Carbon−Hydrogen Bond Activation, C−N Bond Coupling, and Cycloaddition Reactivity of a Three-Coordinate Nickel Complex Featuring a Terminal Imido Ligand

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S *Supporting Information*

ABSTRACT: The three-coordinate imidos (dtbpe)Ni=NR (dtbpe = $^tBu_2PCH_2CH_2P^tBu_2$, R = 2,6-$^iPr_2C_6H_3$, 2,4,6-$Me_3C_6H_2$ (Mes), and 1-adamantyl (Ad)), which contain a legitimate Ni−N double bond as well as basic imido nitrogen based on theoretical analysis, readily deprotonate HC≡CPh to form the amide acetylide species (dtbpe)Ni{NH(Ar)}(C≡CPh). In the case of R = 2,6-$^iPr_2C_6H_3$, reductive carbonylation results in formation of the (dtbpe)Ni(CO)$_2$ along with the N−C coupled product keteneimine PhCH=C=N(2,6-$^iPr_2C_6H_3$). Given the ability of the Ni=N bond to have biradical character as suggested by theoretical analysis, H atom abstraction can also occur in (dtbpe)Ni=N{2,6-$^iPr_2C_6H_3$} when this species is treated with HSn(^nBu)$_3$. Likewise, the microscopic reverse reaction—conversion of the Ni(I) anilide (dtbpe)Ni{NH(2,6-$^iPr_2C_6H_3$)} to the imido (dtbpe)Ni=N{2,6-$^iPr_2C_6H_3$}—is promoted when using the radical Mes*O$^\bullet$ (Mes* = 2,4,6-$^tBu_3C_6H_2$). Reactivity studies involving the imido complexes, in particular (dtbpe)Ni=N{2,6-$^iPr_2C_6H_3$}, are also reported with small, unsaturated molecules such as diphenylketene, benzylisocyanate, benzaldehyde, and carbon dioxide, including the formation of C−N and N−N bonds by coupling reactions. In addition to NMR spectroscopic data and combustion analysis, we also report structural studies for all the cycloaddition reactions involving the imido (dtbpe)Ni=N{2,6-$^iPr_2C_6H_3$}.
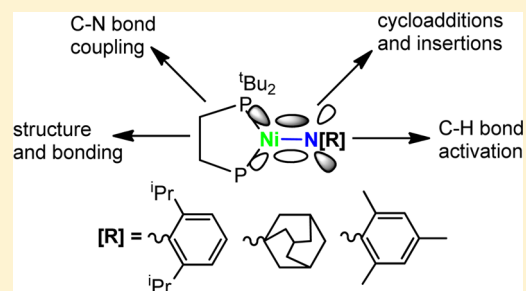
INTRODUCTION

Since the discovery of a three-coordinate terminal nickel imido, (dtbpe)Ni=NAr (dtbpe = $^tBu_2PCH_2CH_2P^tBu_2$, Ar = 2,6-$^iPr_2C_6H_3$, Scheme 1a) in 2001,[1] this class of complexes remains relatively scarce, and their reactivity remains underexplored.[2] The low coordination geometry offered by the strong σ-donating and sterically encumbered chelating bisphosphine ligand allows for optimal σ and π bond formation in a trigonal planar environment without causing π electron−electron repulsion between the electron-rich late transition metal and the π-loaded imido ligand.[3] Three-coordinate nickel(II) imidos can also be prepared with other sterically demanding groups on the imido nitrogen, such as mesityl,[4] 1-adamantyl (Ad),[4] and dmp[5] (dmp = 2,6-dimesitylphenyl, Scheme 1a). The use of a bulky scaffold such as dmp allows the isolation of a three-coordinate Ni(III) imido by virtue of a one-electron oxidation process (Scheme 1b).[5] Warren and co-workers have also found that β-diketiminate ligands can stabilize Ni(III) complexes possessing the terminal imido ligand (Scheme 1c),[6] while Limberg has recently expanded this approach to a diazenido ligand using a more sterically encumbered chelating ligand (Scheme 1d).[7] Other examples of kinetically stabilized Ni(II) imidos have been reported using a sterically encumbering and chelating bis-N-heterocyclic carbene ligand (3,3-methylenebis-(1-tert-butyl-4,5-dimethylimidazoliylidene, Scheme 1e).[8] Terminal imidos are not just restricted to three-coordinate environments. Hillhouse reported examples of linear, two-coordinate imidos using an impressively sterically demanding N-heterocyclic carbene as well as a bulky dmp group on the imido nitrogen (Scheme 1f).[9]

Apart from their fascinating coordination and electronic properties,[5] terminal imido complexes of nickel are also highly reactive and effect H atom-abstraction,[10] engage in C−H bond activation chemistry such as ethylene amination,[9] the amination of allylic groups such as 1,4-cyclohexadiene, and even activation of stronger C−H bonds in substrates such as indane, ethylbenzene, and toluene.[6,11] Warren and co-workers demonstrated that C−H bond activation proceeds via hydrogen atom abstraction and alkyl radical formation, followed by recombination of the latter with a second equivalent of Ni-imido to form primary and secondary nickel(II) amides.[11] The radical nature of some Ni(III) imidos is also manifested in radical recombination to form diphenoquinonediimine-type scaf-

Scheme 1. Terminal Coordinated Ni=N-type Complexes of Nickel
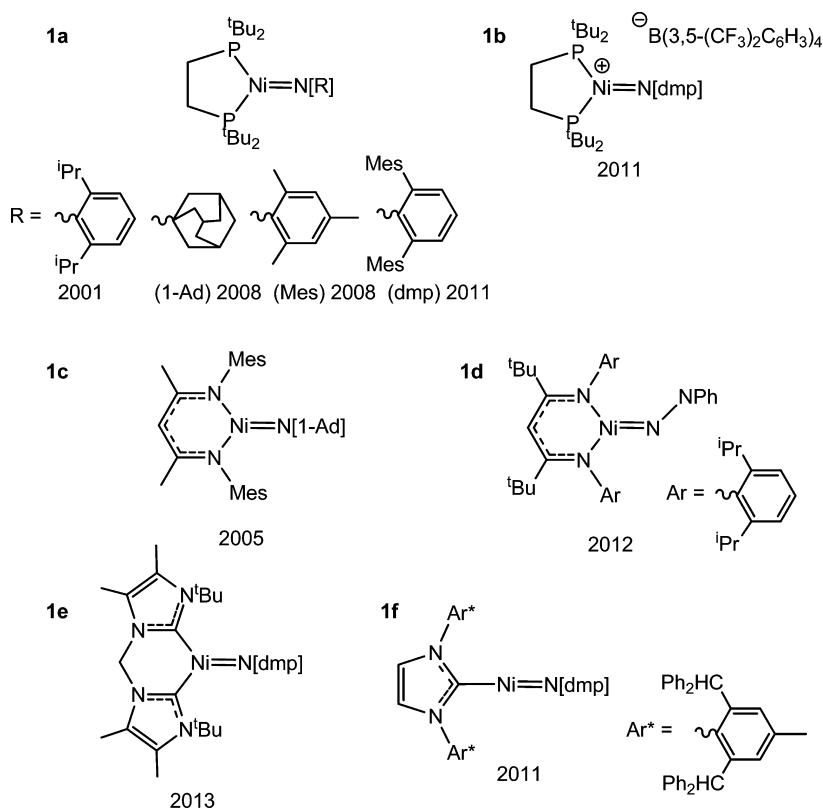
folds.[7,12−14] Lastly, nickel complexes with a terminal imido ligand can also engage in nitrene group transfer to unsaturated molecules such as alkenes,[15] organic azides,[16] C≡O, and C≡NR.[6,17,18] Surprisingly, the reactivity of nickel imidos toward other unsaturated substrates including cumulenes, has not been reported despite the rich chemistry from the similar species (dtbpe)Ni=CPh₂[18] and (dtbpe)Ni=P[dmp].[15,16,20]

In this study, we describe reaction chemistry of the first nickel(II) complexes having a terminally bound imido ligand, (dtbpe)Ni=NR (R = 2,6-iPr₂C₆H₃, 2,3,6-Me₃C₆H₂ (Mes), and Ad) with various small unsaturated molecules. These Ni(II) imidos can abstract an H atom from a reductant such as HSnⁿBu₃,[21] but are also basic enough to heterolytically activate the C−H bond of a terminal alkyne. Other substrates, such as carbon dioxide, isocyanate, aldehyde, and ketene functional groups, engage in [2 + 2] cycloaddition, and sometimes insertion chemistry, across the Ni=N bond to form stable and crystalline 4- and 6-membered ring nickel metallacycles. In addition to activating C−H bonds, it was also discovered that C≡O can promote C−N coupling of anilide with an acetylide to form a transient ynamine, which rearranges to the keteneimine. Theoretical studies, employing both density functional theory and higher-level ab initio simulations, were applied to understand the bonding and reactivity of the nickel-imido ligand.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all operations were performed in an MBraun Lab Master drybox under an atmosphere of purified nitrogen or using high-vacuum and standard Schlenk techniques under an argon atmosphere.[22] Hexanes, petroleum ether, benzene, and toluene were dried by passage through activated alumina and Q-5 columns.[23] Benzene-d_6, deuterated tetrahydrofuran

(THF-d_8), and CD₂Cl₂ were purchased, degassed, and dried over CaH₂ or activated 4 Å molecular sieves and vacuum transferred. Celite, alumina, and 4 Å molecular sieves were activated under vacuum overnight at a temperature above 180 °C. Anhydrous solvents such as THF and diethyl ether were purchased from Acros Organics or Fischer, stirred over sodium metal, and filtered through activated alumina.. All other chemicals were used as received. O=C=CPh₂,[24] [(dtbpe)Ni(μ-Cl)]₂,[1,25] (dtbpe)Ni(COD),[26,27] (dtbpe)Ni{NH-(2,6-iPr₂C₆H₃)},[1] (dtbpe)Ni=N(2,6-iPr₂C₆H₃) (**1**),[1] (dtbpe)Ni=N(Mes) (**2**),[4] Mes*O• radical,[28] MesN=NMes,[29] (dtbpe)NiCl₂,[27] and (dtbpe)Ni=N(1-Ad) (**3**)[4] were prepared according to the literature. For complex **1** an alternative, and optimized, procedure is reported below. HC≡CPh was distilled under reduced pressure and dried over molecular sieves. Infrared data (Fluorolube mulls or solution, CaF₂ plates or in Nujol mulls, KBr plates) were measured by using a Nicolet 670-FT-IR instrument. Elemental analysis was performed by Desert Analytics (Tucson, AZ). ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on Bruker 500 and 400 MHz NMR spectrometers. ¹H and ¹³C NMR are reported with reference to solvent resonances (residual C₆D₅H in C₆D₆, 7.16 and 128.0 ppm; residual CHDCl₂ in CD₂Cl₂, 5.32 and 53.8 ppm; residual proteo THF in THF-d_8, 1.73 and 3.58 ppm, and 65.6 and 23.5 ppm). ¹⁹F NMR spectra were reported with respect to external CCl₃F (0 ppm). ³¹P NMR spectra were reported with respect to external 85% H₃PO₄ (0 ppm). Magnetic susceptibilities were determined by the method of Evans.[30,31] X-ray diffraction data were collected on a Siemens Platform goniometer with a charged coupled device (CCD) detector. Structures were solved by direct or Patterson methods using the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).[32]

Improved Synthesis of 1. A mixture of (dtbpe)Ni{NH(2,6-iPr₂C₆H₃)}[1] (55 mg, 0.1 mmol) and Mes*O• (28 mg, 0.1 mmol) in 10 mL of C₆H₆ was placed in a 20 mL scintillation vial and stirred for 12 h. After removal of volatiles under reduced pressure, the residual solids were extracted with hexanes. The hexanes solution was concentrated, filtered through a plug of Celite, and cooled to −35 °C to generate

pure green crystals of **1** (50 mg, 90%). Spectroscopic characterization matched the previously reported data.[1]

Synthesis of (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)} from 1 and HSn^{n}Bu$_3$. A mixture of **1** (82.8 mg, 0.15 mmol), HSn^{n}Bu$_3$ (43.6 mg, 0.15 mmol), and C$_6$H$_6$ (10 mL) was placed in a Schlenk tube and heated at 75 °C for 12 h. The mixture gradually turned color from emerald green to dark red. After the mixture cooled to room temperature, the volatiles were removed under reduced pressure, and the solids were extracted with toluene. After filtration, crystallization occurred by cooling a concentrated toluene solution stored at −35 °C over a period of 1−2 d. Red crystals were separated by filtration and dried under reduced pressure to yield analytically pure product, (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)} (68 mg, 82%). Spectroscopic characterization matched the previously reported data.[1]

Synthesis of (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)}(C≡CPh) (4). In a vial was dissolved **1** (90 mg, 0.163 mmol) in 15 mL of Et$_2$O, and the green solution was cooled to −35 °C. To the cold solution was added dropwise 5 mL of an Et$_2$O solution containing HC≡CPh (17 mg, 0.167 mmol), which caused darkening of the solution over a period of 2 h after reaching room temperature. The reaction mixture was allowed to stir for an additional 3 h at room temperature. The dark red solution was filtered, concentrated, and cooled to −35 °C overnight to afford (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)}(CCPh) (**4**) in two crops as dark red crystals/powder, which was filtered, washed with cold petroleum ether, and dried under reduced pressure (96 mg, 0.147 mmol, 90% yield). ^{1}H NMR (22 °C, 500.1 MHz, CD$_2$Cl$_2$): δ 6.95 (m, aryl, 3 H), 6.80 (d, aryl, 2 H), 6.49 (m, aryl, 3 H), 4.01 (sept, CH(CH$_3$)$_2$, 2 H), 1.96 (br, NH, 1 H), 1.88 (m, CH_2, 2 H), 1.73 (m, CH_2, 2 H), 1.56 (d, ^{t}Bu, 36 H, J_{HP} = 13 Hz), 1.29 (d, CH(CH_3)$_2$, 6 H), 1.16 (d, CH(CH_3)$_2$, 6 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CD$_2$Cl$_2$): δ 158.21 (s, aryl), 139.12 (s, aryl), 131.04 (s, aryl), 129.59 (s, aryl), 127.49 (s, aryl), 124.35 (s, aryl), 121.83 (s, aryl), 114.41 (s, aryl), 113.85 (d, NiCCPh, $J_{CPtrans}$ = 21 Hz), 106.80 (dd, NiCCPh, $J_{CPtrans}$ = 96 Hz, J_{CPcis} = 41 Hz), 36.75 (s, CH(CH$_3$)$_2$), 36.62 (s, CH(CH$_3$)$_2$), 36.11 (s, C(CH$_3$)$_3$), 36.04 (s, C(CH$_3$)$_3$), 30.91 (s, C(CH$_3$)$_3$), 30.70 (s, C(CH$_3$)$_3$), 28.36 (s, CH(CH$_3$)$_2$), 25.04 (s, CH(CH$_3$)$_2$), 24.68 (t, CH_2CH$_2$, J_{CP} = 15 Hz), 22.74 (s, CH(CH$_3$)$_2$), 21.22 (t, CH$_2$CH_2, J_{CP} = 15 Hz). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, CD$_2$Cl$_2$): δ 82.80 (d, J_{PP} = 26 Hz), 68.84 (d,, J_{PP} = 26 Hz). Anal. Calcd for C$_{38}$H$_{64}$NNiP$_2$: C, 69.73; H, 9.70; N, 2.14. Found: C, 68.83; H, 9.63; N, 2.00%.

Synthesis of (dtbpe)Ni{NH(Mes)}(C≡CPh) (5). A 25 mL round-bottom flask was charged with **2** (83 mg, 0.163 mmol) and 12 mL of Et$_2$O, and then it was cooled to −35 °C. A similarly cold 2 mL solution of HC≡CPh (17 mg, 0.163 mmol) was added dropwise to the nickel solution causing a color change to red-orange. After it was stirred for 45 min at room temperature, the solution was filtered and then cooled to −35 °C overnight to give dark red crystals of **5** (84 mg, 0.132 mmol, 81%). ^{1}H NMR (22 °C, 400 MHz, C$_6$D$_6$): δ 7.23 (t, C$_6$H$_5$, 2 H), 7.19 (s, CH$_2$Me$_3$, 2 H), 7.14 (d, C$_6$H$_5$, 2 H), 6.93 (t, C$_6$H$_5$, 1 H), 2.82 (s, CH$_3$, 6 H), 2.49 (s, CH$_3$, 3 H), 1.44 (d, (CH$_3$)$_3$, 18 H), 1.35 (d, (CH_3)$_3$, 18 H), 1.13 (d, CH_2, 4 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, C$_6$D$_6$): δ 156.7 (t, NiCCPh, J_{CP} = 4.2 Hz), 130.3 (s, Ar), 128.4 (s, Ar), 127.6 (s, Ar), 127.4 (s, Ar), 127.1 (s, Ar), 126.6 (s, Ar), 123.6 (s, Ar), 121.3 (s, Ar), 112.0 (dd, NiCCPh, J_{CP} = 2, 23 Hz), 35.8, 34.5 (m, C(CH$_3$)$_3$, J_{PC} = 16.3 Hz), 35.3 (m, C(CH$_3$)$_3$, J_{PC} = 9.6 Hz), 29.9 (d, (CH$_3$)$_3$, J_{PC} = 3 Hz), 29.7 (d, (CH$_3$)$_3$, J_{PC} = 3.8 Hz), 23.7 (t, CH$_2$, J_{CP} = 15 Hz), 20.5 (s, CH$_3$), 19.6 (s, CH$_3$). The NH resonance could not be located. ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, C$_6$D$_6$): δ 81.0 (d, J_{PP} = 25.2), 67.8 (d, J_{PP} = 25.2). IR (Nujol, KBr): 2092(s ν_{CC}), 1591(m), 1294(w), 1236(s), 1178(m), 1151(m), 1020(m), 851(s), 812(w), 785(w), 755(s), 722(s), 693(m), 683(m), 603(w), 500(m), 454(w) cm^{-1}. Anal. Calcd for C$_{35}$H$_{57}$NiNP$_2$: C, 68.64; H, 9.38; N, 2.29. Found: C, 68.56; H, 9.49; N, 2.20%.

Synthesis of (dtbpe)Ni{NH(1-Ad)}(C≡CPh) (6). A 25 mL round-bottom flask was charged with **3** (31 mg, 0.0589 mmol) and 10 mL of Et$_2$O, and then it was cooled to −35 °C. A similarly cold 2 mL solution of HC≡CPh (6 mg, 0.0589 mmol) was added dropwise to the nickel solution causing a color change to orange-yellow. After it was stirred for 90 min at room temperature, the solution was filtered, concentrated to 3 mL, and cooled to −35 °C overnight to give dark

orange crystals of **6** (32 mg, 0.051 mmol, 86%). ^{1}H NMR (22 °C, 500 MHz, C$_6$D$_6$): δ 7.47 (d, Ph, 2 H), 7.26 (t, Ph, 2 H), 7.03 (t, Ph, 1 H), 2.03 (s, C$_{10}$H$_{15}$, 6 H), 1.96 (s, C$_{10}$H$_{15}$, 3 H), 1.38 (d, C$_{10}$H$_{15}$, 3 H), 1.36 (d, C$_{10}$H$_{15}$, 3 H), 1.33 (m, CH_2, 4 H), 1.25 (d, (CH_3)$_3$, 18 H), 1.10 (d, (CH_3)$_3$, 18 H), ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, C$_6$D$_6$): δ 132.6 (s, Ph), 131.6 (s, Ph), 129.6 (s, Ar), 127.1 (s, Ph), 114.7 (d, NiCCPh, J_{CP} = 21 Hz), 100.6 (dd, NiCCPh, J_{CP} = 91, 34 Hz), 43.6 (t, Ad, J_{PC} = 6.8 Hz), 38.4 (s, Ad), 35.4 (m, C(CH$_3$)$_3$), 32.5, (s, Ad), 30.6 (d, (CH_3)$_3$, J_{PC} = 6.3 Hz), 30.2 (d, (CH_3)$_3$, J_{PC} = 6.3 Hz), 23.9 (m, CH_2). The NH resonance could not be located. ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, C$_6$D$_6$): δ 98.8 (d, J_{PP} = 47.1 Hz), 90.2 (d, J_{PP} = 47.1 Hz). IR (Nujol, KBr): 2153(s ν_{CC}), 1589(s), 1307(w), 1260(w), 1179(s), 1095(m), 1067(w), 1019(m), 935(w), 850(w), 813(s), 755(s), 695(m), 673(m), 658(w) cm^{-1}.

Carbonylation of 4 to Produce (dtbpe)Ni(CO)$_2$ and Keteneimine PhCH=C=N(2,6-^{i}Pr$_2$C$_6$H$_3$). A 25 mL round-bottom flask was charged with **4** (78 mg, 0.0141 mmol), attached to an adapter, and evacuated. Approximately 6 mL of toluene was vacuum-transferred into the flask. Carbon monoxide (1 atm) was introduced into the vessel at −78 °C. Examination of the reaction mixture by ^{31}P NMR spectroscopy revealed clean formation of (dtbpe)Ni(CO)$_2$[17] along with one major organic product (observed by ^{1}H NMR spectroscopy). After 30 min, the gas was evacuated, the flask was opened in air, and the solvent was removed under reduced pressure. The PhCH=C=N(2,6-^{i}Pr$_2$C$_6$H$_3$) residue was passed through a short column of silica with hexanes/EtOAc (4:1) as the eluent to provide a viscous oil (19 mg, 0.68 mmol, 48%). ^{1}H NMR (22 °C, 500.1 MHz, CD$_2$Cl$_2$): δ 6.97 (s, aryl, 3 H), 5.65 (s, CH), 3.65 (sept, CH(CH$_3$)$_2$, 2 H), 1.70 (d, CH(CH_3)$_2$, 12 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CD$_2$Cl$_2$): δ 178.2 (s, CCN), 141.2 (s, aryl), 134.1 (s, aryl), 127.3 (s, aryl), 124.6 (s, aryl), 56.2 (s, CCN), 28.2 (s, CH(CH$_3$)$_2$), 23.5 (s, CH(CH$_3$)$_2$). GC/MS (m/z): 214 (M$^+$), 176, 130, 91.

Synthesis of (dtbpe)Ni{O,C:OC=N(2,6-^{i}Pr$_2$C$_6$H$_3$)CPh$_2$} (7). In a vial was dissolved **1** (100 mg, 0.181 mmol) in 10 mL of Et$_2$O, and to the green solution was added dropwise O=C=CPh$_2$ in 5 mL of Et$_2$O, causing a rapid color change from green to an intense orange-red. After 10 min red precipitate began to form, and after allowing the reaction to stir for an additional 40 min, the mixture was cooled to −35 °C for 20 min, filtered, and the solids washed with cold Et$_2$O. The red solid was dried under reduced pressure to afford crude (dtbpe)Ni{O,C:OC=N(2,6-^{i}Pr$_2$C$_6$H$_3$)CPh$_2$} (127 mg, 0.172 mmol, 95% yield). Analytically pure **7** was obtained by dissolving the solids in a minimum of CH$_2$Cl$_2$, filtering, layering carefully with excess Et$_2$O, and cooling the solution to −35 °C for 1 d. Large dark red blocks of **7** were collected via filtration, washed with cold Et$_2$O, and dried under vacuum (95 mg, 0.127 mmol, 70% yield). ^{1}H NMR (22 °C, 500.1 MHz, CD$_2$Cl$_2$): δ 8.37 (d, aryl, 4 H), 7.24 (t, aryl, 4 H), 7.13 (t, aryl, 2 H), 6.85 (d, aryl, 2 H), 6.74 (t, aryl, 1 H), 2.87 (sept, CH(CH$_3$)$_2$, 2 H), 1.80 (m, CH_2, 2 H), 1.48 (m, CH_2, 2 H), 1.44 (d, ^{t}Bu, 18 H, J_{HP} = 15 Hz), 1.08 (d, ^{t}Bu, 18 H, J_{HP} = 13 Hz), 0.99 (br, CH(CH_3)$_2$, 6 H), 0.86 (br, CH(CH_3)$_2$, 6 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CD$_2$Cl$_2$): δ 175.7 (s, OC=N(2,6-^{i}Pr$_2$C$_6$H$_3$)), 150.2 (s, aryl), 145.2 (s, aryl), 140.5 (s, aryl), 130.6 (s, aryl), 127.4 (s, aryl), 124.0 (s, aryl), 121.5 (s, aryl), 120.6 (s, aryl), 35.79 (CPh$_2$), 35.69 (s, CH(CH$_3$)$_2$), 35.47 (br, C(CH$_3$)$_3$), 30.63 (s, C(CH$_3$)$_3$), 30.40 (s, C(CH$_3$)$_3$), 28.15 (s, CH(CH$_3$)$_2$), 25.24 (m, CH$_2$CH$_2$, J_{CP} = 13 Hz), 23.50 (br, CH(CH$_3$)$_2$), 18.05 (br, CH$_2$CH$_2$). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, CD$_2$Cl$_2$): δ 77.49 (d, J_{PP} = 13 Hz), 66.21 (d, J_{PP} = 13 Hz). IR (CaF$_2$, Fluorolube mull): 3047 (w), 2987 (w), 2953 (w), 2899 (w), 1603 (s, ν_{CN}), 1577 (s), 1482 (m), 1468 (m), 1429 (m), 1391 (w), 1357 (w) cm^{-1}. Anal. Calcd for C$_{44}$H$_{67}$NNiP$_2$O: C, 70.78; H, 9.04; N, 1.88. Found: C, 70.38; H, 9.33; N, 1.92%.

Synthesis of (dtbpe)Ni{O,C:OC=N(Mes)CPh$_2$} (8). A 25 mL round-bottom flask was charged with **2** (48 mg, 0.094 mmol) and 5 mL of Et$_2$O, and then it was cooled to −35 °C. A similarly cold solution of diphenylketene (18 mg, 0.094 mmol) in 4 mL of Et$_2$O was added dropwise to **2**, causing a color change to red-orange. The solution was filtered after 1.5 h of stirring at room temperature, then concentrated to ca. 4 mL and cooled to give orange crystals of **8** (51 mg, 0.068 mmol, 72%). ^{1}H NMR (22 °C, 500 MHz, CD$_2$Cl$_2$): δ 8.22

(d, *Ph*, 4 H), 7.13 (t, *Ph*, 4 H), 7.06 (t, *Ph*, 2 H), 6.58 (s, C*H*$_2$Me$_3$, 2 H), 2.07 (s, C*H*$_3$, 3 H), 1.79 (s, C*H*$_3$, 6 H), 1.34 (m, C*H*$_2$, 4 H), 1.23 (d, (C*H*$_3$)$_3$, 18 H), 1.01 (d, (C*H*$_3$)$_3$, 18 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CD$_2$Cl$_2$): δ 170.2 (s, CO), 133.8 (s, *Ar*), 130.3 (s, *Ar*), 129.8 (s, *Ar*), 127.3 (s, *Ar*), 127.2 (s, *Ar*), 123.7 (s, *Ar*), 122.6 (s, *Ar*), 121.3 (s, *Ar*), 38.1 (t, *C*Ph$_2$, J_{PC} = 15 Hz), 35.4 (m, *C*(CH$_3$)$_3$), 30.4 (d, (*C*H$_3$)$_3$, J_{PC} = 4.6 Hz), 30.1 (d, (*C*H$_3$)$_3$, J_{PC} = 3.7 Hz), 22.7 (m, *C*H$_2$), 22.1 (s, *C*H$_3$), 18.0 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, CD$_2$Cl$_2$): δ 78.5 (d, J_{PP} = 12.4 Hz), 66.9 (d, J_{PP} = 12.4 Hz). IR (Nujol, KBr): 1594(m), 1564(s, ν_{CN}), 1266(m), 1232(w), 1180(m), 1022(m), 859(w), 837(m), 799(w), 786(w), 738(w) 716(m), 694(s), 673(m), 651(w) cm^{-1}. Anal. Calcd for C$_{40}$H$_{61}$NiNOP$_2$: C, 69.37; H, 8.88; N, 2.02. Found: C, 68.87; H, 8.22; N, 2.01%.

Synthesis of (dtbpe)Ni{*O,C*:OC=N(1-Ad)CPh$_2$} (9). A 25 mL round-bottom flask was charged with **3** (95 mg, 0.180 mmol) and 7 mL of Et$_2$O, and then it was cooled to −35 °C. A similarly cold solution of diphenylketene (35 mg, 0.180 mmol) in 2 mL of Et$_2$O was added dropwise to **3**, causing little visible color change. The solution was filtered after 1.5 h of stirring at room temperature, then concentrated to ca. 4 mL and cooled to give dark red blocks of **9** (87 mg, 0.139 mmol, 77%). ^{1}H NMR (22 °C, 500 MHz, C$_6$D$_6$): δ 8.55 (d, *Ph*, 4 H), 7.24 (t, *Ph*, 4 H), 7.10 (t, *Ph*, 2 H), 2.38 (s, C$_{10}$*H*$_{15}$, 6 H), 2.18 (s, C$_{10}$*H*$_{15}$, 3 H), 1.85 (d, C$_{10}$*H*$_{15}$, 3 H), 1.78 (d, C$_{10}$*H*$_{15}$, 3 H), 1.16 (d, (C*H*$_3$)$_3$, 18 H), 1.13 (m, C*H*$_2$, 4 H), 0.88 (d, (C*H*$_3$)$_3$, 18 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, C$_6$D$_6$): δ 179 (br, CO), 141.6 (s, *Ph*), 131 (s, *Ph*), 127.0 (s, *Ph*), 126.3 (s, *Ph*), 48.6 (t, *Ad*, J_{PC} = 6.2 Hz), 38.6 (s, *Ad*), 36.4 (t, *C*Ph$_2$, J_{PC} = 12 Hz), 35.2 (m, *C*(CH$_3$)$_3$), 32.4, (s, *Ad*), 30.2 (d, (*C*H$_3$)$_3$, J_{PC} = 6.5 Hz), 29.3 (d, (*C*H$_3$)$_3$, J_{PC} = 6.7 Hz), 22.1 (m, *C*H$_2$). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, C$_6$D$_6$): δ 77.5 (d, J_{PP} = 19.8 Hz), 62.4 (d, J_{PP} = 19.8 Hz). IR (CaF$_2$, Fluorolube): 1559(s), 1469(s), 1444(m), 1385(w), 1361(s) cm^{-1}.

Synthesis of (dtbpe)Ni{*O,C*:OC=NCH$_2$PhN(2,6-^{i}Pr$_2$C$_6$H$_3$)} (10). In a vial was dissolved **1** (80 mg, 0.145 mmol) in 8 mL of toluene, and the green solution was cooled to −35 °C. To the cold solution was added dropwise 3 mL of a toluene solution containing O=C=NCH$_2$Ph (21 mg, 0.158 mmol) causing darkening of the solution over a period of 2 h at room temperature and with precipitation of green solid. The reaction mixture was allowed to stir for an additional 3 h at room temperature. The dark solution was concentrated, cooled to −35 °C overnight, and then filtered; the green solids were washed with cold Et$_2$O and dried under vacuum to afford crude (dtbpe)Ni{*O,C*:OC=NCH$_2$PhN(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**10**) (89 mg, 131 mmol, 90% yield). The solids were dissolved in a minimum of CH$_2$Cl$_2$, filtered, layered carefully with excess Et$_2$O, and cooled to −35 °C for 2 d. Large dark green blocks of **10** were collected via filtration, washed with Et$_2$O, and dried under vacuum (76 mg, 0.110 mmol, 76% yield). ^{1}H NMR (22 °C, 500.1 MHz, CD$_2$Cl$_2$): δ 7.21 (d, aryl, 2 H), 7.14 (t, aryl, 2 H), 7.01 (t, aryl, 1 H), 6.93 (s, aryl, 3 H), 4.26 (sept, C*H*(CH$_3$)$_2$, 2 H), 4.10 (s, C*H*$_2$Ph, 2 H), 1.65 (m, C*H*$_2$C*H*$_2$, 4 H), 1.58 (d, ^{t}Bu, 18 H, J_{HP} = 13 Hz), 1.24 (d, CH(C*H*$_3$)$_2$, 12 H), 1.23 (d, ^{t}Bu, 18 H, J_{HP} = 13 Hz). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CD$_2$Cl$_2$): δ 173.4 (s, O*C*=NCH$_2$Ph), 147.2 (br, aryl), 146.8 (s, aryl), 128.5 (s, aryl), 127.5 (s, aryl), 124.8 (s, aryl), 123.3 (s, aryl), 122.6 (s, aryl), 47.23 (s, *C*H$_2$Ph), 36.01 (d, *C*(CH$_3$)$_3$, J_{CP} = 15 Hz), 35.51 (d, *C*(CH$_3$)$_3$, J_{CP} = 15 Hz), 30.97 (s, *C*H(CH$_3$)$_2$), 30.40 (s, *C*(CH$_3$)$_3$), 29.23 (s, *C*H(CH$_3$)$_2$), 26.28 (s, *C*H(CH$_3$)$_2$), 24.24 (m, *C*H$_2$CH$_2$), 23.28 (s, *C*H(CH$_3$)$_2$), 21.05 (m, *C*H$_2$CH$_2$). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, CD$_2$Cl$_2$): δ 86.01 (d, J_{PP} = 27 Hz), 83.31 (d, J_{PP} = 27 Hz). Anal. Calcd for C$_{38}$H$_{64}$N$_2$NiP$_2$O: C, 66.57; H, 9.41; N, 4.09. Found: C, 66.17; H, 9.49; N, 3.71%.

Synthesis of (dtbpe)Ni{*O,C*:OCHPhN(2,6-^{i}Pr$_2$C$_6$H$_3$)} (11). In a vial was dissolved **1** (138 mg, 0.250 mmol) in 10 mL of toluene, and the solution was cooled to −35 °C. To the green solution was added dropwise a similarly cold solution of PhHC=O (32 mg, 0.300 mmol) in 3 mL of toluene. The solution was stirred for 7 h at room temperature, during which time the color gradually changed from green to brown to finally a dark navy blue color. The dark solution was filtered, dried under vacuum, extracted with 50 mL of Et$_2$O, filtered, concentrated, and cooled to −35 °C for 2 d to afford large blue needles and powder of (dtbpe)Ni{*O,C*:OCHPhN(2,6-^{i}Pr$_2$C$_6$H$_3$)}

(**11**) (137 mg, 0.207 mmol, 83% yield), which was filtered and washed with cold petroleum ether. Analytically pure **11** was obtained from two consecutive recrystallizations from Et$_2$O. ^{1}H NMR (22 °C, 500.1 MHz, C$_6$D$_6$): δ 8.15 (d, aryl, 2 H), 7.39 (d, aryl, 1 H), 7.33 (t, aryl, 1 H), 7.18 (m, aryl, 2 H), 7.01 (d, aryl, 1 H), 6.63 (d, aryl, 1 H), 4.27 (sept, C*H*(CH$_3$)$_2$, 2 H), 1.94 (d, CH(C*H*$_3$)$_2$, 3 H), 1.88 (d, CH(C*H*$_3$)$_2$, 3 H), 1.57 (d, ^{t}Bu, 9 H, J_{HP} = 13 Hz), 1.45 (d, ^{t}Bu, 9 H, J_{HP} = 12 Hz), 1.30 (d, ^{t}Bu, 9 H, J_{HP} = 12 Hz), 1.27 (d, CH(C*H*$_3$)$_2$, 3 H), 1.09 (br, C*H*$_2$, 2 H), 0.88 (br, C*H*$_2$, 2 H), 0.73 (d, ^{t}Bu, 9 H, J_{HP} = 12 Hz), 0.47 (d, CH(C*H*$_3$)$_2$, 3 H). Note: The OC*H*Ph proton could not be located in the ^{1}H NMR spectrum. ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, C$_6$D$_6$): δ 157.4 (s), 152.8 (s), 148.9 (s, aryl), 147.6 (s, aryl), 127.5 (s, aryl), 126.5 (s, aryl), 124.3 (s, aryl), 122.8 (s, aryl), 122.6 (s, aryl), 114.3 (s, aryl), 35.32 (d, *C*(CH$_3$)$_3$, J_{CP} = 6 Hz), 35.17 (d, *C*(CH$_3$)$_3$, J_{CP} = 6 Hz), 34.78 (d, *C*(CH$_3$)$_3$, J_{CP} = 13 Hz), 34.37 (d, *C*(CH$_3$)$_3$, J_{CP} < 3 Hz), 31.02 (br), 30.47 (br), 30.24 (br), 29.92 (br), 29.79 (br), 27.46 (s, CH(CH$_3$)$_2$), 26.84 (s, CH(CH$_3$)$_2$), 25.50 (s, CH(CH$_3$)$_2$), 23.84 (s, CH(CH$_3$)$_2$), 23.59 (m, CH$_2$CH$_2$), 19.59 (m, CH$_2$CH$_2$). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, C$_6$D$_6$): δ 75.45 (d, J_{PP} = 6 Hz), 69.29 (d, J_{PP} = 7 Hz). Anal. Calcd for C$_{37}$H$_{63}$NNiP$_2$O: C, 67.48; H, 9.64; N, 2.13. Found: C, 67.22; H, 9.78; N, 2.10%.

Synthesis of (dtbpe)Ni{*O,C*:OC(O)N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (12). In a Schlenk flask equipped with a stir bar was dissolved **1** (126 mg, 0.228 mmol) in Et$_2$O, and the solution was degassed and cooled to −78 °C. To the cold green solution was added excess CO$_2$ (25 °C, 1 atm) for several minutes, and the solution was allowed to slowly reach room temperature. Upon reaching 0 °C the solution changed slowly to a pale yellow, and a pale yellow precipitate formed upon reaching room temperature. The solution was allowed to stir for an additional 2 h at room temperature, the solvent was removed under reduced pressure, and the flask was taken into the box. The solids were filtered and washed with cold Et$_2$O/petroleum ether (2:1), and the solids were dried under vacuum to afford crude (dtbpe)Ni{*O,C*:OC(O)N-(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**12**) as a pale yellow solid (128 mg, 0.214 mmol, 94% yield). Analytically pure complex **12** can be obtained by dissolving the crude product in a minimum of CH$_2$Cl$_2$, filtering the golden brown solution, layering the filtrate carefully with excess Et$_2$O, and cooling the solution to −35 °C for 2 d (2 crops, 71 mg, 0.119 mmol, 52% yield). ^{1}H NMR (22 °C, 500.1 MHz, CD$_2$Cl$_2$): δ 6.97 (m, aryl, 3 H), 4.00 (sept, C*H*(CH$_3$)$_2$, 2 H), 1.70 (m, C*H*$_2$, 4 H), 1.65 (d, ^{t}Bu, 18 H, J_{HP} = 13 Hz), 1.25 (d, CH(C*H*$_3$)$_2$, 6 H), 1.21 (d, ^{t}Bu, 18 H, J_{HP} = 13 Hz), 1.18 (d, CH(C*H*$_3$)$_2$, 6 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CD$_2$Cl$_2$): δ 170.5 (br, *C*O$_2$), 147.1 (s, aryl), 144.2 (s, aryl), 124.3 (s, aryl), 122.6 (s, aryl), 36.91 (d, *C*(CH$_3$)$_3$, J_{CP} = 16 Hz), 35.65 (d, *C*(CH$_3$)$_3$, J_{CP} = 16 Hz), 30.35 (s, *C*(CH$_3$)$_3$), 29.48 (s, *C*H(CH$_3$)$_2$), 25.82 (s, *C*H(CH$_3$)$_2$), 24.24 (m, *C*H$_2$CH$_2$, J_{CP} = 12 Hz), 22.86 (s, *C*H(CH$_3$)$_2$), 21.23 (m, *C*H$_2$CH$_2$, J_{CP} = 11 Hz). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, CD$_2$Cl$_2$): δ 89.71 (d, J_{PP} = 28 Hz), 85.67 (d, J_{PP} = 28 Hz). IR (CaF$_2$, Fluorolube): 2955 (w), 1617 (s, ν_{CO}), 1588 (m), 1468 (m), 1431 (m), 1371 (w), 1360 (w), 1321 (w) cm^{-1}. Elemental analysis and single-crystal X-ray diffraction methods were consistent with complex (dtbpe)Ni{κ^2-OC(O)N(2,6-(CHMe$_2$)$_2$C$_6$H$_3$)} retaining one molecule of CH$_2$Cl$_2$. Anal. Calcd for C$_{32}$H$_{53}$Cl$_2$NNiP$_2$: C, 56.41; H, 8.73; N, 2.06. Found: C, 57.72; H, 8.53; N, 2.05%.

Synthesis of (dtbpe)Ni{*O,O*:(OC(O))$_2$N(1-Ad)} (13). A 50 mL round-bottom flask was charged with **3** (80 mg, 0.152 mmol), attached to an adapter, and evacuated. Petroleum ether (10 mL) was vacuum transferred into the flask, and 1 atm CO$_2$ was introduced. The solution became slightly red then lightened to a pale yellow, and a small amount of precipitate formed. After 30 min the CO$_2$ was removed, and the solution was dried under reduced pressure. The solids were extracted with 10 mL of Et$_2$O, filtered, and cooled to −35 °C to provide yellow crystals of **13** (58 mg, 0.094 mmol, 62% yield). ^{1}H NMR (22 °C, 500 MHz, CD$_2$Cl$_2$): δ 2.29 (d, C$_{10}$*H*$_{15}$, 3 H), 2.01 (s, C$_{10}$*H*$_{15}$, 6 H), 1.68 (d, C$_{10}$*H*$_{15}$, 3 H), 1.64 (d, C$_{10}$*H*$_{15}$, 3 H), 1.54 (d, (C*H*$_3$)$_3$, 36 H), 1.52 (d, C*H*$_2$, 4 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CD$_2$Cl$_2$): δ 157.9 (s, *C*O$_2$), 40.9 (s, *Ad*), 38.4 (s, *Ad*), 37.6 (t, *C*(CH$_3$)$_3$, J_{PC} = 6.0 Hz), 31.8, (s, *Ad*), 31.1 (d, (*C*H$_3$)$_3$, J_{PC} = 6.2 Hz), 23.1 (m, *C*H$_2$). ^{31}P{^{1}H} NMR (22 °C, 202.4 MHz, CD$_2$Cl$_2$): δ 87.7 (s). IR (CaF$_2$,

Scheme 2. Original Synthetic Protocols to Prepare the Imido Complexes 1–3
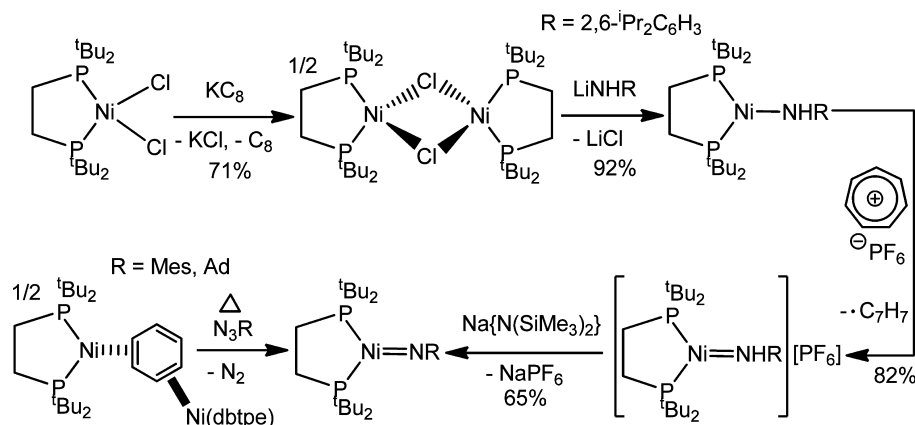
Thermolysis of Complex 2. A Schlenk tube was charged with **2** (76 mg, 0.149 mmol) and 6 mL of benzene. The solution was degassed and heated to 80 °C for 16 h. The tube was then opened in air, and the solvent was removed under reduced pressure. Azomesitylene was purified on a silica gel column with 5:1 hexanes/EtOAc as eluent to give red crystals (16 mg, 0.060 mmol, 40%). ^{1}H NMR (22 °C, 500 MHz, CDCl$_3$): δ 6.95 (s, C$_6$Me$_3$H$_2$, 2 H), 2.40 (s, C$_6$Me$_3$H$_2$, 6 H), 2.32 (s, C$_6$Me$_3$H$_2$, 3 H). ^{13}C{^{1}H} NMR (22 °C, 125.8 MHz, CDCl$_3$): δ 130.3 (s, *Mes*), 129.8 (s, *Mes*), 128.2 (s, *Mes*), 127.6 (s, *Mes*), 22.4 (s, CH$_3$), 21.7 (s, CH$_3$). GC/MS (*m/z*): 266 (M$^+$).

Computational Methods. Computational studies of complex **1** utilized density functional theory (specifically, ONIOM[33](M06[34]/6-311+G(d):[35]UFF[36]); geometry optimizations started from the reported crystal structure,[1] using the Gaussian 09 code.[37] At this optimized geometry, multiconfiguration self-consistent field (MCSCF[38]) computations were performed utilizing the complete active space (CAS) formalism within the GAMESS code.[39]

■ RESULTS AND DISCUSSION

Complex (dtbpe)Ni=N(2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)[1] is a green crystalline species that possesses a Ni–N formal bond order of two and should therefore react similar to the carbene complex (dtbpe)Ni=CPh$_2$[19] or phosphinidene (dtbpe)Ni=P(dmp).[15,16,20] Likewise, the imido relatives (dtbpe)Ni=N(Mes) (**2**, turquoise)[4] and (dtbpe)Ni=N(1-Ad) (**3**, red)[4] can also be prepared, and their chemistry can be similarly explored. Complexes **2** and **3** are obtained by a different route than **1**, using the corresponding organic azide and Ni(0) precursor (Scheme 1). Complex **1** is synthesized via a one-electron oxidation of the three-coordinate Ni(I) complex (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)} with the weak oxidant [C$_7$H$_7$]-[PF$_6$] followed by deprotonation with Na{N(SiMe$_3$)$_2$} (Scheme 2). Although this protocol is reliable, with each reaction being high yielding, it has two disadvantages: (i) It is a stepwise process to remove overall an H atom, and (ii) The synthesis of (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)} involves the use of the precursor [(dtbpe)Ni(μ-Cl)]$_2$,[1,25] a complex prepared in moderate yield from one-electron reduction of (dtbpe)NiCl$_2$[27] with KC$_8$ (Scheme 2).[1,25] The use of a Ni(I) precursor is required given that attempts to transmetallate and dehydrohalogenate (dtbpe)NiCl$_2$ with 2 equiv of Li{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)} resulted in complicated mixtures that contained traces of **1** and other species such as (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)}.[1] To improve the overall yield of [(dtbpe)Ni(μ-Cl)]$_2$, we reported a comproportionation reaction using easy-to-prepare Ni(0) and

Ni(II) complexes, namely, (dtbpe)Ni(COD)[27] and (dtbpe)-NiCl$_2$. Complex [(dtbpe)Ni(μ-Cl)]$_2$ can be prepared quantitatively[21,26] from these two reagents (Scheme 2) akin to Sigman's reported N-heterocyclic carbene complex of Ni(I).[40] Notably, the synthesis of [(dtbpe)Ni(μ-Cl)]$_2$ from this reaction does not require isolation or purification of the Ni(II) and Ni(0) starting materials since it can be produced by simply adding premixed solutions of Ni(COD)$_2$ with dtbpe and NiCl$_2$ with dtbpe over several hours.[21] Likewise, to obviate the need for separate oxidation and deprotonation steps, a H atom-abstraction reaction with the radical Mes*O (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) was used for the direct preparation of **1**.[21,26] Smith[41] and Hillhouse[10] have applied this strategy to prepare cobalt imido and other nickel imido derivatives, respectively. Consequently, a more convenient route to multigram quantities of imido **1** is shown in Scheme 3 via a comproportionation

Scheme 3. Optimized Synthetic Protocol to Prepare Complex 1
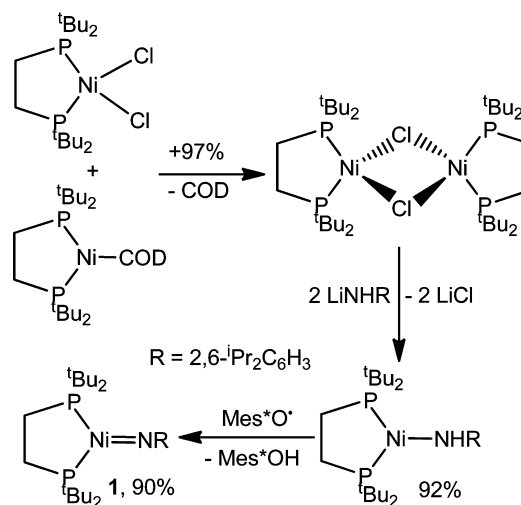
reaction to form [(dtbpe)Ni(μ-Cl)]$_2$, followed by transmetalation with Li{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)} to yield (dtbpe)Ni-{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)} in 92% yield, and then the protocol was completed by H atom abstraction with Mes*O. Separation of **1** from the HOMes byproduct can be achieved by fractional crystallization to provide **1** in 90% yield (Scheme 2).

Preliminary reactivity studies confirmed that the imido ligand in **1** can be readily carbonylated with C≡O to form O=C=
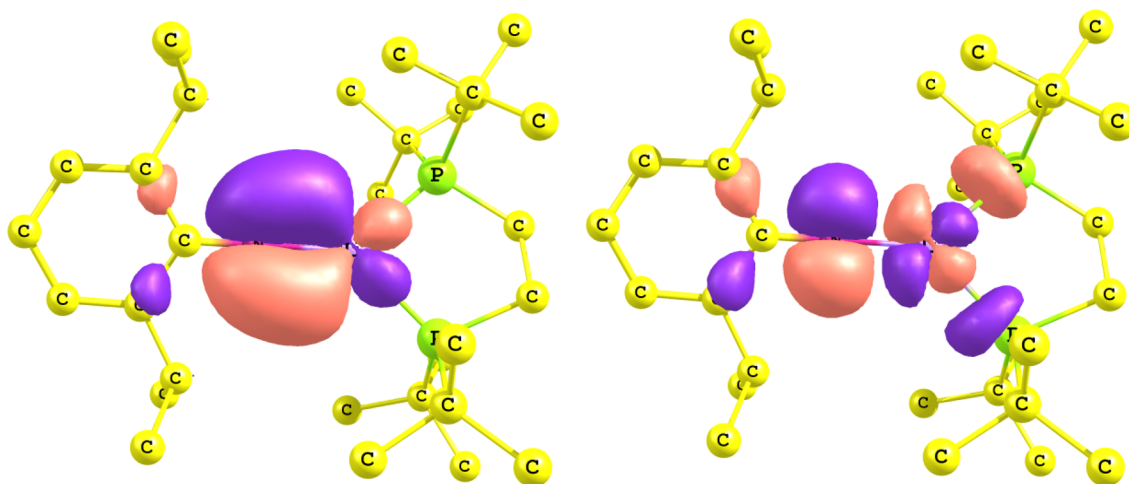
Figure 1. Computed frontier orbitals (π and π^*) of complex **1** in the plane defined by the N and the two P atoms. Hydrogen atoms omitted from figure for clarity.
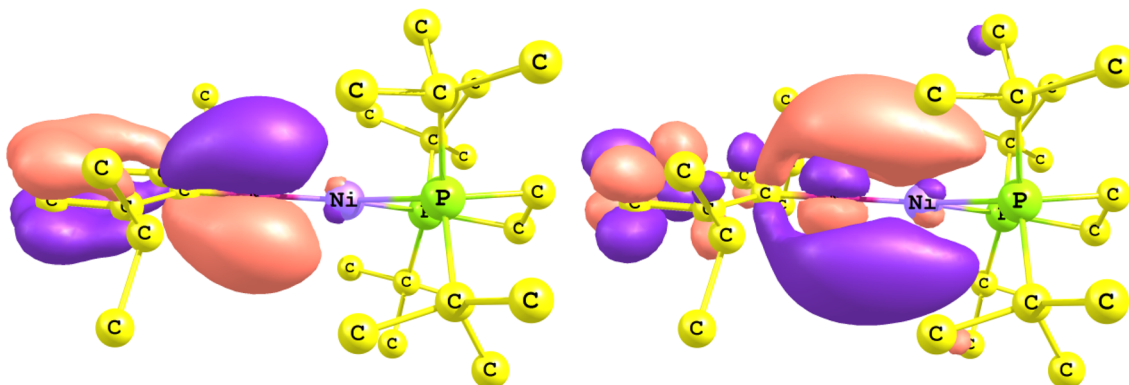

Figure 2. Illustration of the π and π^* orbitals in **1** perpendicular to the plane defined by the N and two P. Hydrogen atoms omitted from figure for clarity.

N(2,6-^{i}Pr$_2$C$_6$H$_3$) or with C≡NCH$_2$Ph to form the asymmetric carbodiimido PhCH$_2$N═C═N(2,6-^{i}Pr$_2$C$_6$H$_3$). Similar reactions have been explored with **2** and **3**.[42] In both reactions, the η^2-isocyanate or η^2-carbodiimido intermediate could be isolated.[16] In addition, [2 + 2] cycloaddition of ethylene across the Ni═N bond in **1** has been shown to be a crucial step in the formation of aziridines,[15] via an elusive azametallacyclobutane intermediate.[43]

The 2001 report by Mindiola and Hillhouse of complex **1**[1] foreshadowed a tremendous upsurge in interest in late transition-metal multiply bonded complexes. The original crystallographic report has several hallmarks of a complex "engineered" to have sufficient stability to permit solid-state analysis—a bulky bidentate supporting ligand, a sterically hindering imido N substituent, and hints of further stabilization of the π-loaded imido nitrogen via resonance with the aryl substituent (cf. the short N$_{imido}$–C$_{ipso}$ distance of 1.355 Å). However, as detailed above, these features belie a remarkable diversity of reactivity for complex **1** encompassing both even- and odd-electron processes as well as reactions involving homolytic (radical) and heterolytic (acid/base) transformations. A previous computational study in 2008,[44] inspired by the original experimental reports by Mindiola and Hillhouse,[1] indicated that subtle changes to the ligands and substituents markedly affect the computed kinetics and thermodynamics for highly desirable reactions such as C−H bond activation. To this

end, the electronic structure of **1** was scrutinized anew using theoretical methods not feasible on such a large complex when the earlier reports were published.

The geometry of **1** was first optimized utilizing hybrid QM/MM methods.[33] The ^{i}Pr and ^{t}Bu substituents on the imidoaryl and dtbpe ligands, respectively, were modeled with the Universal Force Field,[36] while the remainder of the complex was described at the M06/6-311+G(d) level of theory.[34,35] As expected, good agreement with the reported crystal data was obtained (coordinates in Supporting Information), and tests with other functionals—pure (BP86) and hybrid (B3LYP)—gave similar results. The density functional theory-optimized geometry was then used as the basis to analyze the electronic structure of **1** with MCSCF[38,39] techniques employing the CAS approximation with active spaces ranging from two-orbital/two-electron (CAS(2,2)) to 14-orbital/14-electron (CAS(14,14)). The salient features of the frontier natural orbitals are similar among the various CAS calculations; therefore, focus is given to the pertinent orbitals of the latter, largest active space MCSCF simulations.

The first orbitals of interest are the Ni−N$_{imido}$ π and π^* orbitals that lie within the plane defined by the NiP$_2$N coordination plane (Figure 1). The CA(14,14) calculations assign a substantial population to the latter orbital, 0.24 e^-, and thus the correlating π has a natural orbital occupation number (NOON) of 1.76 e^-. These orbitals' NOONs are those
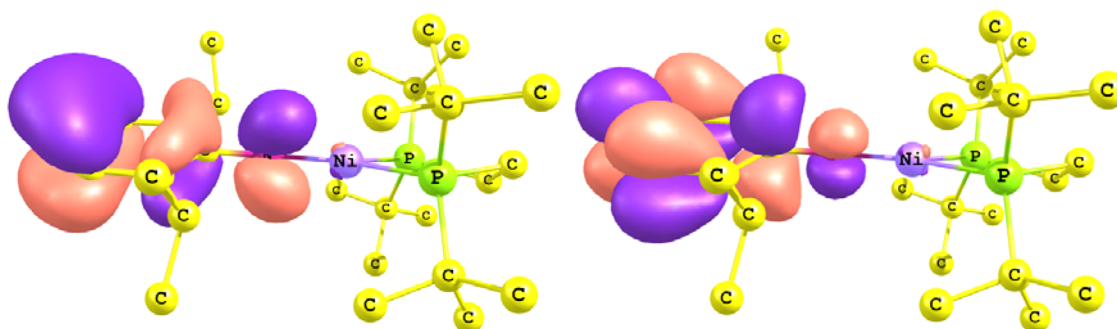
Figure 3. Computed natural orbitals showing delocalization of π-electron density from imido nitrogen of **1** onto the 2,6-^{i}Pr$_2$C$_6$H$_3$ ring: NOON = 1.94 (left) and 0.06 e (right). Hydrogen atoms omitted from figure for clarity.

Scheme 4. C−H Bond Activation of HC≡CPh by Compounds 1−3 to Form 4−6, Respectively, and Subsequent Carbonylation of 4 to Form the Ketenemine

4, R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 90%
5, R = Mes, 81%; **6**, R = Ad, 86%
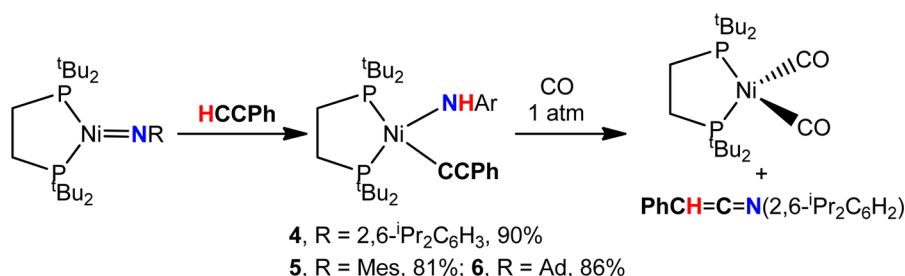
computed to deviate most significantly from the archetypal values of 2 and 0 e^-, and thus the MCSCF calculations are indicative of significant π-biradical character to the Ni-imido moiety, consistent with the ability of **1** to abstract an H atom from HSn(^{n}Bu)$_3$. Additionally, the π-biradical nature of **1** implies a formal bond order of less than three despite the nearly linear coordination of the imido functionality, which obviously assists the [2 + 2] cycloaddition and 1,3-dipolar addition chemistry of complex **1** and its congeners.[1,8,43]

The in-plane NiN π/π^* orbitals just discussed may be contrasted to the perpendicular π orbitals (Figure 2). The π orbital (Figure 2, left; NOON = 1.97 e^-) is heavily polarized toward the imido N with small Ni character but delocalized onto the imido aryl ring, {2,6-^{i}Pr$_2$C$_6$H$_3$}. Electron correlation is not of the bond/antibond variety (cf. Figure 1) but with an orbital that has an additional radial node (Figure 2, right; NOON = 0.03 e^-). The additional radial node in the right diagram in Figure 2 is clear; note that like its bonding counterpart, there is delocalization of electron density onto the imido 2,6-^{i}Pr$_2$C$_6$H$_3$ ring for both members of this correlating pair of orbitals. These MCSCF orbitals imply that in this plane the Ni−N π-bond may be best viewed more as a N$_{imido}$ lone pair, with potentially high nucleophilic or basic reactivity. As with the biradical character, the bonding analysis suggests a further diminution of the nickel−nitrogen bond order below the ideal value of three that a cursory glance at its linear coordination mode might imply.

The final pair of orbitals of interest from the MCSCF computations are plotted below (Figure 3). These orbitals highlight the substantial interaction between the imido N and the π-ring of the aryl substituent. Much of the experimental emphasis on late metal imidos has focused on the steric protection of the metal−nitrogen active site by changing the ortho substituents. The present computations suggest the great potential to synthetically tune the reactivity of these and related

late metal aryl-imido moieties via the introduction of electron-donating and -withdrawing groups onto the *meta* and *para* aryl ring positions. As such, with reduced metal−nitrogen bond orders and synthetic tunability, one may easily envisage derivatives of **1** providing improved routes to C−H bond amination that can complement known metal-catalyzed routes to C−N bond formation.

The observation that the frontier π symmetry orbitals displayed in Figures 1−3 are heavily composed of N$_{imido}$ character suggests that these systems should be quite basic. Because the three-coordinate anilide cation [(dtbpe)Ni═NH(2,6-^{i}Pr$_2$C$_6$H$_3$)][PF$_6$][1] can be deprotonated by NaN-(SiMe$_3$)$_2$, the pK_a of the anilide can be coarsely estimated to be less than 30.[45] We thus examined phenylacetylene as a substrate because its pK_a is slightly less than 30 in dimethyl sulfoxide.[46] Accordingly, treatment of the imidos **1−3** with HC≡CPh in Et$_2$O results in rapid and clean formation of analytically pure phenylacetylidene−amides, as red crystals of (dtbpe)Ni{NH(2,6-^{i}Pr$_2$C$_6$H$_3$)}(C≡CPh) (**4**), (dtbpe)Ni{NH-(Mes)}(C≡CPh) (**5**), and orange crystals of (dtbpe)Ni(NH-{1-Ad})(C≡CPh) (**6**), in 81%, 90%, and 86% isolated yields, respectively (Scheme 4). These results imply that the anilide in [(dtbpe)Ni═NH(2,6-^{i}Pr$_2$C$_6$H$_3$)][PF$_6$] has a pK_a from 29 to 35. Since the imidos **2** and **3** are not prepared by amide deprotonation we do not know their basicity; however, complex **2** most likely has a similar pK_b to **1**. Complexes **4**−**6** were thoroughly characterized spectroscopically in solution. For example, the ^{1}H and ^{13}C NMR spectra of complex **4** reveals the amide (N*H*, 1.93 ppm) and acetylide moieties (C≡C*Ph*, 107 and 114 ppm), respectively. The acetylide α-C reveals diagnostic $^2J_{CP}$ = 96 and 41 Hz, respectively, for trans and cis coupling to dtbpe, which are much greater than the coupling observed for the acetylide β-C $^3J_{CP}$ = 21 Hz to the trans phosphorus. Because of the lack of C_2 symmetry, the ^{31}P NMR spectrum shows a pair of doublets for the dtbpe ligand with the

respective $^2J_{PP}$ values listed in Table 1. Table 1 also lists other salient NMR spectroscopic features for complexes **4−6**.

Table 1. Selected NMR Spectroscopic Data for Complexes 4−13

	^{31}P, Ni−P ($^2J_{PP}$ in Hz)	^{13}C, Ni−C	^{13}C, C=O	^{13}C, C=N	^{13}C, C≡C
4	82.8, 68.8 (26)	106.8	n/a	n/a	113.8
5	81.0, 67.8 (25)	112.0	n/a	n/a	156.7
6	98.8, 90.2 (47)	100.6	n/a	n/a	114.7
7	77.5, 66.2 (13)	35.8	n/a	175.7	n/a
8	78.5, 66.9 (12)	38.1	n/a	170.2	n/a
9	77.5, 62.4 (20)	36.4	n/a	179.0	n/a
10	86.0, 83.3 (27)	n/a	n/a	173.4	n/a
11	75.4, 69.3 (7)	n/a	n/a	n/a	n/a
12	89.7, 85.7 (28)	n/a	170.5	n/a	n/a
13	87.7	n/a	157.9	n/a	n/a

Infrared spectra of **5** and **6** further confirm a terminal acetylide ligand with ν_{CC} = 2091 and 2153 cm^{-1}, respectively. X-ray crystallographic analysis of a single crystal of **4** grown from a saturated Et$_2$O solution cooled to −35 °C reveals a square-planar Ni(II) complex with cis acetylide and anilide ligands (Figure 4). The Ni−N bond length in **4** is significantly longer
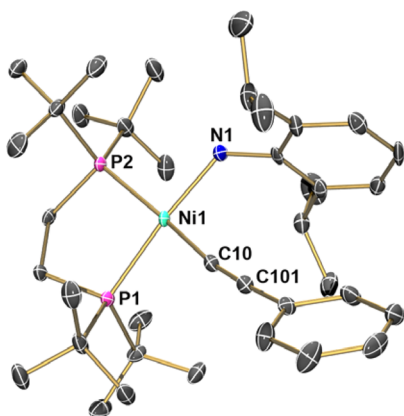

Figure 4. Solid-state structural diagram of complex **4** (thermal ellipsoids at 50% probability). One chemically equivalent but crystallographically independent molecule along with two Et$_2$O molecules confined in the asymmetric unit were omitted for clarity.

at 1.933(3) Å than that observed in [(dtbpe)Ni=N(H)-(2,6-^{i}Pr$_2$C$_6$H$_3$)][PF$_6$] (1.768(14) Å)[1] because of the now filled Ni d-orbital (of b_2 symmetry) in an ideal square planar and C_2 symmetric environment.[3] The lone pair on the anilide nitrogen in **4** can no longer donate to the metal, hence, the pyramidalization. Table 2 depicts selected metrical parameters for complex **4**.

The coupling of amines with alkynes is a relatively difficult, yet synthetically desirable, process for the construction of versatile synthetic precursors.[47] Complexes **4−6** could be considered analogous to intermediates in a reaction coupling these two organic fragments. Consequently, the reductive elimination from complex **4** was investigated further. Accordingly, reaction of **4** with CO (−78 °C, 1 atm) completely converted this nickel species to the known biscarbonyl complex (dtbpe)Ni(CO)$_2$[17] based on ^{31}P NMR spectroscopy. The mass spectrum of the major organic was consistent with the reductive elimination of the alkyne and

amide ligands (Scheme 4). Ynamines, especially those containing a secondary amine as in the case of PhC≡CNHAr, are known to tautomerize to keteneimines spontaneously.[48] The ^{1}H NMR spectrum of this new organic product revealed a diagnostic vinylic singlet at δ 5.62 consistent with the rearranged keteneimine PhCH=C=NAr being produced. This compound was isolated in pure form as an oil in 48% yield.

It has been shown that nickel complexes supporting a terminal imido ligand can engage in some cycloaddition chemistry, and in some cases, the imido can be completely transferred to ethylene,[15] C≡O, and C≡NR.[16,18] Iron and cobalt imidos have been also shown to be reactive with these substrates.[49] Consequently, we examined the reactivity of **4−6** with other unsaturated, small molecules. Accordingly, diphenylketene (O=C=CPh$_2$)[24] smoothly reacted to afford the oxy metallacyclobutane species (dtbpe)Ni{O,C:OC(CPh$_2$)=N(R)} shown in Scheme 5 (R = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**7**), Mes (**8**), 1-Ad (**9**)). Formation of **7−9** is nearly quantitative, although isolated yields can range from 95 to 72%. The ^{31}P NMR spectra reveal two inequivalent phosphorus nuclei with their corresponding $^2J_{PP}$ values between 13 and 20 Hz (Table 1). Because the lowest unoccupied molecular orbital of O=C=CPh$_2$ is augmented mostly with O−C π^* character,[50] one would expect [2 + 2]-cycloaddition to take place by O=C addition across the Ni=N to form an aza oxy metallacyclobutane. Indeed, the ^{13}C NMR spectra of **7−9** show a highly deshielded resonance at ~170 ppm in accord with a carbon atom possessing electron-withdrawing groups (Table 1). To determine unambiguously the type of metallacycle formed, a single-crystal X-ray diffraction study of **7** was performed. To our surprise, the solid-state structure of **7** revealed a square planar oxy nickel cyclobutane species, whereby the imido had virtually undergone insertion into the electrophilic carbon of the ketene (Figure 5). The short C−N = 1.280(2) Å is consistent with a double bond, while all metrical parameters in the metallacycle suggest single bonds in the NiOC$_2$ ring. Formation of **7−9** implies that cycloaddition across the Ni=N took place, though it cannot be distinguished whether initial O=C versus C=C bond addition took place based on these data. Scheme 6 depicts some possible pathways for formation of complexes **7−9**. O,C-Cycloaddition of the ketene group across Ni=N to form metallacycle **A** is the preferred pathway given the frontier orbitals of O=C=CPh$_2$. From **A**, two routes can take place: (i) homo or heterolytic Ni−N bond cleavage and rotation about the C−O bond or (ii) retrocycloaddition to form a nickel−oxo **B** and keteneimine RN=C=CPh$_2$, which can add across the C=C bond to form the NiOC$_2$ ring. The propensity of a terminal nickel−oxo compound to form robust dimers argues against the second pathway.[51] Alternatively, ketene can add via the C−C π^* bond to form the azametallacyclobutane **C**, which, analogously to **A**, can undergo two similar pathways, namely, Ni−N bond rupture or retrocycloaddition (via the nickel carbene **D**), to ultimately form the Ni−O bond.

To isolate an aza oxy metallacyclobutane species such as **A**, the reactivity of **1** with the less sterically hindered isocyanate O=C=NCH$_2$Ph was investigated. Accordingly, it was found that the O,C-cycloaddition product (dtbpe)Ni{O,C:OC=NCH$_2$PhN(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**10**) could be isolated in 90% yield as green-colored crystals (Scheme 5). Salient spectroscopic data for **10** are shown in Table 1, with the most notable feature being the C=N resonance at 173.4 ppm in the ^{13}C

Table 2. Selected Metrical Parameters for Complexes 4, 7, and 10–12[a]

	4	7	10	11	12
Ni–N	1.933(3)		1.939(6)	1.924(4)	1.9334(15)
Ni–C	1.858(4)	2.0786(17)			
Ni–O		1.8548(11)	1.864(5)	1.842(3)	1.8912(13)
Ni–P1	2.1971(10)	2.2457(5)	2.210(2)	2.2313(14)	2.2008(7)
Ni–P2	2.2565(10)	2.2127(5)	2.190(2)	2.2151(14)	2.2223(7)
P1–Ni–P2	89.46(4)	89.894(18)	89.80(8)	89.85(5)	89.63(3)
N–Ni–C	89.39(14)				
N–Ni–O			69.5(2)	73.38(15)	69.24(6)
C–Ni–O		71.33(6)			
P1–Ni–N	173.44(10)		111.47(18)	106.34(11)	160.46(5)
P2–Ni–N	93.16(9)		158.68(18)	163.78(12)	109.72(5)
P1–Ni–C	89.07(11)	158.90(5)			
P2–Ni–C	169.86(11)	111.05(5)			
P1–Ni–O		88.43(4)	173.60(16)	172.43(12)	91.30(4)
P2–Ni–O		170.57(4)	89.24(15)	90.43(10)	177.16(4)

[a]Distances are reported in Å, and angles are in degrees. Solvent was excluded from **4**, **10**, **11**, and **12**.

Scheme 5. [2 + 2]-Cycloaddition and Insertion Chemistry Involving the Ni=N Bond in Complexes 1–3
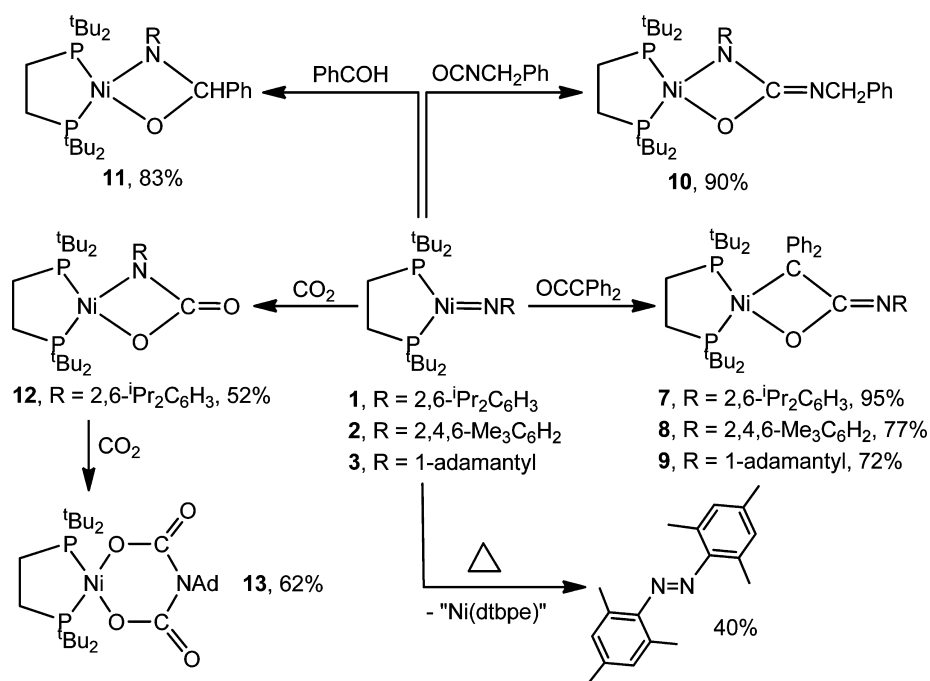
NMR spectrum. Like complexes **4**–**9**, compound **10** also lacks C_2 symmetry but has a stronger $^2J_{PP}$ value of 27 Hz when compared to complex **7**, as a result of the phosphines of the dtbpe ligand not being pushed back due to the sterically congested CPh$_2$ group. Therefore, one would expect less of a distortion from a square planar geometry. A solid-state structure of **10** confirms formation of a rare example of an aza oxy nickel cyclobutane square planar complex with an elongated Ni–N bond (1.939(6) Å) as compared to the imido precursor **1** (Figure 5). Examples of *N,O*-bound ureates resulting from isocyanate cycloaddition across early transition metals having a terminal imido ligand have been reported.[52] The Ni–O bond length (1.864(5) Å) is comparable to those observed in oxy nickel metallacycles.[53] Similar cycloaddition chemistry of **1** was observed with benzaldehyde, which gave the aza oxy nickel cyclobutane complex (dtbpe)Ni{*O,C*:OCHPhN-(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**11**) in 83% yield. Overall, the NMR

spectroscopic features of **11** are similar to those of complex **10**, and the solid-state structure confirms a square planar aza oxy nickel cyclobutane scaffold with Ni–N = 1.924(4) Å and Ni–O = 1.842(3) Å distances that compare favorably to those of **10** (Figure 6).

Exposure of a cold Et$_2$O solution of **1** to 1 atm CO$_2$ resulted in the gradual precipitation of a pale yellow solid containing (dtbpe)Ni{*O,C*:OC(O)N(2,6-^{i}Pr$_2$C$_6$H$_3$)} (**12**) (Scheme 5). The reaction is quantitative by ^{31}P NMR spectroscopy, and yellow solids of **12** can be isolated in 94% yield. In addition to displaying two inequivalent phosphine resonances ($^2J_{PP}$ = 28 Hz) akin to the other nickel metallacycles, the most salient spectroscopic feature in **12** is the presence of a broad ^{13}C NMR resonance at 170.5 ppm in accord with a [2 + 2]-cycloadded CO$_2$ carbon. Likewise, ν_{CO} = 1617 cm^{-1} in the infrared region corroborates the presence of this carbonyl functionality. A solid-state structure of **12** is shown in Figure 6 and again
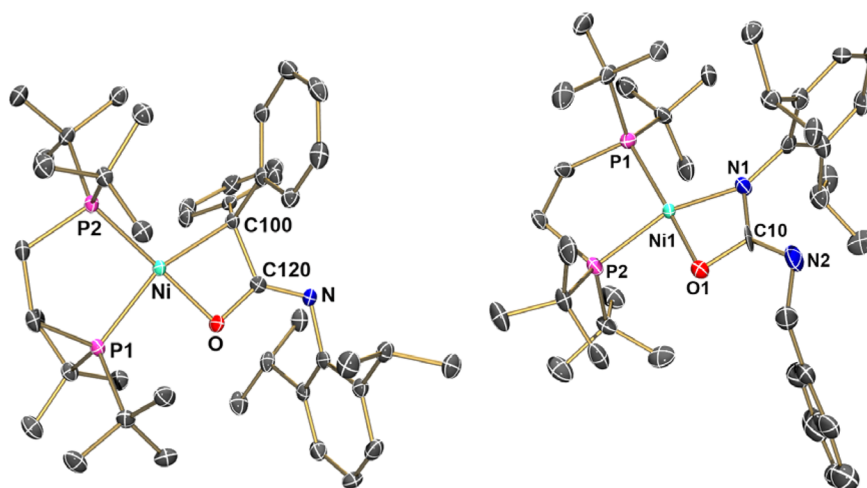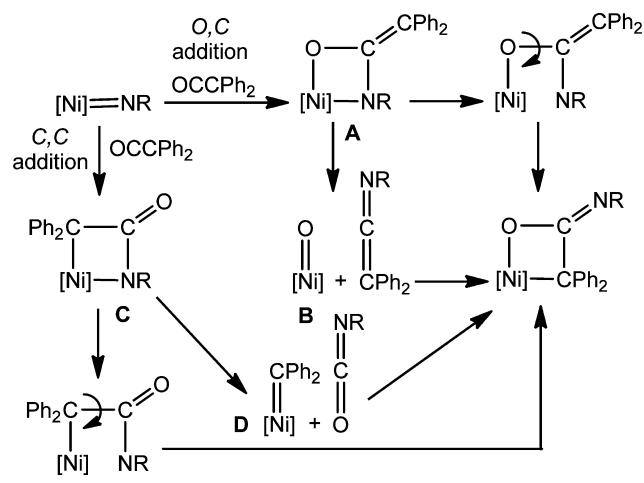
Figure 5. Solid-state structural diagram of complexes **7** (left) and **10** (right) with thermal ellipsoids at 50% probability. One Et$_2$O molecule in the asymmetric unit was omitted from the structure of **10**.

Scheme 6. Proposed Mechanism for Formation of Complexes 7−9

depicts a square planar nickel complex possessing a metallalactam or carbamate framework due to [2 + 2] cycloaddition of CO$_2$ across the Ni≡N bond with distances of Ni−O = 1.9334(15) Å and Ni−N = 1.8912(13) Å. From the metrical parameters, the terminal oxygen (C=O(2) = 1.229(2) Å) is part of a carbonyl functionality, while the "other" half of the CO$_2$ has been reduced to a single bond, C−O(1) = 1.340(2) Å as part of the metallacycle.

When exploring the chemistry of the more electron-rich imido complex **3**, a different outcome is observed. Treating **3** with a bed of CO$_2$ resulted in quick formation of the yellow complex (dtbpe)Ni{O,O:(OC(O))$_2$N(1-Ad)} (**13**) in 62% isolated yield (Scheme 5). Formation of **13** most likely involves a [2 + 2]-cycloaddition intermediate (dtbpe)Ni{O,C:OC(O)-N(1-Ad)}, like **12**, followed by CO$_2$ insertion into the more electron-rich and less-hindered Ni−N bond. The reactivity of CO$_2$ with **3** mirrors that of (dtbpe)Ni≡CPh$_2$, which resulted in six-membered ring formation observed in (dtbpe)Ni{O,O:(OC(O))$_2$CPh$_2$}.[19] NMR spectra of **13** are indicative of a C_{2v}-symmetric complex, while the IR spectrum shows two carbonyl stretches ν_{CO} = 1667 and 1624 cm^{-1}. Attempts to prepare the (dtbpe)Ni{O,C:OC(O)N(1-Ad)} using 1 equiv of CO$_2$ resulted in formation of **13** along with unreacted starting material. Mountford has observed contrasting modes of reactivity between titanium imido complexes and CO$_2$. For example, electron-rich Ti≡N bonds tend to undergo metathesis with CO$_2$ to form the titanium oxo, while aryl-substituted
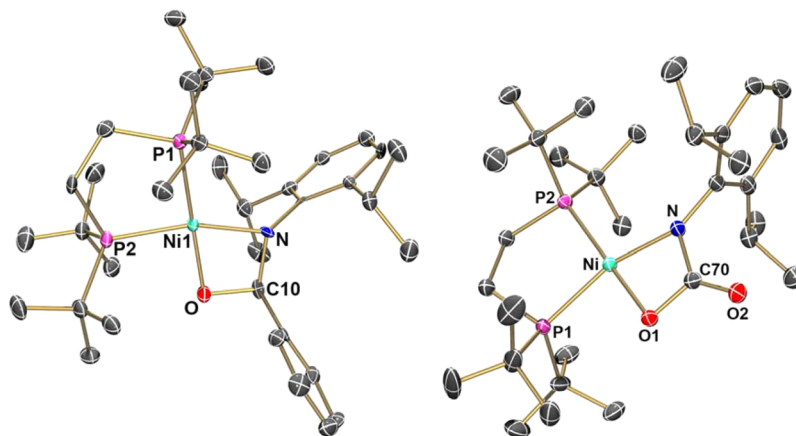

Figure 6. Solid-state structural diagram (thermal ellipsoids at 50% probability) of complexes **11** (left) and **12** (right). One Et$_2$O molecule for **11** and one CH$_2$Cl$_2$ molecule for **12**, found in the asymmetric unit, are excluded for clarity.

imido complexes such as Cp*Ti≡N{2,6-Me₂C₆H₃}{MeC-(NiPr)₂} can undergo cyloaddition of 1 equiv of CO_2 to form the *N,O*-bound carbamate, which can further react with another equivalent of CO_2 to form the azadicarboxylate ligand $[(OC(O))_2N(2,6-Me_2C_6H_3)]^{2-}$.[52]

Lastly, we explored the thermal stability of imido **2** because it is known that (2,2′-bipyridine)NiEt₂ reacts with excess mesitylazide to give azomesitylene (MesN≡NMes).[54] It is proposed in such reactions that a transient "(2,2-bipyridine)-Ni≡NMes" is a key species en route to the formation of the azomesitylene, a hypothesis that partially prompted the synthesis of **1**. Hence, heating a benzene solution of **3** revealed formation of azomesitylene, which can be isolated as red crystals in ∼40% yield (Scheme 5). The thermolysis of **3** demonstrates that the nitrene fragments from a nickel imido can couple to give azoarenes and provides some support to the idea of an imido intermediate in the formal coupling of mesitylazide by (2,2-bipyridine)NiEt₂. This thermolysis is also related to the report that Fe₂(CO)₉ can decompose phenyl-azide to azobenzene.[55]

CONCLUSIONS

In this work we presented three synthetic pathways to mononuclear nickel imido complexes having aliphatic or aromatic groups and reported reactivity involving the Ni≡N motif. A reinvestigation utilizing high-level ab initio quantum chemistry techniques is given for the original Ni-imido complex reported in 2001. The computational analysis of **1**, coupled with the newly disclosed reactivity studies reported herein, paint a picture of this late metal imido complex as being able to effect both one- (i.e., radical) and two-electron (e.g., deprotonation of terminal alkynes) transformations given the biradical and highly N_{imido}-localized nature of the frontier orbitals of **1**. Moreover, delocalization of these same frontier orbitals from the π/π^* orbitals of the NiN_{imido} active site to the aryl−imido substituent suggests considerable potential to tune the reactivity of **1** and other late metal imido complexes among these disparate reactivity manifolds through judicious manipulation of the chemical environment about the active site.

In addition to C−H activation reactions (both homolytically and presumably heterolytically), we include examples of cycloaddition chemistry of **1** with various electrophiles including some cumulenes. Taking advantage of the acidic C−H bond in HC≡CPh, it is shown that imido group in **1** can couple to acetylide to ultimately form a keteneimine. The imido moiety can also engage in cycloaddition and subsequent insertion or isomerization pathways to form unusual nickel metallacycles. While **1** seems to only cycloadd small molecules such as ketenes, isocyanates, aldehydes, and CO_2, more electron-rich alkyl−imidos such as **3** can undergo further Ni−N insertion chemistry. The delocalization of the frontier orbitals between NiN and NAr π/π^* orbitals is also consistent with the greater reactivity of **3** than **1**. In contrast, reducing steric bulk on the arylimido group can allow for reductive coupling.

ASSOCIATED CONTENT

ⓢ Supporting Information

Cartesian coordinates used in calculations of the structure and binding of complex **1** and complete crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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