

Intramolecular C–H Functionalization Followed by a $[2_\sigma + 2_\pi]$ Addition via an Intermediate Nickel–Nitridyl ComplexJack Ghannam,[†] Zhicheng Sun,[‡] Thomas R. Cundari,[‡] Matthias Zeller,[§] Adriana Lugosan,[†] Christopher M. Stanek,[†] and Wei-Tsung Lee^{*,†}[†]Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, Illinois 60660, United States[‡]Department of Chemistry, Center for Advanced Scientific Computing and Modeling (CASCm), University of North Texas, Denton, Texas 76203, United States[§]Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

S Supporting Information

ABSTRACT: Irradiation of a disphenoidal Ni(II) azido complex, $[\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{NiN}_3]$ (**1**), revealed an unprecedented nickel complex, $[\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})(\text{NH}_2\text{--Pyr}^{\text{iPr}})]$ (**2**), in >90% isolated yield. As evidenced by single-crystal X-ray diffraction, **2** is produced by double intramolecular C–H activation of a putative nickel–nitridyl intermediate, $[\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{Ni}\equiv\text{N}^\bullet]$. Calculations support the generation of an intermediate with significant nitridyl radical character after the loss of N_2 , which, in turn, undergoes tandem C–H activations, leading to functionalized intermediates and products. This is an unprecedented example of transient $\text{Ni}\equiv\text{N}^\bullet$ -promoted intramolecular C–H functionalization, followed by a $[2_\sigma + 2_\pi]$ addition, yielding bis-metallacyclic product **2**. Complex **2** is also observed from the reaction of Ni(I) precursor $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{Ni}$ (**3**) and Me_3SiN_3 , suggesting a unique thermal route toward a masked nickel–nitridyl intermediate.

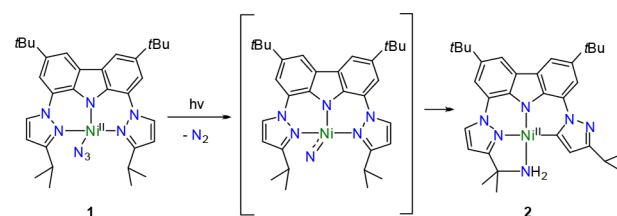
Transition-metal nitrido complexes have long been of interest as putative intermediate species in various organic/inorganic transformations and in biological nitrogen fixation.¹ Whereas most early to mid transition-metal nitrido complexes have proven to be both thermodynamically stable and kinetically inert, the isolation of late transition-metal nitrido counterparts, especially those of groups 9 to 11, has proven to be very challenging.^{1c,2} This is proposed to be due to the population of metal–nitrogen π -antibonding molecular orbitals, leading to thermodynamic destabilization and kinetic labilization (via diradical character at the nitrido nitrogen) of such a species.^{1a} An intriguing aspect of late transition-metal nitrido compounds is their potential applications in C–N and H–N bond formation, which has encouraged continued investigation.³ Tomson,^{3f} Chirik,^{3g} and coworkers have provided evidence of cobalt nitride intermediates being capable of intramolecular activation of aliphatic and benzylic C–H bonds. Sun et al. reported density functional theory (DFT) calculations that suggest that cobalt- and nickel-nitrido complexes are capable of the activation and functionalization of strong alkane C–H bonds.^{3h}

Thus far, there are only two literature precedents for putative nickel nitrido species, each generated by the photolysis of square planar (PNP)NiN₃ complexes in which the N of the supporting pincer is an anionic amide. For instance, Vreeken et al. described the C–H activation of benzene,⁴ whereas the formation of carbodiimides via nitrogen atom transfer was reported by Yao et al.^{3c} Inspired by these examples, we set out to extend this chemistry to species with different supporting ligands. Recently, we have synthesized and fully characterized a monoanionic NNN pincer ligand, $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2^-$, which is capable of supporting rare examples of disphenoidal Ni(II) complexes.⁵ It was reasoned that $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2^-$ would provide a unique coordination environment for supporting nickel nitrido species, which, in turn, might afford unusual reactivity.

The reaction of $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{NiBr}$ with NaN_3 leads to the formation of a new complex that has been proposed as $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{NiN}_3$ (**1**) based on its ¹H NMR and IR spectra ($\nu_{\text{N}_3} = 2080 \text{ cm}^{-1}$). B3LYP/6-31+G(d)/gas calculations of $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{NiN}_3$ place this stretch at 2153 cm^{-1} , which is ~3 to 4% higher than the experimental value, as expected from anharmonicity and basis set effects.⁶

The irradiation of azido compound **1** results in an orange solid, which was recrystallized to afford single crystals of **2** in 91% yield (Scheme 1). The ¹H NMR spectrum of **2** suggests *C*₁ molecular symmetry, indicating that the supporting ligand, $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2^-$, has been modified (see below). The molecular structure of **2** was revealed by X-ray diffraction (XRD) (Figure 1), which confirms an unprecedented double-intramolecularly C–H-activated Ni(II) complex. Interestingly, a direct C–H

Scheme 1



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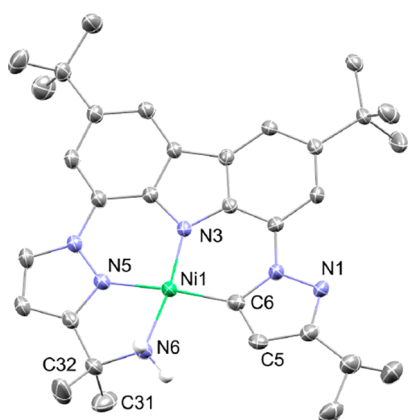
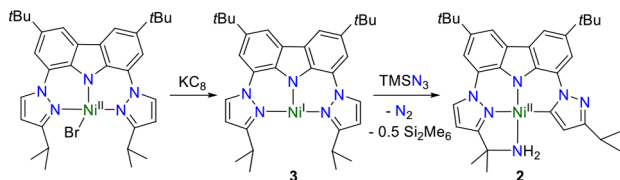


Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Noncoordinated solvent molecules and some hydrogen atoms are omitted for clarity. Color key: turquoise, Ni; blue, N; gray, C.

amination occurs on the methine position ($C_{sp^3}-H$) of the isopropyl substituent of one of the Pyr^{iPr} arms. A “rollover” C–H activation of the other Pyr^{iPr} arm yields a metallacycle.⁷ In agreement with the assignment of the solid-state structure, notable features in the 1H NMR spectrum include a singlet for the methyl groups that signal the loss of the methine proton. Nitrogen atom insertion is evident by a broad N–H peak, accounting for two protons located at 2.48 ppm in the 1H NMR spectrum of **2**, and a characteristic band that was observed at 3424 cm^{-1} by IR spectroscopy. Moreover, two unusual upfield shifts of the protons on C5 (4.83 ppm) and C31/C32 (0.54 ppm) in the 1H NMR spectrum of **2** suggest that these protons are closer to the nickel center,⁸ resulting from both C–H amination and pendant arm-flipping.

Even more striking, **2** can also be produced via a proposed Ni(III)–imido intermediate. To our knowledge, this would be the first thermal route to an intermediate that is functionally equivalent to a nickel–nitrido complex. Note that related intramolecular C–H aminations via terminal Co(III)–imido intermediates were reported by Theopold, Betley, and Mindiola.⁹ The reduction of $Cz^{tBu}(Pyr^{iPr})_2NiBr$ with 1.5 equiv of KC_8 under an inert gas atmosphere afforded the new complex $Cz^{tBu}(Pyr^{iPr})_2Ni$ (**3**) (Scheme 2). Complex **3** was

Scheme 2



characterized by paramagnetic 1H NMR spectroscopy, which suggests an $S = 1/2$ ground state according to the Evans' method ($\mu_{eff} = 1.8(2)\mu_B$ in C_6D_6), and its electron paramagnetic resonance (EPR) spectrum with $g = [2.30, 2.16, 2.04]$ is shown in Figure S1.¹⁰ A single-crystal XRD study revealed the structure of **3** as a rare example of a three-coordinate Ni(I) NNN–pincer complex.¹¹ The Ni(I) center adopts a slightly distorted T-shaped geometry about the Ni(I) central ion and is coordinated by two pyrazole nitrogen atoms on the axial positions and the carbazole nitrogen atom on the equatorial site (Figure S2). The reduction of the Ni–N(ave)

bond of $1.908(3)\text{ \AA}$ in **3** relative to **2** does not reflect a larger ionic radius of the Ni(I) center compared with its Ni(II) analogues ($2.002(2)$, $1.990(2)$, and $1.981(1)\text{ \AA}$ in $Cz^{tBu}(Pyr^{iPr})_2NiCl$, $Cz^{tBu}(Pyr^{iPr})_2NiBr$, and $Cz^{tBu}(Pyr^{iPr})_2NiI$, respectively).⁵ Rather, this can be attributed to increased steric hindrance around the Ni(II) center in four-coordinate **2** or the change in spin state from **3** (doublet) to **2** (singlet).

An immediate color change and gas evolution was observed when treating **3** with Me_3SiN_3 at ambient temperature (Scheme 2). The 1H NMR spectrum of the reaction mixture suggests that complex **2** is formed as a major product (68% isolated yield).

Organoazides are often useful reagents for preparing terminal imido late transition-metal complexes.¹² A Co(III)–silylimido intermediate, $Tp^{R,R}Co=NSiMe_3$, has been postulated to be capable of abstracting hydrogen atoms from alkyl groups and yielding a “Co–N(H)SiMe₃” product.^{9a} Nickel imidyl complexes have been shown by Wiese et al. to be capable of activating C–H bonds.¹³ The conversion of metal–silylimido into metal–nitride has been reported for early transition-metal complexes, $[Cp^*M\{N(iPr)C(Me)N(iPr)\}Cl_2]$ ($Cp^* = \eta^5-C_5Me_5$, $M = Mo$ and W), although an additional substrate is required for the removal of the $SiMe_3$ group.¹⁴ The loss of the trimethylsilyl group was monitored by in situ 1H NMR spectroscopy, where hexamethyldisilane was observed. Note that the reaction of **3** with Me_3SiN_3 yielded $Cz^{tBu}(Pyr^{iPr})_2NiN_3$, which then converted to corresponding **2** via a nitridyl intermediate.^{15,16} However, this pathway for **3**/ Me_3SiN_3 reactivity is unlikely given that the reaction proceeds under thermal rather than photochemical conditions.

To gain further insight into the possible formation of **2** via different routes, DFT calculations were performed. As shown in Figure S6, the release of N_2 from $Cz^{tBu}(Pyr^{iPr})_2NiN_3$ (**1**) is the starting point for the calculations. **1** is calculated to be the most stable in its triplet configuration, consistent with experimental measurements. The nickel–nitridyl intermediate (**B**) is more stable in a triplet spin state (10 kcal/mol lower than an open-shell singlet); this intermediate is 23.6 kcal/mol higher in free energy than triplet azide **1**. The release of N_2 to form a high-energy Ni–nitrido intermediate is endergonic and thus requires energy input (irradiation). The coordination geometry of triplet $Cz^{tBu}(Pyr^{iPr})_2NiN$ is closer to disphenoidal than square planar. The calculated Ni–N_{nitridyl} bond length (B3LYP/6-31+G(d): 1.74 \AA) is longer than that observed for many structurally characterized Ni=N_{imide} complexes.¹⁷ A Mulliken population analysis shows significant spin density on the terminal N atom in the triplet ground electronic state of the Ni “nitridyl” ($2.16\text{ }e^-$ on N and $-0.17\text{ }e^-$ on Ni) (Figure 2a). Vreeken et al. proposed that significant nitridyl radical character represents the admixture of resonance structures: $Ni^{IV}(N^{3-}) \leftrightarrow Ni^{III}(N^{2-}) \leftrightarrow Ni^{II}(N^{1-})$.³ Both DFT and MCSCF (CAS(12,12)) calculations suggest that the $Cz^{tBu}(Pyr^{iPr})_2NiN$ intermediate is perhaps best described as $[(L^-)(d^8-Ni^{2+})(N^-)]$, although the electronic structure of this nitridyl is complicated, and one might better characterize it as either a N-centered biradical or perhaps a metallanitrene. Importantly, the calculations suggest significant delocalization of the frontier orbitals among the metal (Ni), supporting $(Cz^{tBu}(Pyr^{iPr})_2)^-$, and actor (N) ligands in the nitridyl intermediate, which may underlie the metastability of $Cz^{tBu}(Pyr^{iPr})_2NiN$.

The calculated thermodynamics of the intramolecular C–H activation process to make a triplet amide intermediate (**D**) is

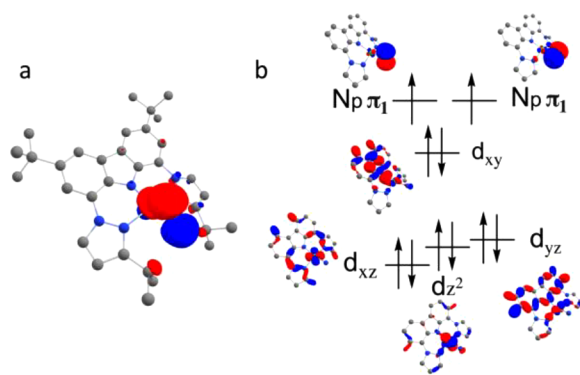


Figure 2. (a) Mulliken spin density of Ni-nitridyl (B) triplet. (b) MCSCF (CAS(12, 12)) calculated Ni-nitridyl orbitals.

energetically quite favorable (**D** is ~ 60 kcal/mol lower in free energy than the triplet Ni-nitridyl). A transition-state search shows that C–H activation of one of the Pyr^{iPr} arms on the ligand (**TS1**) is facile, with only an 11.1 kcal/mol computed barrier (B3LYP), leading to the formation of a high-spin quintet radical (**C**). The initial C–H activation transition state is reasonably insensitive to functional choice, ranging from 7 (PBE0, BP86) to 13.5 kcal/mol (M06, M06L, MN12L). For the “rollover” C–H activation to occur between the amido N and the other Pyr^{iPr} arm, calculations suggest **C6** of **2** (Figure 1), and the attached H can form an agostic intermediate (**E**), with only 8.1 kcal/mol invested (B3LYP). Despite using multiple functionals and basis sets, bond length/angle restraints, and different initial geometry guesses, an oxidative addition transition state (**TS**) could not be found, and all searches converge to a $[2\sigma + 2\pi]$ addition **TS** (**TS2**) that leads to the observed final product **2**. Previous research indicates that electrophilic transition-metal complexes with nucleophilic actor ligands tend to favor a metal–ligand centered pathway for C–H activation via a four-centered transition state.^{3h} Mulliken population analysis shows that for intermediate **D** (a triplet), there is uniform delocalization of the spin density on both the Ni and the amidyl N. DFT calculations with B3LYP revealed that the second C–H activation barrier (**D** \rightarrow **TS2** \rightarrow **2**) leading to **TS2** is 40.8 kcal/mol relative to intermediate **D**. Interestingly, **TS2** is much more sensitive than **TS1** to functional choice ($\Delta G^\ddagger = 28 \pm 7$ kcal/mol for the 11 functionals tested), with values as low as 17 kcal/mol (MN12L). The lower end of this range seems more consistent with experimental observations. The formation of the Ni amine complex (**2**) is not as energetically favorable as the formation of a Ni-amidyl intermediate (-60 vs -13 kcal/mol, Figure S6), which further supports the proposal that the second “rollover” C–H activation is the rate-determining step.

As for Me_3SiN_3 reactivity, Warren and coworkers reported an interesting example whereby the reaction of a Ni(I) synthon with Me_3SiN_3 yielded a Ni(II)–azido complex.¹⁸ DFT calculations (details below) place the reaction of Ni(I) complex **3** with Me_3SiN_3 to form $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{NiN}_3 + \text{Me}_3\text{Si}^\bullet$ ($\Delta G_{\text{calc}} = +36.2$ kcal/mol; $\Delta G_{\text{calc}} = +5.9$ kcal/mol if it is assumed that 1/2 equiv of $\text{Me}_3\text{Si}^\bullet$ is formed) at a distinct thermodynamic disadvantage relative to the formation of $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{Ni}^\bullet\text{N}^\bullet\text{SiMe}_3 + \text{N}_2$ ($\Delta G_{\text{calc}} = -17.8$ kcal/mol). Calculations suggest that scission of the N–SiMe₃ bond is more facile (by ~ 20 kcal/mol) after the initial C–H insertion by the Ni-imidyl intermediate, as opposed to homolysis of this bond in $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{Ni}^\bullet\text{N}^\bullet\text{SiMe}_3$. There-

fore, the Ni-terminal imidyl intermediate, $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{Ni}^\bullet\text{N}^\bullet\text{SiMe}_3$ (spin density calculated for quartet imidyl ground state: $1.4 e^-$ (Ni), $1.3 e^-$ (N_{im})), is proposed to be initially generated, which is followed by C–H insertion, the removal of the trimethylsilyl group, and then “rollover” C–H activation to produce **2**.¹³

In conclusion, we describe an unprecedented reaction involving C–H functionalization followed by $[2\sigma + 2\pi]$ addition that yields nickel bis-metalocyclic complex **2**. Theoretical calculations suggest that the formation of **2** is via a transient Ni-nitridyl species, which can be generated by the photolysis of $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{NiN}_3$. The reaction of Ni(I) starting material **3** with Me_3SiN_3 also results in the formation of **2**; DFT calculations suggest that the key intermediate in this second reaction is a Ni-imidyl, $\text{Cz}^{\text{tBu}}(\text{Pyr}^{\text{iPr}})_2\text{Ni}^\bullet\text{N}^\bullet\text{SiMe}_3$. The spectroscopic validation of intermediates and investigation of intermolecular C–H activation are currently ongoing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00168.

Experimental details of the preparation of **1–3**, crystallography, computational methods, NMR, and EPR spectra (PDF)

Accession Codes

CCDC 1875204–1875205 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Berry, J. F. Terminal Nitrido and Imido Complexes of the Late Transition Metals. *Comments Inorg. Chem.* **2009**, *30*, 28–66. (b) Lancaster, K. M.; Roemelt, M.; Ettenhuber, P.; Hu, Y.; Ribbe, M. W.; Neese, F.; Bergmann, U.; DeBeer, S. X-ray Emission Spectroscopy Evidences a Central Carbon in the Nitrogenase Iron-Molybdenum Cofactor. *Science* **2011**, *334*, 974–977. (c) Friedle, S.; Reisner, E.; Lippard, S. J. Current Challenges of Modeling Diiron Enzyme Active Sites for Dioxygen Activation by Biomimetic Synthetic Complexes. *Chem. Soc. Rev.* **2010**, *39*, 2768–2779. (d) Krebs, C.; Galonić Fujimori, D.; Walsh, C. T.; Bollinger, J. M. Non-Heme Fe(IV)–Oxo Intermediates. *Acc. Chem. Res.* **2007**, *40*, 484–492. (e) Smith, J. M. Reactive Transition Metal Nitride Complexes. *Prog. Inorg. Chem.* **2014**, *58*. DOI: 10.1002/9781118792797.ch06
- (2) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds: The Chemistry of Transition Metal Complexes Containing Oxo, Nitrido, Imido, Alkylidene, or Alkylidyne Ligands*; John Wiley and Sons Ltd.: New York, 1988.
- (3) (a) Suarez, A. I. O.; Lyaskovskyy, V.; Reek, J. N. H.; van der Vlugt, J. I.; de Bruin, B. Complexes with Nitrogen-Centered Radical Ligands: Classification, Spectroscopic Features, Reactivity, and Catalytic Applications. *Angew. Chem., Int. Ed.* **2013**, *52*, 12510–12529. (b) Maity, A. K.; Murillo, J.; Metta-Magaña, A. J.; Pinter, B.; Fortier, S. A Terminal Iron(IV) Nitride Supported by a Super Bulky Guanidinate Ligand and Examination of Its Electronic Structure and Reactivity. *J. Am. Chem. Soc.* **2017**, *139*, 15691–15700. (c) Yao, C.; Wang, X.; Huang, K.-W. Nitrogen Atom Transfer Mediated by a New PN3P-Pincer Nickel Core via a Putative Nitrido Nickel Intermediate. *Chem. Commun.* **2018**, *54*, 3940–3943. (d) Scepianiak, J. J.; Young, J. A.; Bontchev, R. P.; Smith, J. M. Formation of Ammonia from an Iron Nitrido Complex. *Angew. Chem., Int. Ed.* **2009**, *48*, 3158–3160. (e) Scepianiak, J. J.; Vogel, C. S.; Khusniyarov, M. M.; Heinemann, F. W.; Meyer, K.; Smith, J. M. Synthesis, Structure, and Reactivity of an Iron(V) Nitride. *Science* **2011**, *331*, 1049–1052. (f) Cui, P.; Wang, Q.; McCollom, S. P.; Manor, B. C.; Carroll, P. J.; Tomson, N. C. Ring-Size-Modulated Reactivity of Putative Dicobalt-Bridging Nitrides: C–H Activation versus Phosphinimide Formation. *Angew. Chem.* **2017**, *129*, 16195–16199. (g) Hojilla Atienza, C. C.; Bowman, A. C.; Lobkovsky, E.; Chirik, P. J. Photolysis and Thermolysis of Bis(imino)pyridine Cobalt Azides: C–H Activation from Putative Cobalt Nitrido Complexes. *J. Am. Chem. Soc.* **2010**, *132*, 16343–16345. (h) Sun, Z.; Hull, O. A.; Cundari, T. R. Computational Study of Methane C–H Activation by Diiminopyridine Nitride/Nitridyl Complexes of 3d Transition Metals and Main-Group Elements. *Inorg. Chem.* **2018**, *57*, 6807–6815.
- (4) Vreeken, V.; Siegler, M. A.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. C–H Activation of Benzene by a Photoactivated Ni^{II}(azide): Formation of a Transient Nickel Nitrido Complex. *Angew. Chem., Int. Ed.* **2015**, *54*, 7055–7059.
- (5) Ghannam, J.; Al Assil, T.; Pankratz, T. C.; Lord, R. L.; Zeller, M.; Lee, W.-T. A Series of 4- and 5-Coordinate Ni(II) Complexes: Synthesis, Characterization, Spectroscopic, and DFT Studies. *Inorg. Chem.* **2018**, *57*, 8307–8316.
- (6) Scott, A. P.; Radom, L. Harmonic Vibrational Frequencies: An Evaluation of Hartree–Fock, Møller–Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. *J. Phys. Chem.* **1996**, *100*, 16502–16513.
- (7) (a) Bailey, W. D.; Luconi, L.; Rossin, A.; Yakhvarov, D.; Flowers, S. E.; Kaminsky, W.; Kemp, R. A.; Giambastiani, G.; Goldberg, K. I. Pyrazole-Based PCN Pincer Complexes of Palladium(II): Mono- and Dinuclear Hydroxide Complexes and Ligand Rollover C–H Activation. *Organometallics* **2015**, *34*, 3998–4010. (b) Lin, H.-J.; Lutz, S.; O’Kane, C.; Zeller, M.; Chen, C.-H.; Al Assil, T.; Lee, W.-T. Synthesis and Characterization of an Iron Complex Bearing a Hemilabile NNN-Pincer for Catalytic Hydrosilylation of Organic Carbonyl Compounds. *Dalton Trans* **2018**, *47*, 3243–3247.
- (8) Horak, K. T.; VanderVelde, D. G.; Agapie, T. Tuning of Metal Complex Electronics and Reactivity by Remote Lewis Acid Binding to π -Coordinated Pyridine Diphosphine Ligands. *Organometallics* **2015**, *34*, 4753–4765.
- (9) (a) Thyagarajan, S.; Shay, D. T.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. Intramolecular C–H Activation by Inferred Terminal Cobalt Imido Intermediates. *J. Am. Chem. Soc.* **2003**, *125*, 4440–4441. (b) King, E. R.; Sazama, G. T.; Betley, T. A. Co(III) Imidos Exhibiting Spin Crossover and C–H Bond Activation. *J. Am. Chem. Soc.* **2012**, *134*, 17858–17861. (c) Grant, L. N.; Carroll, M. E.; Carroll, P. J.; Mindiola, D. J. An Unusual Cobalt Azide Adduct That Produces a Nitrene Species for Carbon–Hydrogen Insertion Chemistry. *Inorg. Chem.* **2016**, *55*, 7997–8002.
- (10) (a) Schneck, F.; Ahrens, J.; Finger, M.; Stückl, A. C.; Würtele, C.; Schwarzer, D.; Schneider, S. The Elusive Abnormal CO₂ Insertion Enabled by Metal-ligand Cooperative Photochemical Selectivity Inversion. *Nat. Commun.* **2018**, *9*, 1161. (b) Yoo, C.; Lee, Y. A T-Shaped Nickel(I) Metalloradical Species. *Angew. Chem., Int. Ed.* **2017**, *56*, 9502–9506.
- (11) (a) Wenz, J.; Rettenmeier, C. A.; Wadepohl, H.; Gade, L. H. Catalytic C–F bond Activation of Geminal Difluorocyclopropanes by Nickel(I) Complexes via a Radical Mechanism. *Chem. Commun.* **2016**, *52*, 202–205. (b) Rettenmeier, C.; Wadepohl, H.; Gade, L. H. Stereoselective Hydrodehalogenation via a Radical-Based Mechanism Involving T-Shaped Chiral Nickel(I) Pincer Complexes. *Chem. - Eur. J.* **2014**, *20*, 9657–9665.
- (12) (a) Kogut, E.; Wiencko, H. L.; Zhang, L.; Cordeau, D. E.; Warren, T. H. A Terminal Ni(III)–Imide with Diverse Reactivity Pathways. *J. Am. Chem. Soc.* **2005**, *127*, 11248–11249. (b) Jenkins, D. M.; Betley, T. A.; Peters, J. C. Oxidative Group Transfer to Co(I) Affords a Terminal Co(III) Imido Complex. *J. Am. Chem. Soc.* **2002**, *124*, 11238–11239. (c) Waterman, R.; Hillhouse, G. L. η^2 -Organoazide Complexes of Nickel and Their Conversion to Terminal Imido Complexes via Dinitrogen Extrusion. *J. Am. Chem. Soc.* **2008**, *130*, 12628–12629. (d) Otten, B. M.; Figg, T. M.; Cundari, T. R. The Curious Case of Mesityl Azide and Its Reactivity with bpyNiEt_2 . *Inorg. Chem.* **2014**, *53*, 11633–11639.
- (13) Wiese, S.; McAfee, J. L.; Pahls, D. R.; McMullin, C. L.; Cundari, T. R.; Warren, T. H. Functionalization Reactivity of a Nickel–Imide. *J. Am. Chem. Soc.* **2012**, *134*, 10114–10121.
- (14) Keane, A. J.; Farrell, W. S.; Yonke, B. L.; Zavalij, P. Y.; Sita, L. R. Metal-Mediated Production of Isocyanates, $\text{R}_3\text{EN}=\text{C}=\text{O}$ from Dinitrogen, Carbon Dioxide, and R_3ECl . *Angew. Chem., Int. Ed.* **2015**, *54*, 10220–10224.
- (15) (a) Ngai, R.; Wang, Y. H. L.; Reed, J. L. Photochemistry of Nickel(II) Azido Complexes: Singlet Nitrene. *Inorg. Chem.* **1985**, *24*, 3802–3807. (b) Yu, Y.; Sadique, A. R.; Smith, J. M.; Dugan, T. R.; Cowley, R. E.; Brennessel, W. W.; Flaschenriem, C. J.; Bill, E.; Cundari, T. R.; Holland, P. L. The Reactivity Patterns of Low-Coordinate Iron–Hydride Complexes. *J. Am. Chem. Soc.* **2008**, *130*, 6624–6638.
- (16) Other important examples of late transition-metal nitridyl: (a) Scheibel, M. G.; Abbeneth, J.; Kinauer, M.; Heinemann, F. W.; Würtele, C.; de Bruin, B.; Schneider, S. Homolytic N–H Activation of Ammonia: Hydrogen Transfer of Parent Iridium Ammine, Amide, Imide, and Nitride Species. *Inorg. Chem.* **2015**, *54*, 9290–9302. (b) Scheibel, M. G.; Wu, Y.; Stückl, A. C.; Krause, L.; Carl, E.; Stalke, D.; de Bruin, B.; Schneider, S. Synthesis and Reactivity of a Transient, Terminal Nitrido Complex of Rhodium. *J. Am. Chem. Soc.* **2013**, *135*, 17719–17722. (c) Scheibel, M. G.; Askevold, B.; Heinemann, F. W.; Reijerse, E. J.; de Bruin, B.; Schneider, S. Closed-shell and Open-shell Square-planar Iridium Nitrido Complexes. *Nat. Chem.* **2012**, *4*, 552. (d) Gloaguen, Y.; Rebreyend, C.; Lutz, M.; Kumar, P.; Huber, M.; van der Vlugt, J. I.; Schneider, S.; de Bruin, B. An Isolated Nitridyl Radical-Bridged $\{\text{Rh}(\text{N}^\bullet)\text{Rh}\}$ Complex. *Angew. Chem., Int. Ed.* **2014**, *53*, 6814–6818.
- (17) (a) Köthe, C.; Metzinger, R.; Herwig, C.; Limberg, C. Reductive Deprotonation and Dehydrogenation of Phenylhydrazine at a Nickel Center To Give a Nickel Diazenido Complex. *Inorg. Chem.* **2012**, *51*, 9740–9747. (b) Harrold, N. D.; Corcos, A. R.; Hillhouse, G. L. Synthesis, Structures, and Catalytic Reactivity of Bis(N-

Heterocyclic Carbene) Supported Diphenyldiazomethane and 1-Azidoadamantane Complexes of Nickel. *J. Organomet. Chem.* **2016**, 813, 46–54.

(18) Wiese, S.; Aguila, M. J. B.; Kogut, E.; Warren, T. H. β -Diketiminato Nickel Imides in Catalytic Nitrene Transfer to Isocyanides. *Organometallics* **2013**, 32, 2300–2308.