduct, which was isolated simply by removing solvent under vacuum. To establish the chemical formula, the Ni content of the tan product was determined by precipitation with dimethylglyoxime.[14] Depending on the length of reflux time, the amount of coordinated THF varied from 0.7 to 1.6 molecules, with a reaction time of 24 h or more reproducibly giving a stoichiometry of NiCl$_2$THF$_{1.5}$.[15] The precise amount of coordinated THF, however, did not influence the products of the following reactions.

Syntheses and Solid-State Structures of Ni(II) Chloride Complexes. When equimolar amounts of LiL^{Me} and NiCl$_2$-
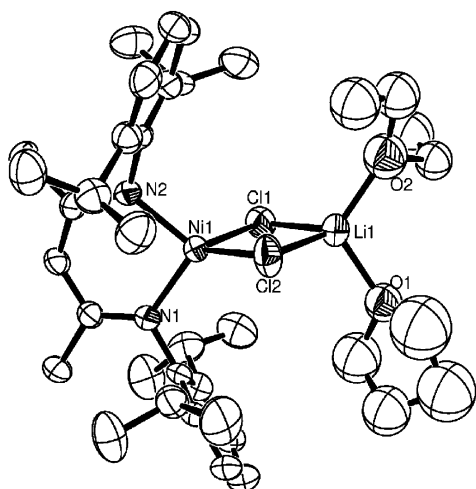
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(15) The reported synthesis of L^{tBu}NiCl (ref 8) used NiCl$_2$THF$_{0.7}$, but NiCl$_2$-THF$_{1.5}$ works equally well.

Figure 2. ORTEP drawing of $[L^{Me}NiCl]_2$. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Ni1−N11 1.938(3), Ni1−N12 1.946(3), Ni1−Cl1 2.324(1), Ni1−Cl2 2.349(1), Ni−Ni 3.458(3), N11−Ni−N12 93.7(1), Cl1−Ni−Cl2 84.56(4).

THF$_n$ were stirred in hot toluene, a bright blue solution was formed. When extracted into CH$_2$Cl$_2$, the solution was dark green, but dark blue crystals could be isolated in moderate yield, and one was subjected to crystallographic analysis. The molecular structure of $[L^{Me}NiCl]_2$ is shown in Figure 2 (Table 1). There is a crystallographic C_2 axis of symmetry that makes the two $L^{Me}NiCl$ units equivalent. The Ni−Cl distances of 2.324(1) and 2.349(1) Å are longer than typical Ni(II)−μ-Cl bonds,[16] perhaps due to the sterically imposing β-diketiminate and the high-spin Ni(II). The Ni−Ni distance is 3.458(1) Å, suggesting that there is no direct metal−metal interaction. The bite angle (N−Ni−N) of 93.7(1)° is typical for β-diketiminate complexes.[1,2,8−11]

Interestingly, when the reaction of LiL^{Me} and NiCl$_2$THF$_n$ was carried out in THF at room temperature, deep purple crystals were obtained from Et$_2$O. The molecular structure is shown in Figure 3 (Table 1). The product, $L^{Me}NiCl_2Li$-(THF)(OEt$_2$), is structurally analogous to the recently described Fe(II) and Co(II) compounds $L^{Me}MCl_2Li(ether)_2$.[2e,i] The Ni−Cl distances are slightly shorter in $L^{Me}NiCl_2Li$-(THF)(OEt$_2$) (average 2.29 Å) than $[L^{Me}NiCl]_2$. The geometry about nickel in $L^{Me}NiCl_2Li(THF)(OEt_2)$ is tetrahedral, like that of $[L^{Me}NiCl]_2$, and the bond angles are similar

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Figure 3. ORTEP drawing of $L^{Me}NiCl_2Li(THF)(OEt_2)$. Thermal ellipsoids are shown at 50% probability. The diethyl ether ligand was modeled with two disorder components in a 55:45 ratio, and the major component is shown. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Ni−N1 1.950(5), Ni−N2 1.943(5), Ni−Cl1 2.284(2), Ni−Cl2 2.295-(2), Ni−Li 3.144(1), N1−Ni−N2 94.7(2), Cl1−Ni−Cl2 95.15(7).

including the bite angle of the β-diketiminate. The Ni−Li distance of 3.144(1) Å again suggests that there is no direct metal−metal interaction.

It is interesting to observe the structural differences enforced by different backbone substituents on β-diketiminate ligands. L^{tBu} gives a three-coordinate, trigonal planar chloride complex, with a Ni−Cl distance of 2.137(2) Å and an average Ni−N distance of 1.815(3) Å.[8] These are 0.1−0.2 Å shorter than the analogous distances in the nickel chloride complexes of L^{Me}, consistent with the lower coordination number of the metal. $L^{tBu}NiCl$ possesses a bite angle of 97.3-(2)°, while $L^{Me}NiCl_2Li(THF)(OEt_2)$ and $[L^{Me}NiCl]_2$ have much smaller bite angles, 94.2 ± 0.5°. This suggests that larger backbone substituents increase the bite angle of diketiminates. With L^{tBu}, the *tert*-butyl groups push the aryl groups toward the metal, forcing the metal deeper into the NN binding pocket and enlarging the bite angle relative to the L^{Me} analogue. We can further observe the effect of backbone substituents on diketiminate bite angle by comparing the C−N−C bond angles of the diketiminates. $L^{Me}NiCl_2$-Li(THF)(OEt_2) has a C−N−C angle of 121.1(5)°, with an analogous angle of 116.4(3)° for $[L^{Me}NiCl]_2$. For $L^{tBu}NiCl$, the angle is 130.4(4)°, nearly 10° larger than in either complex of L^{Me}! Similar bite angle perturbations have been observed in the analogous Fe diketiminate complexes.[2e]

Properties of Ni(II) Complexes in Solution. The nickel chloride complexes show interesting solvent-dependent behavior, which has been monitored using ^{1}H NMR spectroscopy (all the compounds have distinct, paramagnetically shifted spectra) and UV−vis spectrophotometry. Scheme 1 shows our interpretation of the interconversions, and Table 2 lists estimates of the equilibrium populations in ~10 mM solution at room temperature. The rationale for our assignments follows.

In the solid state, $[L^{Me}NiCl]_2$ is blue (λ_{max} = 580, 710 nm; Figure 4). However, dissolving $[L^{Me}NiCl]_2$ in methylene chloride gave green solutions with ^{1}H NMR and UV−vis
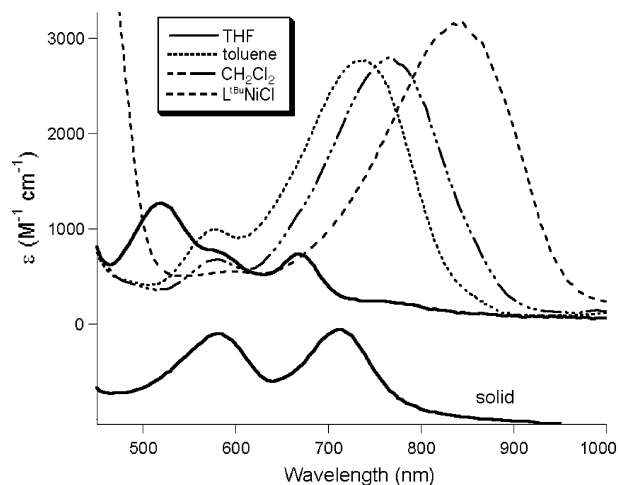
Figure 4. UV−vis spectra of $[L^{Me}NiCl]_2$ in 0.3 mM solutions. The solid-state spectrum is on an arbitrary scale.

Scheme 1
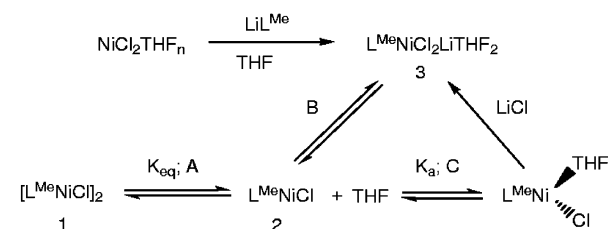
**Table 2.** Populations of ~10 mM Samples at Room Temperature

	equilib A		equilib B	
	% **1**	% **2**	% **2** + LiCl	% **3**
solid	100	0	0	100
C_6H_6/toluene	50	50	20	80
CH_2Cl_2	0	100	95	5

spectra similar to three-coordinate $L^{tBu}NiCl$ (Figure 4).[8] ^{1}H NMR spectra of CD_2Cl_2 solutions of $L^{tBu}NiCl$[8] and of $[L^{Me}$-NiCl]_2$ are similar, although the signals for $[L^{Me}NiCl]_2$ are spread over a larger frequency range. For example, the isopropyl methyl proton sets appear at 5.6 and 4.1 ppm in $L^{tBu}NiCl$, while they are found at 9.7 and 8.5 ppm in CD_2-Cl_2 solutions of $[L^{Me}NiCl]_2$. The signals from the ligand appear in the same order for both compounds, except the different backbone alkyl substituents. The similar spectroscopic properties of $[L^{Me}NiCl]_2$ and $L^{tBu}NiCl$ in CH_2Cl_2 strongly suggest that $[L^{Me}NiCl]_2$ dissociates into monomeric $L^{Me}NiCl$, which has an intense electronic absorption at 765 nm.

In benzene or toluene, blue solutions of $[L^{Me}NiCl]_2$ had two sets of signals in their ^{1}H NMR spectra. One set was nearly identical to that assigned as $L^{Me}NiCl$ above, and the other set had slightly shifted peaks. These are assigned as $L^{Me}NiCl$ and $[L^{Me}NiCl]_2$, respectively. The ratio between the two sets of peaks was dependent on concentration and temperature, as expected for a monomer/dimer equilibrium. At room temperature with low concentrations we observed only the monomer and could not attain high enough concentrations to observe $[L^{Me}NiCl]_2$ without some $L^{Me}NiCl$ present. UV−vis spectra of $[L^{Me}NiCl]_2$ in aromatic solvents at low concentration support the presence of both monomeric
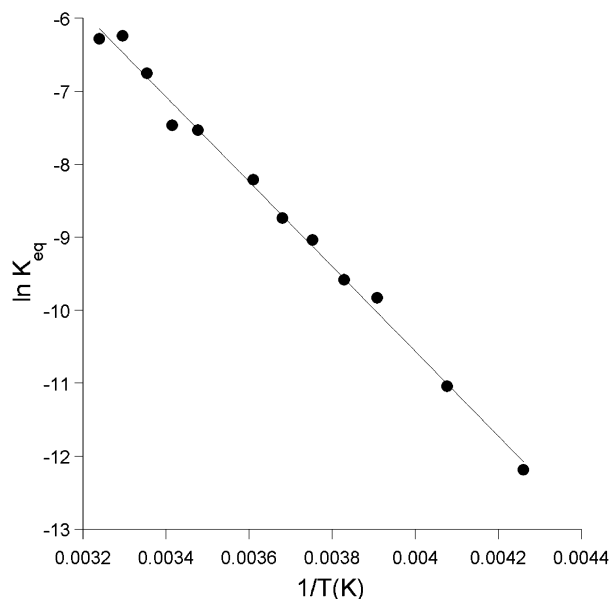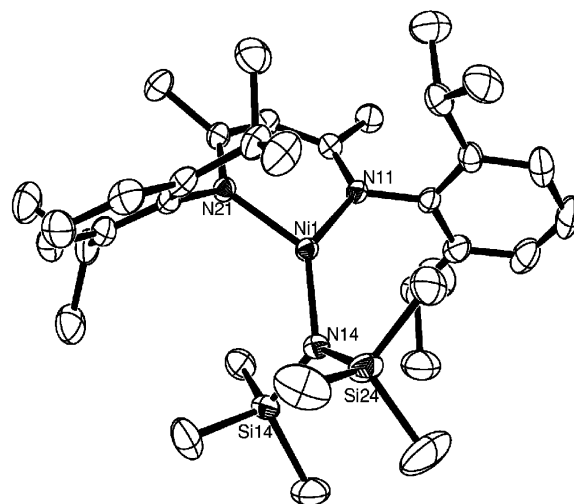
Figure 5. van't Hoff plot of data from a 10.5 mM sample of [L^{Me}NiCl]$_2$ in toluene-d_8 from −49 to 46 °C.

Figure 6. ORTEP drawing of L^{Me}NiN(SiMe$_3$)$_2$. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Ni−N11 1.911(2), Ni−N21 1.953(2), Ni−N14 1.873(2), N11−Ni1−N21 94.86(9), N11−Ni1−N14 133.25(9), N21−Ni1−N14 128.86(9).

L^{Me}NiCl (λ_{max} = 740 nm) and dimeric [L^{Me}NiCl]$_2$ (λ_{max} = 580 nm) (Figure 4). To further examine this equilibrium in solution, we monitored ^{1}H NMR spectra at various temperatures. Above 46 °C only the monomer was detected, and below −49 °C only the dimer was observed. Between these temperatures, the measured equilibrium constants for the dissociation of dimer into monomer (K_{eq}; equilibrium A in Scheme 1) gave ΔH = +51(5) kJ/mol and ΔS = +116(15) J/(mol·K) (Figure 5). As observed with other transition metal dimer−monomer equilibria, equilibrium A (cleavage of dimer) is enthalpically disfavored but entropically favored.[17]

The monomer/dimer equilibrium bears a resemblance to those recently reported in (β-diketiminato)copper(II) halide complexes. Both L^{tBu}CuCl and L^{Me}CuCl are monomers at all temperatures in aromatic solvents.[2b,2h] With diketiminate L′ (substantially smaller than L^{Me}, with *ortho*-methyl substitution rather than *ortho*-isopropyl substitution on the aryl rings), a dimer was crystallographically characterized, and the equilibrium between monomer and dimer was monitored using EPR and UV−vis techniques.[2h,18] [L′CuCl]$_2$ is a monomer above −55 °C in toluene, a temperature similar to that at which [L^{Me}NiCl]$_2$ begins to dissociate. Thus, roughly the same dissociation temperature is evident in electronically similar complexes of copper with a smaller ligand and nickel with a larger ligand. We conclude that nickel β-diketiminate complexes have a greater tendency to dimerize than their copper analogues.

In THF solution, [L^{Me}NiCl]$_2$ became purple and the ^{1}H NMR and UV−vis spectra were similar to those of L^{Me}NiCl$_2$-Li(THF)(OEt$_2$) in THF. We suggest that this more drastic spectroscopic change results from dissociation of the dimer 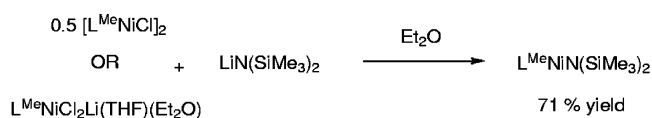and THF coordination to form L^{Me}NiCl(THF). To determine the association constant of THF to L^{Me}NiCl (K_a; equilibrium C in Scheme 1), we utilized UV−vis spectrophotometry in CH$_2$Cl$_2$. Linear Scatchard plots[19] of data at several concentrations yielded K_a = 1.2(0.2) M^{-1} at 21 °C.[20] Thus our data support the observation that [L^{Me}NiCl]$_2$ is fully converted to L^{Me}NiCl(THF) when dissolved in THF.

The two Ni(II) chloride complexes were easily interconverted. When solutions of [L^{Me}NiCl]$_2$ in THF were treated with excess LiCl (followed by ultrasound irradiation to facilitate LiCl incorporation), ^{1}H NMR and electronic spectra suggested formation of L^{Me}NiCl$_2$Li(THF)(OEt$_2$). Conversely, when L^{Me}NiCl$_2$Li(THF)(OEt$_2$) was dissolved in CD$_2$Cl$_2$, we observed ^{1}H NMR signals from both L^{Me}NiCl and L^{Me}NiCl$_2$-Li(ether)$_2$ (Supporting Information). On a preparative scale, the conversion of L^{Me}NiCl$_2$Li(THF)(OEt$_2$) to [L^{Me}NiCl]$_2$ may be effected by heating in toluene at 100 °C for several hours, extracting, and crystallizing from CH$_2$Cl$_2$.

Scheme 2

0.5 [L^{Me}NiCl]$_2$

OR + LiN(SiMe$_3$)$_2$ $\xrightarrow{\text{Et}_2\text{O}}$ L^{Me}NiN(SiMe$_3$)$_2$

L^{Me}NiCl$_2$Li(THF)(Et$_2$O)   71 % yield

Synthesis of a Three-Coordinate Nickel(II) Amido Complex. The suitability of [L^{Me}NiCl]$_2$ and L^{Me}NiCl$_2$Li-(THF)(OEt$_2$) as starting materials for low-coordinate nickel-(II) complexes was evaluated by adding lithium bis-(trimethylsilyl)amide to ethereal solutions of these nickel(II) complexes (Scheme 2). Starting from either complex, this reaction cleanly gave a single product as judged by ^{1}H NMR spectroscopy. X-ray crystallographic analysis of the product

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(18) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Le Pape, L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307−6321.
(19) Connors, K. A. *Binding Constants: The Measurements of Molecular Complex Stability*; John Wiley & Sons: New York, 1987; pp 59−101 and 141−187.
(20) Scatchard plots from data collected at −5 and −20 °C gave K_{eq} values within experimental error of K_{eq} at room temperature. This suggests that ΔH for the reaction is roughly zero and the bond dissociation energy (BDE) for the Ni−O(THF) bond is equal to the sum of the decreases in other bond energies from increased coordination number.

Table 3. Relevant Distances and Angles for Three-Coordinate M(II) Diketiminate Bis(trimethylsilyl)amido Compounds[a]

	Mn	Fe	Co	Ni
M−N(diketiminate) (Å)	2.073(1)	2.008(1)	1.965(1)	1.932(2)
M−N(amido) (Å)	1.992(1)	1.928(1)	1.903(1)	1.873(2)
bite angle (N−M−N) (deg)	92.57(5)	94.33(4)	96.60(4)	94.86(9)
fold angle[b] (deg)	164.2	164.8	165.3	168.8(2)
M−N₂C₃ dist[c] (Å)	0.394	0.365	0.340	0.281(3)

[a] All data for Mn, Fe, and Co compounds taken from ref 2i. [b] Fold angle is defined as the angle between MN_2 and N_2C_3 planes. [c] Distance from M to the N_2C_3 plane.
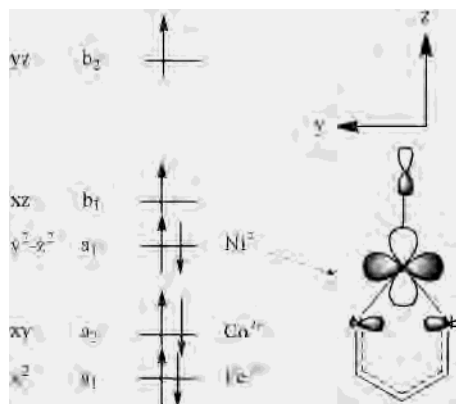
Figure 7. Molecular orbitals of $L^{Me}MX$ (adapted from ref 8).

showed that it was $L^{Me}NiN(SiMe_3)_2$ (Figure 6, Table 1), which has a three-coordinate geometry. A similar procedure was employed by Mindiola and Hillhouse to synthesize a three-coordinate Ni(II) amido complex from $[(dtbpe)NiCl]_2$.[5f]

The Ni−N(amido) distance of 1.873(2) Å is similar to that of the homoleptic amido compound $[Ni(NPh_2)_3]^-$ (1.889(3) Å)[5b] and the heteroleptic (dtbpe)NiNH(diisopropylphenyl) (1.881(2) Å).[5f] $L^{Me}NiN(SiMe_3)_2$ is isoleptic with Power's very recently reported compounds $L^{Me}MN(SiMe_3)_2$ (M = Mn, Fe, Co), and these compounds possessing identical ligand sets show a monotonic decrease in M−N(amido) distance from Mn to Ni.[2i] This trend is similar to the one we have found in three-coordinate $L^{tBu}MCl$ complexes.[8] The Ni(II) amido compound is nearly planar at the metal (356.97-(9)°) as well as the amido nitrogen (358.9(2)°), as found for the $^-N(SiMe_3)_2$ compounds of the other metals.[2i] Table 3 compares key distances and angles for the $L^{Me}MN(SiMe_3)_2$ series. There is an increase in diketiminate bite angle (N−M−N) from Mn to Co and then a dropoff for Ni. The decreased nickel bite angle in three-coordinate chloride complexes was previously explained through either onset of diketiminate ligand folding or through occupation of molecular orbitals with N---N bonding character.[8] In the amido complexes, it is possible to distinguish between these two explanations. Because the ligand folding is similar in all of the amido complexes (Table 3), the major influence on bite angle is likely to be occupation of the a_1-symmetry molecular orbital that has some N---N bonding (Figure 7).

Conclusion

We have synthesized Ni(II) complexes of a bulky β-diketiminate ligand and examined their solvatochromic behavior.

There is an equilibrium that shifts between the monomer, the dimer, and four-coordinate adducts, depending on solvent. Equilibrium constants and thermodynamic data are consistent with the proposed equilibria. Structural comparisons to the recently reported $L^{tBu}NiCl$[8] show that the structural differences can be attributed to the steric effects of the backbone substituents. Due to the leaving ability of the chloride groups in $[L^{Me}NiCl]_2$ and $L^{Me}NiCl_2Li(THF)(OEt_2)$, these compounds are expected to be useful precursors for three-coordinate Ni-(II) β-diketiminate complexes.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere by standard Schlenk techniques or in an M. Braun glovebox maintained at or below 1 ppm of O_2 and H_2O. Glassware was dried at 150 °C overnight. NMR data were recorded on a Bruker Avance 400 spectrometer (400 MHz) at 22 °C and referenced to residual protiated solvent (C_6D_5H, 7.15 ppm; $CDHCl$, 5.32 ppm; C_7D_7H, 2.09 ppm; C_4D_7HO, 1.73 ppm). IR spectra were recorded on a Mattson Instruments 6020 Galaxy Series FTIR using solution cells with CsF windows. UV−vis spectra were measured on a Cary 50 spectrophotometer, using screw-cap or Schlenk-adapted cuvettes. Solution magnetic susceptibilities were determined by the Evans method.[21] Elemental analyses were determined by Desert Analytics, Tucson, AZ.

Pentane, diethyl ether, tetrahydrofuran (THF), dichloromethane, and toluene were purified by passage through activated alumina and "deoxygenizer" columns obtained from Glass Contour Co. (Laguna Beach, CA). Deuterated benzene was first dried over CaH_2, then over Na/benzophenone, and then vacuum transferred into a storage container. Before use, an aliquot of each solvent was tested with a drop of sodium benzophenone ketyl in THF solution. Celite was dried overnight at 200 °C under vacuum. CD_2Cl_2 was dried over CaH_2 and used without further testing.

$[L^{Me}NiCl]_2$. $NiCl_2THF_{0.7}$ (230 mg, 1.28 mmol) and LiL^{Me} (0.60 g, 1.4 mmol) were dissolved in toluene (20 mL). The flask was heated at 100 °C for 24 h, and then the volatile materials were removed in vacuo. The blue residue was extracted with CH_2Cl_2 (10 mL), and the dark green solution was filtered through Celite. $[L^{Me}NiCl]_2$ was crystallized at −35 °C from CH_2Cl_2 and isolated as dark blue crystals in two crops (291 mg, 44% yield). ^1H NMR (CD_2Cl_2, 400 MHz): δ_H 58 (4H, $CH(CH_3)_2$ or m-Ar), 36 (4H, $CH(CH_3)_2$ or m-Ar), 9.7 (12H, CH(CH_3)₂), 8.5 (12H, CH(CH_3)₂), −27 (2H, p-Ar), −90 (6H, CH_3), −284 (1H, backbone-H) ppm. At room temperature in toluene-d_8 both monomer and dimer were observed in a ∼1:1 ratio on the basis of integration. ^1H NMR (tol-d_8, 400 MHz): δ_H 57 (4H, $CH(CH_3)_2$ or m-Ar), 45 (4H, $CH(CH_3)_2$ or m-Ar), 36 (4H, $CH(CH_3)_2$ or m-Ar), 22 (4H, $CH(CH_3)_2$ or m-Ar), 12 (24H, CH(CH_3)₂), 9.3 (24H, CH(CH_3)₂), −16 (2H, p-Ar), −27 (2H, p-Ar), −81 (6H, CH_3), −89 (6H, CH_3), −268 (1H, CH), −273 (1H, CH) ppm. ^1H NMR (THF-d_8, 400 MHz): δ_H 43 (4H, $CH(CH_3)_2$ or m-Ar), 25 ($CH(CH_3)_2$ or m-Ar), 6.5 (12H, CH(CH_3)₂), 6.1 (12H, CH(CH_3)₂), −19 (2H, p-Ar), −56 (6H, CH_3), −154 (1H, CH) ppm. UV−vis (solid): 580, 710 nm. UV−vis (CH_2Cl_2): 575 (680 M^{-1} cm^{-1}), 765 (2800 M^{-1} cm^{-1}) nm. UV−vis (toluene): 580 (1200 M^{-1} cm^{-1}), 740 (2800 M^{-1} cm^{-1}) nm. UV−vis (THF): 520 (1300 M^{-1} cm^{-1}), 670 (830 M^{-1} cm^{-1}) nm. μ_{eff} (CD_2Cl_2): 2.4 ± 0.3 μ_B/Ni. μ_{eff} (THF-d_8): 3.3 ± 0.3 μ_B/Ni. μ_{eff} (tol-d_8): 3.1 ± 0.3 μ_B/Ni. Anal. Calcd: C, 68.06; N, 5.47; H, 8.07. Found: C, 66.37; N, 5.58; H, 8.02.

(21) Schubert, E. M. *J. Chem. Ed.* **1992**, *69*, 62.

L^{Me}NiCl$_2$Li(THF)(OEt$_2$). NiCl$_2$THF$_{0.7}$ (3.23 g, 17.9 mmol) and LiL^{Me} (8.00 g, 18.8 mmol) were dissolved in THF (40 mL). The mixture was stirred at room temperature for 24 h. The volatile materials were removed in vacuo. The purple residue was dissolved in Et$_2$O (40 mL) and filtered through Celite. The purple Et$_2$O solution was concentrated (15 mL) and cooled to −35 °C. The product was isolated as dark purple crystals in three crops (8.4 g, 64% yield). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ_H 4 5 (4H, CHMe$_2$ or *m*-Ar), 26 (4H, CH(CH$_3$)$_2$ or *m*-Ar), 8.3 (12H, CH(CH_3)$_2$), 6.8 (12H, CH(CH_3)$_2$), −19 (2H, *p*-Ar), −62 (6H, CH_3), −81 (1H, CH) ppm. UV−vis (THF): 535 (910 M^{-1} cm^{-1}), 665 nm (400 M^{-1} cm^{-1}). μ_{eff} (THF-d_8): 3.1 ± 0.3 μ_B. Anal. Calcd: C, 63.45; H, 8.49; N, 4.00. Found: C, 63.42; H, 8.66; N, 3.96.

L^{Me}NiN(SiMe$_3$)$_2$. L^{Me}NiCl$_2$Li(THF)(OEt$_2$) (2.0 g, 2.9 mmol) and LiN(SiMe$_3$)$_2$ (0.49 g, 2.9 mmol) were dissolved in Et$_2$O (15 mL) and stirred for 12 h. The dark green solution was filtered through Celite, and all volatile materials were removed in vacuo. The residue was extracted with pentane (40 mL), filtered, concentrated to 20 mL, and cooled to −35 °C. L^{Me}NiN(SiMe$_3$)$_2$ was isolated as dark green needlelike crystals (1.3 g, 71%). L^{Me}NiN(SiMe$_3$)$_2$ can be synthesized from [L^{Me}NiCl]$_2$ using the same workup procedure, in 81% yield. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ_H 49 (4H, *m*-Ar), 35 (4H, CH(CH$_3$)$_2$), 8.1 (12H, CH(CH_3)$_2$), 5.5 (12H, CH(CH_3)$_2$), −3.9 (18H, Si(CH$_3$)$_3$), −11 (2H, *p*-Ar), −66 (6H, CCH$_3$) ppm. UV−vis (pentane): 655 nm (1200 M^{-1} cm^{-1}). μ_{eff} (C$_6$D$_6$): 2.5 ± 0.3 μ_B. Anal. Calcd: C, 66.10; N, 6.61; H, 9.36. Found: C, 65.49; N, 6.36; H, 9.13.

Supporting Information Available: Proton NMR and UV−vis spectra of complexes and crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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