Agostic Complexes

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Oxidation State Dependent Coordination Modes: Accessing an Amidate-Supported Nickel(I) δ-bis(C–H) Agostic Complex

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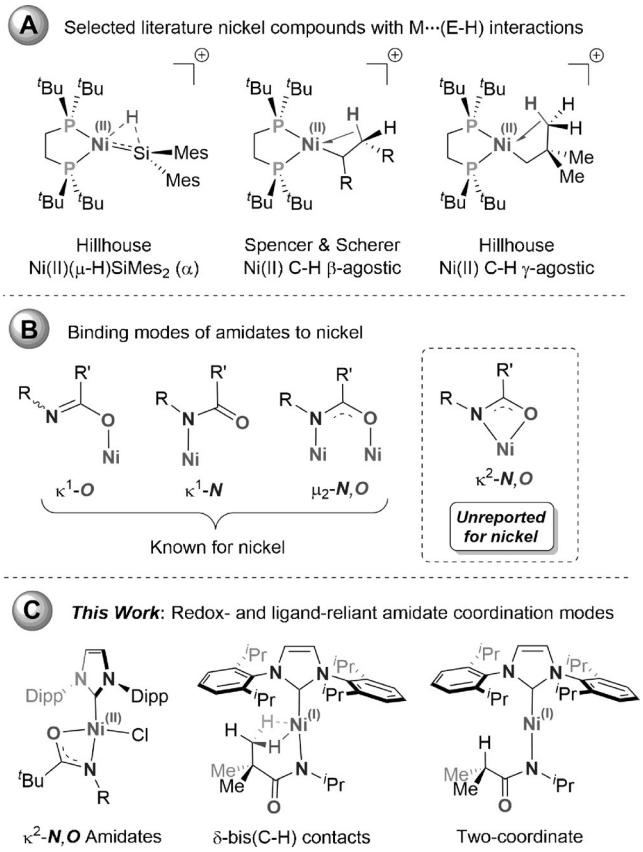
Abstract: *Amidate-supported two- and three-coordinate Ni^{I} complexes were synthesized by reduction of the corresponding Ni^{II} precursors. A dramatic change in binding mode is observed upon reduction from Ni^{II} to Ni^{I}. The Ni^{I} derivatives include an unprecedented Ni^{I} bis(C–H) agostic complex and a two-coordinate Ni^{I} complex.*

Transition metal (TM) systems incorporating transient metal-centered unsaturation have proven ubiquitous for myriad catalytic transformations including olefin metathesis,[1] olefin polymerization,[2] cross-coupling,[3] and hydrogenation.[4] Thus, low-coordinate complexes are often targeted as highly reactive species. In the absence of other stabilizing contacts, coordinatively unsaturated complexes can interact with sigma (σ) bonds (e.g. C–H bonds)[5] in a 3-center-2-electron (3c-2e) manner to form agostic or sigma complexes. From a mechanistic standpoint, understanding the interactions of σ-bonds with TMs is critical, as it is understood that these interactions are requisite for bond activation processes.[5a,6]

In particular, nickel C–H agostic species are invoked in nickel-catalyzed ethylene polymerizations,[7] and β-elimination processes.[8] Well characterized C–H agostic complexes for Ni^{0}[9] and Ni^{II}[10] have been reported. For instance, Spencer,[10a] Hillhouse,[10c] and Scherer[10e] have shown that cationic Ni^{II} C–H agostic complexes (Scheme 1 a) may be synthesized via protonation of Ni^{0} olefin complexes. To our knowledge, there are no reports of C–H agostic or σ-type complexes of Ni^{I}, though such species have been proposed in aryl C–H bond activation using Ni^{I}.[11]

Agostic and σ-complexes of other E–H (E = Si, B) bonds have been reported for Ni^{I}. McGrady and co-workers[12] reported a Ni^{I} η^2:η^2-bis(B–H) borohydride σ-complex formed from salt metathesis with $NaBH_4$. Multinuclear nickel(I)–silyl complexes with Si–H agostic interactions have also been isolated.[13] More recently, Uyeda and colleagues reported a dinickel(I) complex having geminal $\sigma_{Si\text{-}H}$ interactions, which are reactive intermediates in catalytic alkene hydrosilylation.[13c] These investigations containing Ni^{I} sigma complexes are important for understanding how Ni^{I} can activate element–H bonds.



Scheme 1. a) Ni compounds with M···(E–H) interactions, prepared by Hillhouse,[10c,16] Spencer,[10a] and Scherer.[10e] b) Binding modes of amidates to nickel. c) This work.

Recently, we have begun to explore the coordination chemistry of 1,3-*N*,*O* chelating ligands on late TMs.[14] In particular, we have found that monoanionic LX-type amidates $[RNCOR']^-$ can be used to advantage in the formation of square planar Rh^{I} complexes that can access a range of new amidate coordination modes.[14a] In addition, we disclosed an unsaturated Cp^*Ir^{III} phosphoramidate $[RN(P{=}O)(OR)_2]^-$ complex which promotes a range of E–H (E = H, B, C, Si) activation processes.[14b,c]

In light of these reports, we expanded our studies to nickel, with the goal of stabilizing low-coordinate nickel amidate species which might also facilitate the activation of E–H bonds. To date, amidates are known ligands for Ni^{II} and Ni^{III},[15] and the currently reported amidate binding modes for Ni are limited to κ^1-*N*,[15a–j] κ^1-*O*,[15f] and μ_2-*N*,*O*[15k] (Sche-

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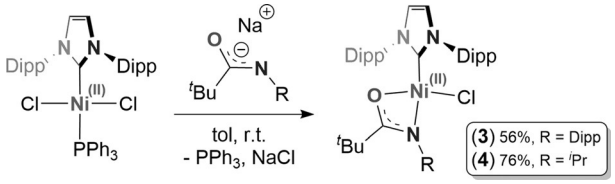
me 1b). Herein, we demonstrate the first examples of amidates bonded in a κ^2-*N,O* fashion to Ni^{II} which undergo changes in coordination mode upon reduction to Ni^{I} (Scheme 1c). In one case, the reduction yields a Ni^{I} amidate complex which contains δ-bis(C–H) agostic contacts; the first example of a well characterized Ni^{I} C–H agostic complex. These dual $\sigma_{C\text{-}H}$ contacts have also been studied by density functional theory (DFT) using natural bond order (NBO) and Atoms in Molecules (AIM) analyses. Studying agostic interactions within paramagnetic compounds is challenging without the use of standard NMR spectroscopic techniques,[17] thus agostic contacts in paramagnetic compounds are comparably less studied.

With the aim of selectively accessing unique binding modes based on rational ligand design, we first set out to explore the coordination chemistry of *N*-aryl and *N*-alkyl substituted amidates. Amide proligands **1** and **2** were chosen, in which both *N*-(Dipp) **1** and *N*-(^{i}Pr) **2** (Dipp = 2,6-diisopropylphenyl) substituted amides are supported by a pivaloyl backbone (RNHCO^{t}Bu).

Ni^{II} amidates are prepared from the easily accessed Ni^{II} starting material,[18] $Ni(IPr)(PPh_3)Cl_2$ (IPr = *N,N*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). Addition of Na[**1**] or Na[**2**] to $Ni(IPr)(PPh_3)Cl_2$ results in the loss of NaCl and PPh_3, affording distorted square planar complexes **3** and **4** in 56% and 76% yields, respectively (Scheme 2). Complexes **3** and **4** were characterized by multinuclear NMR spectroscopy, elemental analysis (EA), EI-MS, and single-crystal X-ray diffraction (XRD).



Scheme 2. Synthesis of complexes **3** and **4** via salt metathesis.

The solution $^{13}C\{^1H\}$ NMR spectra of **3** and **4** show carbonyl shifts ($\delta = 187.6$ and 186.5, respectively) characteristic of κ^2-*N,O*-amidate coordination.[14a,19] The κ^2-*N,O* assignment is corroborated in the solid state (Figure 1a,b), wherein the amidate N-atom in both structures is oriented *trans* to the bulky IPr coligand; **3** [C(1)-Ni(1)-N(1) 167.89(5)°] and **4** [C(1)-Ni(1)-N(1) 171.04(8)°]. We propose that this isomer is favored due to the sterically demanding amidate *N*-substituent. The N-Ni-O bite angles **3** [N(1)-Ni(1)-O(1) 68.48(5)°] and **4** [N(1)-Ni(1)-O(1) 68.58(7)°] are significantly strained from the ideal 90° for square planar complexes. Further analysis of the crystal structures of **3** and **4** reveals delocalization of charge through the O(1)-C(28)-N(1) π-system as seen by the similar O(1)–C(28) [**3**, 1.3098(17) Å; **4**, 1.321(2) Å] and N(1)–C(28) [**3**, 1.3035(18) Å; **4**, 1.305(3) Å] bond lengths. This data is consistent with our reports of κ^2-*N,O* amidates bound to other TMs.[14a,19]

Having established a reliable protocol for accessing Ni^{II} amidate precursors, we next sought to develop the chemistry

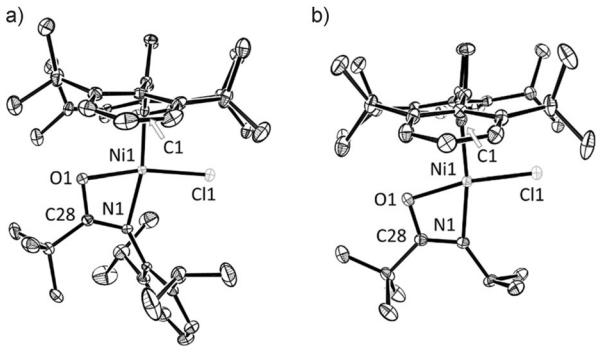
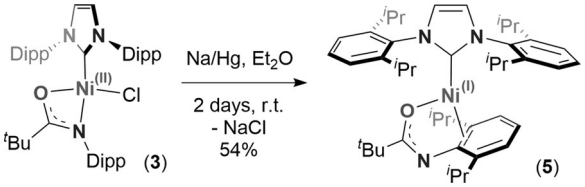


Figure 1. ORTEP depictions (ellipsoids at 50% probability, hydrogens omitted, selected bond lengths [Å] and angles [°]) of the solid-state structures of a) complex **3**: Ni1–Cl1 2.1563(4), Ni1–O1 1.9134(10), Ni1–N1 1.9215(12); C1-Ni1-N1 167.89(5), N1-Ni1-O1 68.48(5); b) complex **4**: Ni1–Cl1 2.1600(6), Ni1–O1 1.9206(15), Ni1–N1 1.9280(17); C1-Ni1-N1 171.04(8), N1-Ni1-O1 68.58(7).



Scheme 3. Accessing complex **5** from reduction of **3** with Na/Hg.

of related Ni^{I} species. Combining **3** and 1.1 equiv of (0.5%) Na/Hg amalgam results in the loss of NaCl and formation of **5**, which was isolated as a paramagnetic yellow crystalline solid in 54% yield (Scheme 3). Alternately, complex **5** can be prepared via salt metathesis using Na[**1**] and 0.5 equiv of Sigman's dimer[20] $[(IPr)Ni(\mu\text{-}Br)]_2$ in 85% yield (see the Supporting Information (SI)). A C_6D_6 solution of **5** displays a $\mu_{eff} = 1.71\ \mu_B$ (Evans method, 25 °C), consistent with a one electron paramagnet [c.f. $\mu_{(spin\text{-}only)} = 1.73\ \mu_B$]. X-ray analysis reveals a T-shaped amidate binding mode (Figure 2a), reminiscent of known Ni^{I} thiolate[21] and amide[22] complexes.

Similar to complex **3**, in complex **5**, bond lengths [C(28)–N(1) 1.306(3) Å] and [C(28)–O(1) 1.295(3) Å] are consistent with delocalization of charge throughout the amidate back-

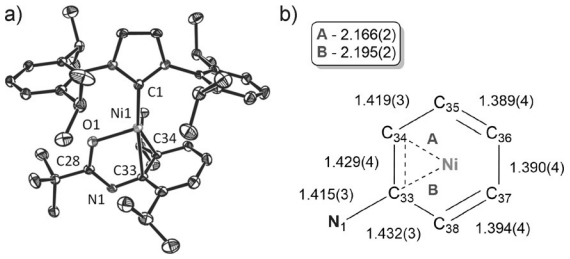
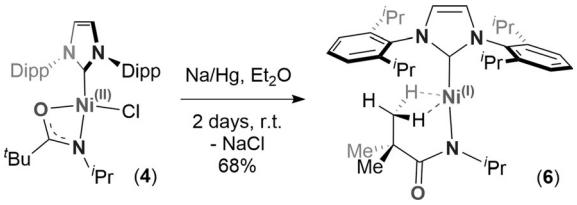


Figure 2. a) ORTEP depiction of the solid-state structure of **5** (ellipsoids at 50% probability, hydrogens omitted). Selected bond lengths [Å] and angles [°]: Ni1–C33 2.195(2), Ni1–C34 2.166(2), Ni1–O1 1.9633(18); C1-Ni1-C33 171.82(9), C1-Ni1-C34 141.93(10), C1-Ni1-O1 107.90(8). b) View orthogonal to amidate *N*-aryl plane showing bond lengths [Å] of aryl ring and nickel η^2-aryl contacts.

bone. Consistent with the change in oxidation state, the Ni–O bond distance [Ni(1)–O(1) 1.9633] is somewhat lengthened in **5** relative to **3** [Δ(Å) = 0.0499(21)]. Bond distances [C(33)–C(34) 1.429(4) Å] and [C(33)–C(38) 1.432(3) Å] are elongated from the proteo-ligand [c.f. 1.403(3) Å, see SI], indicating some back-bonding into the aryl ring (Figure 2b).

Having accessed the π-stabilized Ni^{I} *N*-aryl substituted amidate complex **5**, we were eager to prepare the Ni^{I} *N*-alkyl substituted amidate from complex **4**. The single electron reduction of **4** (under identical conditions as above) affords complex **6** as a paramagnetic yellow crystalline solid in 68% yield (Scheme 4).[23] Like complex **5**, **6** can also be independently prepared via salt metathesis using Na[**2**] and 0.5 equiv of Sigman's dimer[20] in 95% yield (see SI). Evans measurements (μ_{eff} = 1.87 μ_B, C_6D_6 at 25 °C) further support the preparation of a metalloradical having one unpaired electron.



Scheme 4. Accessing complex **6** from reduction of **4** with Na/Hg.

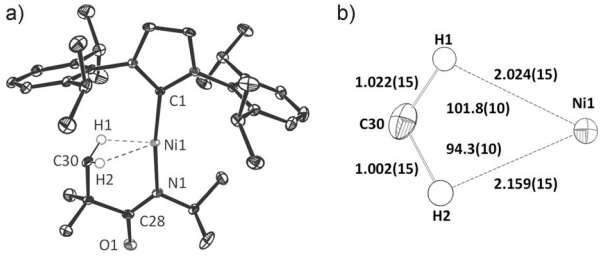


Figure 3. a) ORTEP depiction of the solid-state structure of **6** (ellipsoids at 50% probability, hydrogens omitted). H1 and H2 were freely located and refined from the electron density map. Selected bond lengths [Å] and angles [°]: Ni1–C1 1.9119(9), Ni1–N1 1.9149(8), Ni1–C30 2.4476(10), C28–N1 1.3392(13), C28–O1 1.2515(12); N1-Ni1-C1 172.12(4). b) View orthogonal to C(30)-H-Ni(1) agostic contacts showing bond lengths [Å] and angles [°].

Importantly, single-crystal X-ray analysis (Figure 3a) indicates the formation of a κ^1-*N* bound species, having dual supporting δ-bis(C–H) agostic (or bifurcated η^3-H_2C) contacts resulting in a pseudo-T-shaped geometry. These bifurcated η^3-H_2C interactions are rare for sp^3 C–H agostic complexes, but have been noted previously.[24] To our knowledge, complex **6** represents the first example of a Ni^{I} C–H agostic complex. It is noteworthy that the data was of sufficient quality allowing for free location and refinement of the *t*Bu hydrogen atoms, giving [Ni(1)–H(1) 2.024(15)] and [Ni(1)–H(2) 2.159(15) Å], respectively (Figure 3b). These Ni–H contacts and C(30)-H-Ni angles are within the values accepted for TM C–H agostic complexes (Figure 3b).[5a] Unlike complexes **3**–**5**, the amidate bond lengths [C(28)–N(1) 1.3392(13) Å] and [C(28)–O(1) 1.2515(12) Å] in **6** suggest localization of charge at N(1). Similar to related Ni^{I} amido[25] and alkyl[20b] structures, the C(1)-Ni(1)-N(1) angle of 172.12(4)° indicates quasi-linearity.

The gas-phase geometry of **6** was calculated and optimized using DFT (Figure 4a).[26] The optimized geometry of **6**

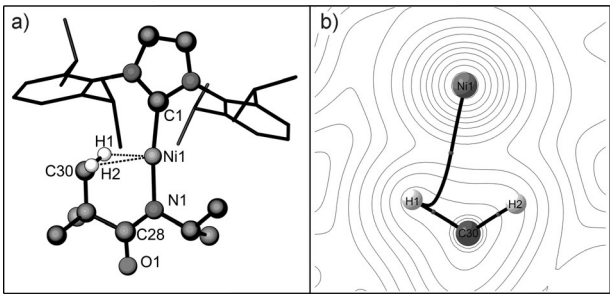


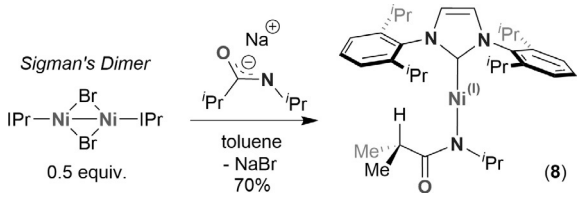
Figure 4. a) DFT-optimized structure of **6**. b) AIM contour map of the electron density in the Ni1-H1-C30 plane of **6** showing bcps as gray dots and bond paths as black lines.

differs from the X-ray structure in that the NHC imidazole and amidate O(1)-C(28)-N(1) planes deviate from coplanarity [29.3°],[27] but the N(1)–Ni(1) [1.900 Å], C(1)–Ni(1) [1.922 Å] bond lengths and C(1)-Ni(1)-N(1) angle [172.6°] are consistent with solid state observations. Two inequivalent C–H···Ni interactions are observed [d(H(1)···Ni(1)) = 2.119 Å; d(H(2)···Ni(1)) = 2.189 Å]. The elongation of the C(28)–H(1) and C(28)–H(2) bonds relative to those in the non-interacting *t*Bu groups was small [C(28)–H(1): 0.011 Å; C(28)–H(2): 0.006 Å], indicating the weak nature of the C–H···Ni interactions. Optimization of hydrogen atom positions in **6** while constraining heavy atom positions to those determined by XRD did not result in significantly larger C–H bond elongation (see SI). NBO and AIM analyses were applied to **6** to substantiate the putative bis-σ_{C-H} bonding mode. Second order perturbation analysis performed in the NBO analysis reveals donation from the β-spin C–H σ-bond orbital to an sd hybrid on the Ni^{I} center [$E^{(2)}$: 5.7 kcal mol^{-1} (H1), 5.1 kcal mol^{-1} (H2)]. These interactions are non-negligible, but weak compared to those reported previously for Ni^{II} agostic interactions.[10e] AIM theory is useful in cases where bonding modes are ambiguous, as searching for bond critical points (bcps) in electron density maps provides a criterion for the presence of a chemical bond. The electron density topology in **6** in the plane of the CH_2···Ni motif is shown in Figure 4b. A bond critical point was located for the C(30)–H(1)···Ni(1) interaction, whereas no bcp was found between Ni and the more distal C(30)–H(2) bond. The H(1)–Ni(1) bond critical point properties (see SI) are similar to those found for weak C–H···Pd interactions found in a series of unsaturated Pd^{II} phosphine complexes by Hartwig and coworkers.[28]

Despite the lack of a bcp, the similarity in $E^{(2)}$ values for the two C–H···Ni interactions suggests that the C(30)–H(2) bond is interacting with Ni in the same fashion, and the absence of bcps for agostic interactions is a phenomenon that has been noted previously.[29] Taken together, the NBO and

AIM data are consistent with our assignment of a bis-$\sigma_{C\text{-}H}$ binding motif.

Crabtree et al. have reported similar weak C–H agostic interactions to **6** in an Ir^{III} system when a ligand ^{t}Bu group was brought into close proximity.[30] When an ^{i}Pr group was employed, the agostic interaction was no longer evident by NMR spectroscopy, nor in the solid-state due to several competing ligand-ligand interactions. To similarly probe the C–H agostic interactions in our system, we prepared amide **7**, (^{i}Pr)NHCO^{i}Pr. Combining Sigman's dimer (0.5 equiv) and Na[**7**] affords paramagnetic pale yellow crystals of **8** in 70% yield (Scheme 5).[23] Evans method measurements of **8** (μ_{eff} = 2.20 μ_B, C_6D_6, 25 °C) are again consistent with a one-electron species. The large range of magnetic moments for two coordinate TM species has been addressed previously.[31]



Scheme 5. Generation of complex **8** through reaction of Na[**7**] with 0.5 equiv of Sigman's dimer.

X-ray crystallographic analysis of **8** confirms a structure (Figure 5) nearly identical to complex **6** (Figure 3a). However, in the absence of a quaternary carbon α to the carbonyl, a methine C–H bond is parallel to the nickel-nitrogen bond, eliminating any agostic contributions. Thus, **8** is formally a two-coordinate Ni^I species [C(1)-Ni(1)-N(1) 169.0(5)°]. This example illustrates an unusual case where the removal of steric bulk from complex **6** (^{t}Bu) to **8** (^{i}Pr) results in a lower-coordinate species. Based on these results we propose that the weak C–H agostic interactions observed in complex **6** are due to a steric bias.[32]

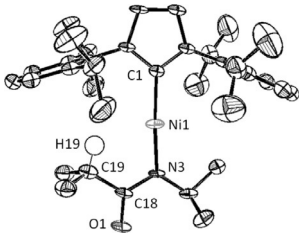
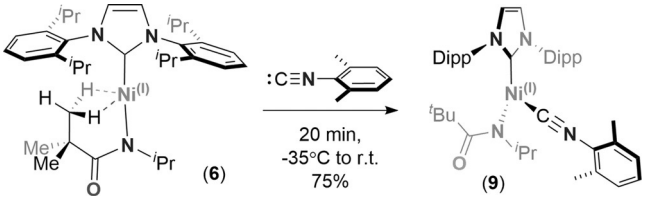


Figure 5. ORTEP depiction of the solid-state structure of **8** (ellipsoids at 50% probability, hydrogens omitted). Selected bond lengths [Å] and angles [°]: Ni1–N3 1.85(2), N3–C18 1.381(19), O1–C18 1.255(13), H19–Ni1(calc) 2.295; C1-Ni1-N3 169.0(5).

Our calculations on complex **6**, and the observation that complex **8** does not have agostic interactions, are both consistent with weak C–H agostic interactions from H(1) and H(2) to the low-coordinate Ni^I center of complex **6**. In an effort to displace the weak agostic contacts in **6** to afford a three coordinate Ni^I species, we next probed the reactivity of **6** with two-electron donors. Markedly, no addition reaction was observed by NMR spectroscopy between **6** and a variety of Lewis bases including THF, CH_3CN, pyridine, PPh_3, and PCy_3 at room temperature or with extensive heating (110 °C, 4 days). Moreover, recrystallization of **6** at −35 °C in the presence of excess THF, pyridine, PPh_3, or PCy_3 did not result in an increase of coordination number to the Ni^I metal center. However, the joint σ-donating/π-accepting isonitrile CNXyl (Xyl = 2,6-dimethylphenyl) was observed to rapidly react with **6**, affording an orange solution of the three coordinate Ni^I complex **9** in 75% yield (Scheme 6).



Scheme 6. Reaction of **6** with isonitrile CNXyl at low temperature affords **9**.

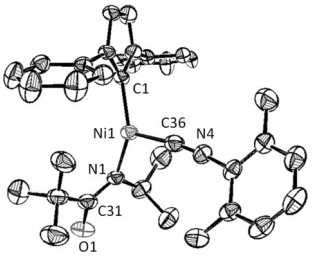


Figure 6. ORTEP depiction of the solid-state structure of **9** (ellipsoids at 50% probability, hydrogens, second molecule of **9**, solvent, and NHC(^{i}Pr) groups omitted) Selected bond lengths [Å] and angles [°]: Ni1–Ni1 1.952(5), Ni1–C36 1.856(6), C36–N4 1.168(7); C1-Ni1-C36 105.1(2), C1-Ni1-N1 147.3(2).

Evans method measurements (μ_{eff} = 1.58 μ_B, C_6D_6, 25 °C) are consistent with a one-electron paramagnet. Amidate distances [C(31)–N(1) 1.324(8) Å] and [C(31)–O(1) 1.276-(7) Å] (Figure 6) suggest localization of charge at the amidate N(1). The metal center back-donates to the isonitrile π*(C≡N), as evidenced by the red shifted [ν_{CN} = 2063 cm^{-1}] infrared (IR) stretching frequency [c.f. 2123 cm^{-1}; free isonitrile]. The ready coordination of π-accepting CNXyl to the electron rich Ni^I metal center points towards opportunities in small molecule activation.

We have synthesized a variety of nickel amidates in the +1 and +2 oxidation states. Our findings include the first examples of κ^2-*N*,*O* amidate nickel complexes (**3** and **4**), a rare two-coordinate nickel complex (**8**) and the first rigorously characterized Ni^I C–H agostic complex (**6**). Of importance is the difference in binding modes accessed for the simple amidate ligands, as well as the effect of oxidation state on these binding modes. These complexes highlight the coordinative flexibility of 1,3-*N*,*O* chelating ligands. Future work in our group focuses on the application of these low-coordinate Ni^I complexes in small molecule activation processes.

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