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

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Ⓢ *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_2 from a bulky aryl azide in its reaction with (IPr*)Ni(η^6-C_7H_8) (**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(dπ)−N(pπ) interactions, resulting in two nearly degenerate singly occupied molecular orbitals (SOMOs) that are Ni−N π^* in character. Reaction of **2** with CO resulted in nitrene-group transfer to form (dmp)NCO and (IPr*)Ni$(CO)_3$ (**3**). Net C−H insertion was observed in the reaction of **2** with ethene, forming the vinylamine (dmp)NH(CH═CH_2) (**5**) via an azanickelacyclobutane intermediate, (IPr*)Ni{*N*,*C*:κ^2-N(dmp)CH_2CH_2} (**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_2 reduction to ammonia.[1−6] A prerequisite for transition-metal-element π-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 π-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.[7] Utilizing the massive steric profile of IPr* [IPr* = 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene],[8] we were able to prepare (IPr*)Ni(η^6-C_7H_8) (**1**) via heterogeneous Mg reduction of (IPr*)(THF)NiCl_2 in the presence of toluene (Scheme 1). Installation of an imide (RN^{2-}) fragment is often achieved through dinitrogen extrusion from organoazides (N_3R).[1,9,10] 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_3(dmp) (dmp = 2,6-dimesitylphenyl) resulted in vigorous N_2 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 ^{1}H NMR spectroscopy. While **2** decomposes in CH_2Cl_2 solution, it is stable in toluene or Et_2O 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).[11−13] Other than the two coordination points, there are no short, stabilizing contacts between Ni and the IPr* or (dmp)N^{2-} 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 π bonding between the imido ligand and nickel(II). A dihedral angle of ~41°, defined by the NHC core and the central C_6H_3 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,[11,13] complex **2** exhibits a solid-state magnetic moment of 2.77μ_B (SQUID, 60−300 K; Figure 2), indicative of the triplet ground state of a high-spin d^8 Ni center with a large zero-field splitting ($D = 24$ 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 π bonding dominates. An otherwise σ^* 3d_{z^2} Ni orbital is greatly stabilized by symmetry-allowed mixing with the 4s Ni orbital, increasing its nonbonding character.[14] Additionally, the short Ni−N distance allows for a strong π interaction, which destabilizes the π^* molecular orbitals (Ni 3d_{xz} and 3d_{yz} character) beyond the "nonbonding" 3d_{z^2} orbital. The resulting orbital ordering, in which the two nearly degenerate singly occupied molecular orbitals ($\Delta = 0.03$ eV) are π^* in nature, similar to Fe{N(*tert*-butyl)$_2$}$_2$,[15] was corroborated by density functional theory (DFT) calculations at the B3LYP/6-311+G-(d) level (Figure 2)[16] and gives a formal Ni−N bond order of 2.

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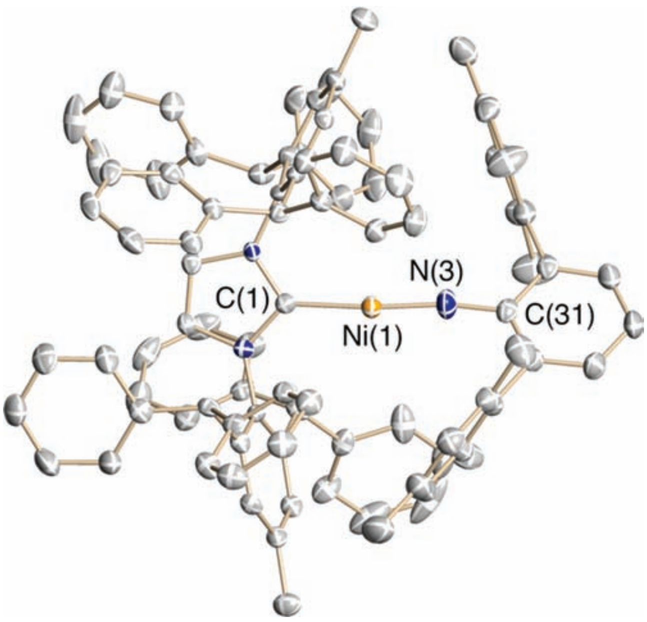
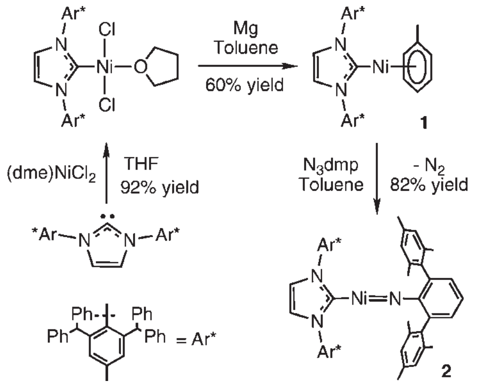


Figure 1. Perspective view of the molecular structure of **2** (50% thermal ellipsoids). H atoms and cocrystallized solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **2**: Ni(1)−N(3), 1.663(3); C(1)−Ni(1), 1.917(3); N(3)−C(31), 1.351(4); C(1)−Ni(1)−N(3), 174.24(13); 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{NMes(BMes$_2$)}$_2$ and Ni{NHC$_6$H$_3$(2,6-(isopropyl)$_2$-C$_6$H$_3$)$_2$}$_2$,[17] where standard Ni−N single-bond distances[11,18] 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*)Ni(CO)$_3$ (**3**; ν(CO) = 2048, 1968 cm^{-1}) and the aryl isocyanate (dmp)NCO. Related group transfers to give aryl isocyanates are known for several late-metal imides.[19] 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$_2$) (**5**) during the 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)Ni(η^2-CH$_2$CH$_2$)$_2$ (**6**), which was characterized by ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction.

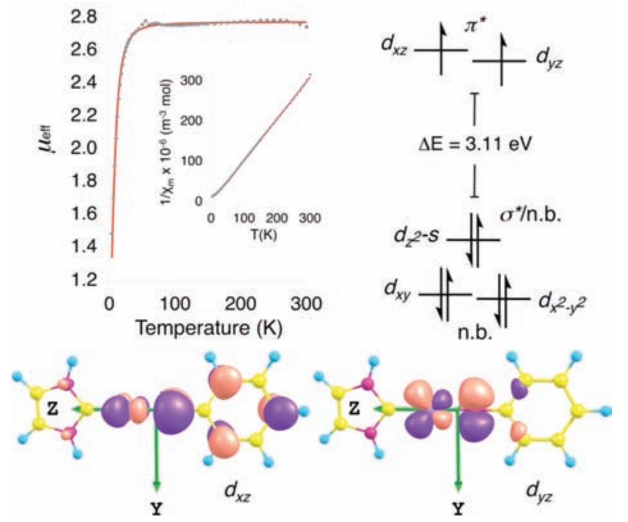
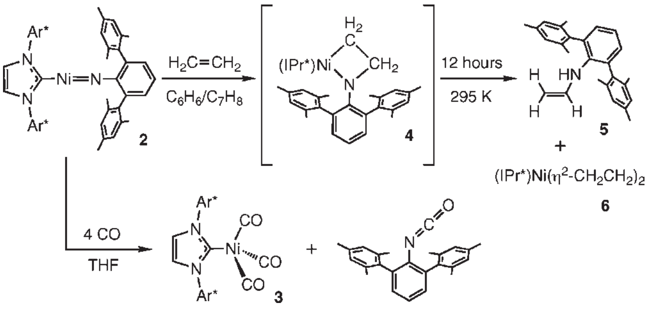


Figure 2. (top left) Effective magnetic moment of **2** at 4−300 K and 0.5 T. The inset shows the inverse molar magnetic susceptibility (4−300 K at 0.5 T). The raw data are shown as gray ◆ and the JulX fits as red lines. (top right) Qualitative MO diagram for **2**. (bottom) π^* SOMO orbitals of **2**.

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



^{1}H and ^{13}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_s symmetry that was spectroscopically identified as the azametallacyclobutane complex (IPr*)Ni{*N*,*C*:κ^2-N(dmp)CH$_2$CH$_2$} (**4**). Two triplets (δ 3.34, 0.62; $^3J_{HH}$ = 7.0 Hz) consistent with a [2 + 2]-cycloaddition intermediate were detected in the alkyl region of the ^{1}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*:κ^2-NTsCH$_2$CH$_2$) (**7**; Ts = O$_2$SC$_6$H$_4$CH$_3$).[20] Reaction of ^{13}C$_2$-labeled ethene with **2** allowed for observation and unambiguous characterization of the thermally sensitive azametallacycle (IPr*)-Ni{*N*,*C*:κ^2-N(dmp)^{13}CH$_2$^{13}CH$_2$} (**4-^{13}C**). The ^{13}C NMR spectrum of **4-^{13}C** in toluene-d_8 displayed two characteristic resonances at δ 54.8 (dt, $^1J_{CH}$ = 137 Hz, $^1J_{CC}$ = 35.4 Hz) and δ −13.5 (dt, $^1J_{CH}$ = 145 Hz, $^1J_{CC}$ = 35.4 Hz), in agreement with the corresponding resonances in **7** (δ 54.4, −12.2). When warmed, **4-^{13}C** cleanly eliminated (dmp)NH(^{13}CH=^{13}CH$_2$) (**5-^{13}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[21] or β-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 $\{(tert\text{-butyl})_2PCH_2CH_2P(tert\text{-butyl})_2\}Ni{=}N\text{-}\{2,6\text{-}(isopropyl)_2C_6H_3\}$ (**8**), which requires an elevated temperature (70 °C) and long reaction times (8 days).[22] 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.[23] The exceptional steric demands presented by the IPr* and $(dmp)N^{2-}$ ligands, coupled with the strong σ-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[23,24] 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 π 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

Ⓢ Supporting Information. Experimental, spectroscopic, computational, and analytical details; complete crystallographic details for $(IPr^*)(THF)NiCl_2$, **2**, and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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