

# A Two-Coordinate Nickel Imido Complex That Effects C–H Amination

Carl A. Laskowski,<sup>†</sup> Alexander J. M. Miller,<sup>‡</sup> Gregory L. Hillhouse,<sup>\*,†</sup> and Thomas R. Cundari<sup>\*,§</sup>

<sup>†</sup>Gordon Center for Integrative Science, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, United States

<sup>‡</sup>Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, United States

<sup>§</sup>Center for Advanced Scientific Computing and Modeling, Department of Chemistry, University of North Texas, Denton, Texas 76203, United States

**S** Supporting Information

**ABSTRACT:** An exceptionally low coordinate nickel imido complex, (IPr\*)Ni=N(dmp) (**2**) (dmp = 2,6-dimesitylphenyl), has been prepared by the elimination of N<sub>2</sub> from a bulky aryl azide in its reaction with (IPr\*)Ni( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>) (**1**). The solid-state structure of **2** features two-coordinate nickel with a linear C–Ni–N core and a short Ni–N distance, both indicative of multiple-bond character. Computational studies using density functional theory showed a Ni=N bond dominated by Ni(d $\pi$ )–N(p $\pi$ ) interactions, resulting in two nearly degenerate singly occupied molecular orbitals (SOMOs) that are Ni–N  $\pi^*$  in character. Reaction of **2** with CO resulted in nitrene-group transfer to form (dmp)NCO and (IPr\*)Ni(CO)<sub>3</sub> (**3**). Net C–H insertion was observed in the reaction of **2** with ethene, forming the vinylamine (dmp)NH(CH=CH<sub>2</sub>) (**5**) via an azanickelacyclobutane intermediate, (IPr\*)Ni{N,C: $\kappa^2$ -N(dmp)CH<sub>2</sub>CH<sub>2</sub>} (**4**).

Transition-metal complexes containing multiple bonds with main-group elements constitute an important class of organometallic reagents, exemplified by the active species in olefin and alkane metathesis, aziridination, epoxidation, vicinal diamination and oxyamination, and N<sub>2</sub> reduction to ammonia.<sup>1–6</sup> A prerequisite for transition-metal-element  $\pi$ -donor multiple bonding is the availability of empty d orbitals on the metal center that are of the correct symmetry and energetic disposition to accept  $\pi$ -electron density from the main-group element. Traditional synthetic strategies have employed high oxidation states and/or coordinatively unsaturated complexes, both of which lower the valence-electron count and increase the number of unoccupied metal d orbitals. Extension of these principles suggests that two-coordinate complexes might be well-suited for the formation of multiple bonds, and because of their extreme coordinative unsaturation, such complexes should show enhanced reactivity.

The accessibility of low-coordinate complexes supported by a single neutral N-heterocyclic carbene (NHC) has accelerated our research efforts directed toward two-coordinate late-metal complexes.<sup>7</sup> Utilizing the massive steric profile of IPr\* [IPr\* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene],<sup>8</sup> we were able to prepare (IPr\*)Ni( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>) (**1**) via heterogeneous Mg reduction of (IPr\*)(THF)NiCl<sub>2</sub> in the presence of toluene (Scheme 1). Installation of an imide (RN<sup>2–</sup>) fragment is often achieved through dinitrogen extrusion from organoazides

(N<sub>3</sub>R).<sup>1,9,10</sup> Protection of the Ni=N bond is crucial, and “capping” of the (IPr\*)Ni subunit was accomplished with a large terphenyl-substituted azide. Reaction of **1** with N<sub>3</sub>(dmp) (dmp = 2,6-dimesitylphenyl) resulted in vigorous N<sub>2</sub> evolution and the clean formation of (IPr\*)Ni=N(dmp) (**2**), a 14-electron species, as an olive-green solid (Scheme 1). **2** was characterized by X-ray diffraction, superconducting quantum interference device (SQUID) magnetometry, elemental analysis, and <sup>1</sup>H NMR spectroscopy. While **2** decomposes in CH<sub>2</sub>Cl<sub>2</sub> solution, it is stable in toluene or Et<sub>2</sub>O and does not change color or exhibit signs of instability in THF.

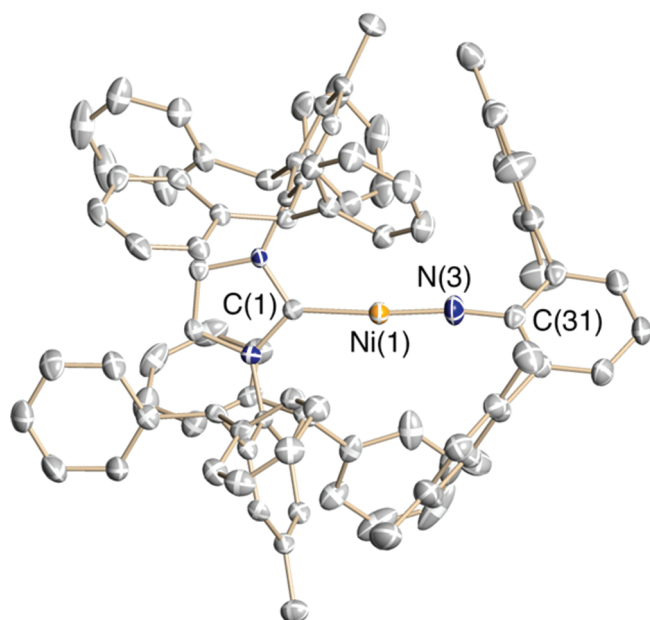
X-ray studies of **2** showed a rigorously two-coordinate Ni center whose very short Ni–N bond of 1.663(3) Å is among the shortest reported to date (Figure 1).<sup>11–13</sup> Other than the two coordination points, there are no short, stabilizing contacts between Ni and the IPr\* or (dmp)N<sup>2–</sup> ligands. The linear C–Ni–N [174.24(13)°] core is as expected for a coordination number of 2, and the linear [171.6(3)°] Ni–N–C unit reflects  $\pi$  bonding between the imido ligand and nickel(II). A dihedral angle of ~41°, defined by the NHC core and the central C<sub>6</sub>H<sub>3</sub> aromatic group of dmp, positions the dmp group in a twisted conformation relative to IPr\*.

While three-coordinate Ni(II) imido complexes have singlet ground states,<sup>11,13</sup> complex **2** exhibits a solid-state magnetic moment of 2.77 $\mu_B$  (SQUID, 60–300 K; Figure 2), indicative of the triplet ground state of a high-spin d<sup>8</sup> Ni center with a large zero-field splitting ( $D = 24 \text{ cm}^{-1}$ ). The high-spin configuration of **2** magnifies the impact of the frontier orbitals' composition on bond order, as electrons are promoted to antibonding orbitals, providing a formal Ni=N double bond.

Orbital mixing accounts for the short Ni–N distance in **2**, a multiple bond in which  $\pi$  bonding dominates. An otherwise  $\sigma^*$  3d<sub>z<sup>2</sup></sub> Ni orbital is greatly stabilized by symmetry-allowed mixing with the 4s Ni orbital, increasing its nonbonding character.<sup>14</sup> Additionally, the short Ni–N distance allows for a strong  $\pi$  interaction, which destabilizes the  $\pi^*$  molecular orbitals (Ni 3d<sub>xz</sub> and 3d<sub>yz</sub> character) beyond the “nonbonding” 3d<sub>z<sup>2</sup></sub> orbital. The resulting orbital ordering, in which the two nearly degenerate singly occupied molecular orbitals ( $\Delta = 0.03 \text{ eV}$ ) are  $\pi^*$  in nature, similar to Fe{N(*tert*-butyl)<sub>2</sub>}<sub>2</sub>,<sup>15</sup> was corroborated by density functional theory (DFT) calculations at the B3LYP/6-311+G-(d) level (Figure 2)<sup>16</sup> and gives a formal Ni–N bond order of 2.

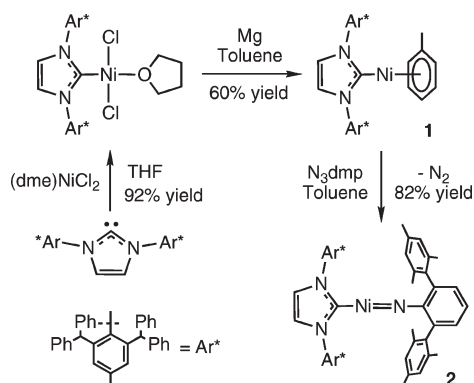
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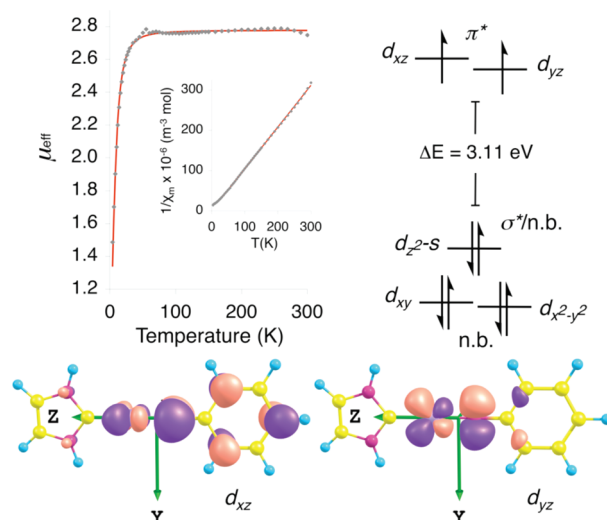
**Figure 1.** Perspective view of the molecular structure of **2** (50% thermal ellipsoids). H atoms and cocrystallized solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **2**: Ni(1)–N(3), 1.663(3); C(1)–Ni(1), 1.917(3); N(3)–C(31), 1.351(4); C(1)–Ni(1)–N(3), 174.24(13); Ni(1)–N(3)–C(31), 171.6(3).

**Scheme 1. Synthesis of a Two-Coordinate Nickel Imido Complex through Dinitrogen Elimination from 2,6-Dimesitylphenyl Azide**



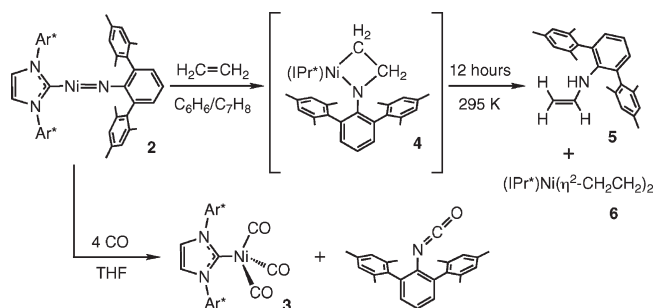
Different bonding situations are found in the Ni(II) bis(amido) complexes Ni{NMe<sub>2</sub>(BMes<sub>2</sub>)<sub>2</sub>}<sub>2</sub> and Ni{NHC<sub>6</sub>H<sub>3</sub>(2,6-(isopropyl)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>}<sub>2</sub>,<sup>17</sup> where standard Ni–N single-bond distances<sup>11,18</sup> of 1.867(2)–1.818(2) Å have been observed. The lack of significant multiple bonding in the latter complex is possibly a consequence of the steric requirements of the amido substituents, which result in an eclipsed conformation that requires the nitrogen lone pairs to donate into the same Ni d orbital.

Group transfer of the imido functionality in **2** occurred in the presence of CO or ethene (Scheme 2). Exposure of **2** to 1 atm CO resulted in the rapid formation of (IPr<sup>\*</sup>)Ni(CO)<sub>3</sub> (**3**;  $\nu(\text{CO}) = 2048, 1968 \text{ cm}^{-1}$ ) and the aryl isocyanate (dmp)NCO. Related group transfers to give aryl isocyanates are known for several late-metal imides.<sup>19</sup> Complex **2** also mediated net C–H insertion into ethene (1 atm), forming (via an observable intermediate **4**; see below) the vinylamine (dmp)NH(CH=CH<sub>2</sub>) (**5**) during the



**Figure 2.** (top left) Effective magnetic moment of **2** at 4–300 K and 0.5 T. The inset shows the inverse molar magnetic susceptibility (4–300 K at 0.5 T). The raw data are shown as gray  $\blacklozenge$  and the  $\mu_{\text{eff}}$  fits as red lines. (top right) Qualitative MO diagram for **2**. (bottom)  $\pi^*$  SOMO orbitals of **2**.

**Scheme 2. Reactions of 2 with Carbon Monoxide and Ethene That Result in Nitrene-Group Transfer**



course of 12 h at room temperature. The resulting Ni(0) fragment is trapped by ethene to give a labile 16-electron bis(ethene) complex, (IPr<sup>\*</sup>)Ni( $\eta^2$ -CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (**6**), which was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and single-crystal X-ray diffraction.

<sup>1</sup>H and <sup>13</sup>C NMR studies conducted immediately after combining ethene and **2** at low temperature showed the rapid and clean formation of a new, diamagnetic complex with C<sub>s</sub> symmetry that was spectroscopically identified as the azametallacyclobutane complex (IPr<sup>\*</sup>)Ni{N,C: $\kappa^2$ -N(dmp)CH<sub>2</sub>CH<sub>2</sub>} (**4**). Two triplets ( $\delta$  3.34, 0.62; <sup>3</sup>J<sub>HH</sub> = 7.0 Hz) consistent with a [2 + 2]-cycloaddition intermediate were detected in the alkyl region of the <sup>1</sup>H NMR spectrum, and the chemical shifts and couplings were in close agreement with those for the previously isolated azametallacyclobutane complex (2,2'-bipyridine)Ni(N,C: $\kappa^2$ -NTsCH<sub>2</sub>CH<sub>2</sub>) (**7**; Ts = O<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>).<sup>20</sup> Reaction of <sup>13</sup>C<sub>2</sub>-labeled ethene with **2** allowed for observation and unambiguous characterization of the thermally sensitive azametallacyclobutane complex (IPr<sup>\*</sup>)Ni{N,C: $\kappa^2$ -N(dmp)<sup>13</sup>CH<sub>2</sub><sup>13</sup>CH<sub>2</sub>} (**4**-<sup>13</sup>C). The <sup>13</sup>C NMR spectrum of **4**-<sup>13</sup>C in toluene-*d*<sub>8</sub> displayed two characteristic resonances at  $\delta$  54.8 (dt, <sup>1</sup>J<sub>CH</sub> = 137 Hz, <sup>1</sup>J<sub>CC</sub> = 35.4 Hz) and  $\delta$  -13.5 (dt, <sup>1</sup>J<sub>CH</sub> = 145 Hz, <sup>1</sup>J<sub>CC</sub> = 35.4 Hz), in agreement with the corresponding resonances in **7** ( $\delta$  54.4, -12.2). When warmed, **4**-<sup>13</sup>C cleanly eliminated (dmp)NH(<sup>13</sup>CH=CH<sub>2</sub>) (**5**-<sup>13</sup>C),

whose NMR spectra were consistent with its formulation and isotopic composition.

These results indicate that formation of **5** results from the three-coordinate azametallacyclobutane **4**, possibly via a 1,2-hydride shift<sup>21</sup> or  $\beta$ -hydride elimination followed by N–H reductive elimination but not from H-atom abstraction by the triplet diradical **2** or direct C–H insertion involving ethene. The lower coordination number of **2** reveals distinct reactivity: the room-temperature C–H amination of ethene contrasts with aziridination observed in the reaction of ethene with the three-coordinate imide  $\{(tert\text{-butyl})_2\text{PCH}_2\text{CH}_2\text{P}(tert\text{-butyl})_2\}\text{Ni}=\text{N}\{2,6\text{-}(\text{isopropyl})_2\text{C}_6\text{H}_3\}$  (**8**), which requires an elevated temperature (70 °C) and long reaction times (8 days).<sup>22</sup> DFT calculations support a mechanism for aziridine formation from **8** that involves a four-coordinate azametallacyclobutane intermediate (like **7**). Reductive elimination to form a C–N bond proceeds from a three-coordinate, T-shaped azametallacyclobutane intermediate formed by dissociation of one of the arms of the phosphine ligand.<sup>23</sup> The exceptional steric demands presented by the IPr\* and (dmp)N<sup>2-</sup> ligands, coupled with the strong  $\sigma$ -donor characteristics of IPr\* (which disfavor its adoption of a trans arrangement with respect to the alkyl or amide substituents of the metallacycle), likely prevent **4** from assuming the T-shaped configuration favoring C–N reductive elimination.<sup>23,24</sup> Thus, an alternate, low-energy hydride-migration pathway ultimately affords vinylamine **5** instead of the corresponding aziridine.

In summary, the first two-coordinate transition-metal complex containing an imido ligand has been prepared and studied. Its solid-state structure features a linear core with a very short Ni–N distance indicative of strong  $\pi$  bonding. The low coordination number results in a triplet ground state for this Ni(II) complex and engenders dramatically enhanced group-transfer reactivity in comparison with higher-coordinate analogues.

## ASSOCIATED CONTENT

**S** Supporting Information. Experimental, spectroscopic, computational, and analytical details; complete crystallographic details for (IPr\*)(THF)NiCl<sub>2</sub>, **2**, and **6** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

g-hillhouse@uchicago.edu; t@unt.edu

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