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Terminal Amido and Imido Complexes of Three-Coordinate Nickel

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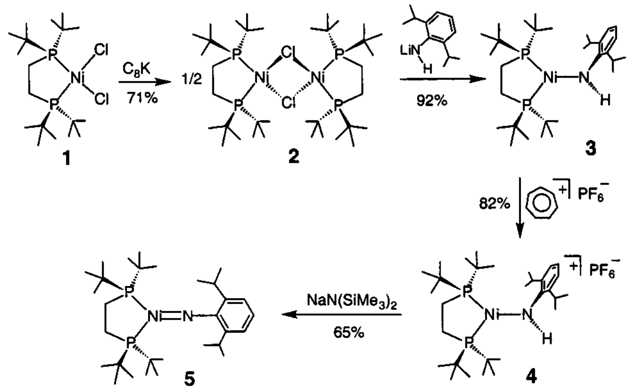
The chemistry of late-transition-metal complexes possessing amido (NR_2^-) and imido (NR^{2-}) ligands is much less developed than that of the early- and mid-transition elements.[1] This is particularly true of the nickel triad, where the contrast between these hard, nitrogen-donor ligands and the soft, electron-rich metals is considered to be energetically destabilizing and is exacerbated by the general lack of stabilizing π-donor interactions involving the ligand lone pair(s) that are commonly found with terminal amides and imides of the early- and mid-transition metals. There has been increasing research activity in this area by us and others,[2−4] and it has been demonstrated that amido complexes of Ni and Pd play key roles in a range of important reactions.[5] Imido complexes of the Ni triad are limited to a few bimetallic and trimetallic examples possessing bridging (μ_2 and μ_3) NR^{2-} moieties.[6,7] Stone's 1970 report of $(Ph_2MeP)_2M{=}NCF_2CFHCF_3$ (M = Pd, Pt) complexes incorporating an imido ligand with a strongly electron-withdrawing fluoropropyl substituent provides the only examples of terminal Group 10 imido derivatives, although characterization was limited to ^1H and ^{19}F NMR spectroscopic data, and the exact nature of these compounds is unclear.[8] To date, the only structurally characterized examples of late-metal complexes possessing terminal imido ligands are Bergman's Ir derivatives of the general formulation $Cp^*Ir{\equiv}NR$ (R = aryl, alkyl, silyl).[9]

Scheme 1



In the course of our studies of the reactions of aryl azides with Ni(II) alkyls to give amide moieties,[2] we have noted that azides with bulky substituents (i.e., mesityl azide) yield products that suggest involvement of nitrene (or imido) intermediates.[10] Moreover, a recent report from Jones and Vicic presented compelling evidence that a reactive terminal sulfido complex of Ni(II) was generated on thermolysis of $(PR_2CH_2CH_2PR_2)Ni(SH)(Ph)$, although it was unstable with respect to dimerization via Ni−S−Ni bridges.[11] Herein we report a successful synthetic strategy for the preparation of monomeric, three-coordinate nickel complexes containing the chelating 1,2-bis(di-*tert*-butylphosphino)ethane (dtbpe) ligand and an amido or imido nitrogen-donor ligand, along with the structural characterization of the first terminal imido complex of nickel, a species which features a nickel−nitrogen multiple bond.

Our initial approach to preparing a terminal imido complex of Ni(II) involved a modification of Jones' method for the synthesis of the transient "$L_2Ni{=}S$"(described above).[11] Specifically, we wished to effect deprotonation or dehydrohalogenation of an appropriate Ni(II) amide (i.e., $L_xNi(NHR)X$). To inhibit imido bridging, we used bulky substituents in both the ancillary phosphine ligand (dtbpe) as well as at nitrogen. Reaction of $(dtbpe)NiCl_2$ (**1**)[12] with 1 equiv of lithium 2,6-di-*iso*-propylphenylamide ($LiNH(2,6\text{-}(CHMe_2)_2C_6H_3)$) gives a mixture of products, including paramagnetic species. Reduction of **1** with KC_8 in THF at −35 °C gives red crystals of the Ni(I) monochloride $[(dtbpe)NiCl]_2$ (**2**) in 71% yield.[13] Related Ni(I) chlorides of chelating diphosphine ligands have been reported.[14] In contrast to **1**, toluene solutions of **2** react cleanly at −35 °C with Et_2O solutions of lithium 2,6-di-*iso*-propylphenylamide to afford the paramagnetic arylamido complex $(dtbpe)Ni\{NH(2,6\text{-}(CHMe_2)_2C_6H_3)\}$ (**3**) as beet-red crystals in 92% yield (Scheme 1). This Ni(I) complex has been characterized by elemental analysis, IR and ^1H NMR spectroscopic methods,[13] and by single-crystal X-ray diffraction.[15] The molecular structure of **3** features a planar, three-coordinate

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[13] See the Supporting Information for complete spectroscopic and analytical details for **2**−**5** and solution magnetic moments for **2** and **3**.

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[15] Crystal data for **3**: $C_{30}H_{58}NNiP_2$, orthorhombic, $P2_12_12_1$, $a = 10.8603(9)$ Å, $b = 16.6536(14)$ Å, $c = 17.3090(14)$ Å, $Z = 4$, μ(Mo Kα) = 7.40 cm^{-1}, $T = 100$ K, $V = 3130.6(4)$ Å^3, $\lambda = 0.71073$ Å, $D_c = 1.174$ mg/mm^3. Of 19258 data collected (red crystal, $1.70 \le \theta \le 28.29$) 7365 were independent and observed with $I > 2\sigma(I)$. Flack *x* parameter = −0.004, 0.010 esd. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were idealized except for the H attached to N, which was located and refined isotropically. $R(F) = 0.035$ and $R(wF^2) = 0.063$.

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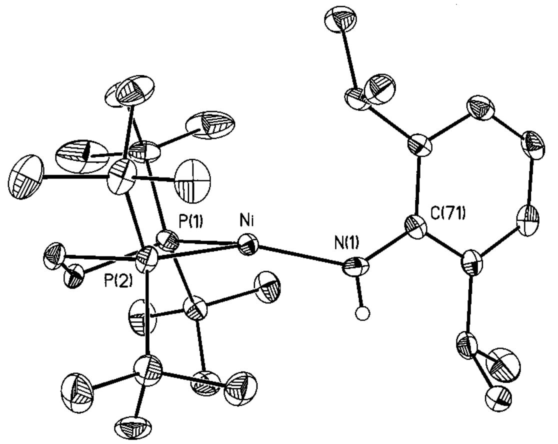

Figure 1. A perspective view of the molecular structure of **3** showing the atom-labeling scheme. H-atoms (except H(1)) have been omitted for clarity. Selected metrical parameters: Ni−P(1) = 2.2094(8), Ni−P(2) = 2.2012(7), Ni−N(1) = 1.881(2), N(1)−C(71) = 1.373(3), N(1)−H(1) = 0.82(2) Å; P(1)−Ni−P(2) = 91.91(3), P(1)−Ni−N(1) = 123.18(7), P(2)−Ni−N(1) = 140.41(7), Ni−N(1)−C(71) = 134.6(2), Ni−N(1)−H(1) = 111(2), C(71)−N(1)−H(1) = 109(2)°.

nickel and a terminal, planar amido ligand (Ni−N(1) = 1.881(2) Å) (see Figure 1). The {P(1), P(2), Ni} and {N(1), C(71), H(1)} planes are orthogonal with a 91° dihedral angle. The Ni−N distance is comparable to those found for other terminal Ni amides, such as the related three-coordinate Ni(I) complex $(PPh_3)_2$-Ni{$N(SiMe_3)_2$} (Ni−N = 1.88(1) Å)[3a] and several diverse Ni(II) examples having $(Ni{-}N)_{avg} \approx 1.88$ Å (ranging from 1.93 to 1.82 Å).[3c−e,h,4b]

Recognizing that moving from the Ni(I) to Ni(II) manifold should prove advantageous in preparing a terminal imido moiety since a three-coordinate, d^8 species could be stabilized by ligand-to-metal π-donation, we sought to chemically oxidize **3** by one electron. Common oxidants such as Cp_2Fe^+, Ag^+, or I_2 gave myriad decomposition products, consistent with observations that these oxidants are competent in triggering oxidatively induced reductive elimination from alkyl Ni(II) amides and alkoxides via Ni(III) intermediates.[2,16] A cyclic voltammogram of a solution of **3** (THF/TBAH) shows two closely spaced, quasireversible oxidations at $E_{1/2} = -0.90$ V and −0.52 V (relative to Fc/Fc^+) for the Ni(I)/Ni(II) and Ni(II)/Ni(III) couples, respectively. These electrochemical data suggest that to effect the oxidation of **3** to Ni(II), a very weak oxidant whose potential lies in this narrow range is required to avoid over-oxidation to Ni(III). Inspection of tabulations of oxidation potentials of reagents indicated a good choice might be tropylium, having $E^{0'} = -0.65$ V in acetonitrile.[17] Accordingly, oxidation of THF solutions of **3** with tropylium hexafluorophosphate at −35 °C gives the diamagnetic Ni(II) amido salt [(dtbpe)Ni{$NH(2,6\text{-}(CHMe_2)_2C_6H_3)$}$^+$][$PF_6^-$] (**4**) as dark-green crystals in 82% isolated yield (Scheme 1). **4** was characterized by elemental analysis, IR and NMR (^{1}H, ^{13}C, ^{19}F, ^{31}P) spectroscopy,[13] and single-crystal X-ray diffraction. Although disordered, the structure of **4** shows well-separated cations and anions; the coordination geometry about Ni is similar to that observed in **3**, with a Ni−N bond length of 1.768(14) Å.[18]

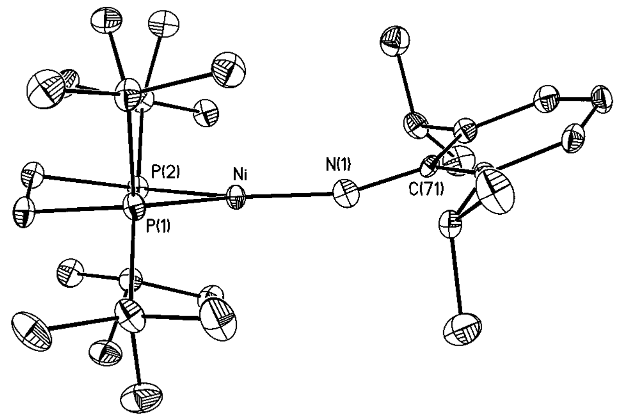

Figure 2. A perspective view of the molecular structure of **5** showing the atom-labeling scheme. H-atoms have been omitted for clarity. Selected metrical parameters: Ni−P(1) = 2.1815(8), Ni−P(2) = 2.1887(8), Ni−N(1) = 1.702(2), N(1)−C(71) = 1.355(3) Å; P(1)−Ni−P(2) = 90.94(3), P(1)−Ni−N(1) = 132.50(7), P(2)−Ni−N(1) = 136.46(7), Ni−N(1)−C(71) = 162.8(2)°.

Treatment of THF solutions of **4** with sodium bis(trimethylsilyl)amide at −35 °C results in deprotonation of **4** at nitrogen, affording emerald-green crystals of the diamagnetic arylimido complex (dtbpe)Ni{$N(2,6\text{-}(CHMe_2)_2C_6H_3)$} (**5**) in 65% isolated yield. **5** was characterized by elemental analysis and IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy,[13] and its monomeric structure was confirmed by single-crystal X-ray diffraction.[19]

The molecular structure of **5** is shown in Figure 2. The most salient structural features are a planar, three-coordinate nickel(II) center and a terminal imido ligand with a short Ni−N(1) bond (1.702(2) Å). The Ni−N(1) bond length is comparable to the value of 1.68 Å predicted by Pauling for a Ni−N bond order of two[20] and is consistent with a symmetry-allowed π-bonding interaction between a nitrogen lone pair and the empty in-plane Ni d-orbital of π-symmetry. The imido ligand is significantly bent at nitrogen (Ni−N(1)−C(71) = 162.8(2)°) out of the Ni coordination plane (as required by the in-plane π-bond). Steric interactions between the imido's aryl substituent and the phosphine's *tert*-Bu groups might be responsible for preventing this angle from being more acute.

In summary, we have shown that a cationic Ni(II)−amido complex can serve as a precursor to a Ni(II)−imido complex containing a terminal imido moiety. It is noteworthy that while **5** is air-sensitive, it does not exhibit unusual thermal instability (in fact, it is thermally robust), and it is somewhat surprising that related three-coordinate complexes of Ni(II) with hard π-donor ligands have not been previously prepared. We are currently exploring the reaction chemistries of these three-coordinate nickel complexes.

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Supporting Information Available: Experimental, spectroscopic, and analytical details; crystallographic details; atomic coordinates; bond angles and distances; anisotropic thermal parameters; hydrogen atom coordinates; least-squares planes; torsion angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] The structure of **4** suffered from conformational disorder of the *tert*-Bu and CH_2 groups of the dtbpe ligand, and the *iso*-Pr groups of the amido ligand. A highly disordered THF of solvation was also confined in the asymmetric unit, resulting in a poor quality structure. Details are included as Supporting Information, but not reported here, except for selected metrical parameters for the inner coordination sphere of Ni for comparison with **3** and **5**.

[19] Crystal data for **5**: $C_{30}H_{57}NNiP_2$, triclinic, $P\bar{1}$, $a = 10.8639(10)$ Å, $b = 11.1092(10)$ Å, $c = 14.5704(14)$ Å, $\alpha = 67.700(2)°$, $\beta = 72.419(2)°$, $\gamma = 75.351(2)$ °, $Z = 2$, μ(Mo Kα) = 7.56 cm^{-1}, $T = 100$ K, $V = 1531.8(2)$ Å^3, $\lambda = 0.71073$ Å, $D_c = 1.198$ mg/mm^3. Of 8973 data collected (emerald green crystal, $1.55 \le \theta \le 28.28$) 6199 were independent and observed with $I > 2\sigma(I)$. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were placed in idealized positions. $R(F) = 0.0475$ and $R(wF^2) = 0.0947$.

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