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Nickel Complexes of *N*/*O*-Functionalized N-Heterocyclic Carbenes as Precatalysts for Michael Reactions in Air at Room Temperature Under the Much Preferred Base-Free Conditions

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A series of several new nickel precatalysts supported over *N*/*O*-functionalized N-heterocyclic carbenes (NHC) for the Michael reactions of β-dicarbonyl, β-keto ester, β-diester, and α-cyano ester compounds with α,β-unsaturated carbonyl compounds in air at ambient temperature under the much preferred base-free conditions are reported. Specifically, the nickel complexes, [1-(R^1-aminocarbonylmethyl)-3-R^2-imidazol-2-ylidene]$_2$Ni [R^1 = 2-C_6H_4(OMe); R^2 = Me (**1b**), *i*Pr (**2b**), CH_2Ph (**3b**) and R^1 = 2-$CH_2C_4H_3O$; R^2 = Me (**4b**), CH_2Ph (**5b**)] carried out the highly convenient base-free Michael addition of the activated C–H compounds across α,β-unsaturated carbonyl compounds in air at room temperature. The complexes **1b**–**5b** were synthesized by the direct reaction of the respective imidazolium chloride salt with $NiCl_2$·$6H_2O$ in CH_3CN in the presence of K_2CO_3 as a base. The exceptional stability of **1b**–**5b** has been attributed to the deeply buried nickel–NHC σ-bonding molecular orbitals as evidenced from the density functional theory (DFT) studies.

Introduction

Though widely accepted as a useful methodology for the construction of C–C bonds, the Michael reaction, which involves the addition of the β-dicarbonyl compounds with acceptor-activated olefins, suffers from certain limitations that arise from its strongly basic reaction conditions.[1] In particular, the classic Michael reaction is often catalyzed by a Brønsted base, which apart from yielding the desired Michael addition products, also promotes a host of unwanted side reactions like, the aldol-cyclization, retro-Claisen type decomposition, ester solvolyses, hetero Diels–Alder dimerization, Knoevenagel reaction, etc. and as a consequence of which, the yields of the preferred Michael addition products are severely affected.[2] Hence, a major challenge in this area lies in reducing or even completely eliminating the formation of the undesired side products of the classic base-catalyzed Michael reaction. Towards this objective, several strategies that have been successfully employed involve the use of a weak Brønsted base[3] or those that focus on achieving milder reaction conditions by employing basic zeolites,[4] alumina,[5] the phase-transfer catalysis,[6] or solid-phase catalysis.[7] In this context, the base-free Michael reaction under neutral conditions assumes significance as it offers the possibility of completely eliminating the unwanted side products of the classic base-catalyzed Michael reaction.[8] It is worth noting that the transition-metal-catalyzed Michael reactions indeed exhibit superior chemoselectivity by virtue of its milder and also neutral reaction conditions in comparison to the classic base-catalyzed reaction.[9] Furthermore, compared to the base-catalyzed Michael reactions, the transition-metal-catalyzed Michael reactions enjoy certain additional advantages as they often do not require inert or anhydrous conditions,[10] can be performed in the absence of solvents,[11] or may even provide near quantitative conversions at ambient temperatures.[12] In light of the above facts we became interested in developing the chemistry of base-free Michael reactions, in particular by designing highly efficient transition-metal-based catalysts.

Of late N-heterocyclic carbenes have been phenomenally successful in homogeneous catalysis and in this regard we have recently designed several *N*/*O*-functionalized N-heterocyclic carbene-based[13] catalysts for a host of important transformations ranging from their use in producing biodegradable polymers by ring-opening polymerization (ROP) of L-lactides[14] to a variety of C–C cross-coupling reactions, namely the Suzuki–Miyaura[15] and the Sonogashira coupling reactions.[16] Apart from catalysis, we have also explored the utility of these *N*/*O*-functionalized N-heterocyclic carbene compounds in biomedical applications, particularly with regard to their anticancer and antimicrobial properties.[17] The necessary impetus for our efforts towards employing N-heterocyclic carbenes in base-free Michael re-

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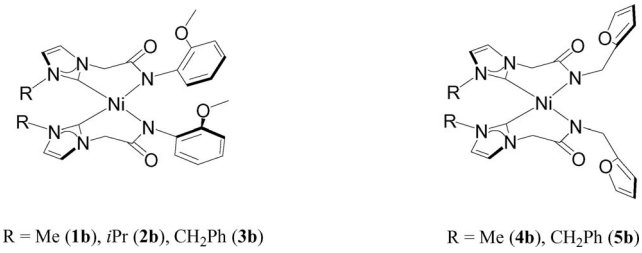
actions came from the fact that despite unprecedented successes seen by the N-heterocyclic carbenes in numerous catalytic reactions recently, their utility in the base-free Michael reaction have largely remained unexplored.[18] Hence, we set out to design new *N*/*O*-functionalized N-heterocyclic carbene-based precatalysts for the base-free Michael reaction.

Here in this contribution, we report a series of highly efficient nickel complexes, **1b**–**5b**, (Figure 1) supported over amido-functionalized N-heterocyclic carbene ligands, for the base-free Michael reaction of β-dicarbonyl, β-keto ester, β-diester, and α-cyano ester compounds with α,β-unsaturated carbonyl compounds in air at ambient temperature. The air and moisture stability of these precatalysts has been attributed to deeply buried NHC–Ni σ-bonding orbitals as seen from the density functional theory studies.



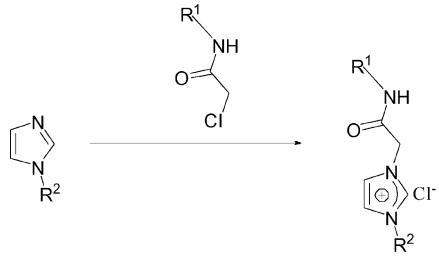
R = Me (**1b**), *i*Pr (**2b**), CH_2Ph (**3b**) R = Me (**4b**), CH_2Ph (**5b**)

Figure 1. Nickel complexes of the amido-functionalized N-heterocyclic carbene, **1b**–**5b**.

Results and Discussion

With an eye on exploring the utility of N-heterocyclic carbenes in Michael reactions, particularly under the much preferred base-free conditions, we set out to design metal-based precatalysts of *N*/*O*-functionalized N-heterocyclic carbenes. Our choice of nickel for the study was based on prior reports of the use of simple nickel precursors under "ligand-assisted catalysis" (LAC) conditions, in which the catalytically active species were generated in situ during the course of the Michael reaction.[10,19] It is worth mentioning that classic Michael reactions exhibit certain limitations like the need for the use of a base, or requiring anhydrous reaction conditions or high temperatures and even then on many occasions the reactions proceed in low yields. In light of these facts, we focused on designing well-defined, robust nickel precatalysts supported over *N*/*O*-functionalized N-heterocyclic carbenes for their utility in Michael reactions under the highly desired base-free conditions. Additionally, we also explored the possibility of this catalysis occurring under amenable conditions like in air and at ambient temperature.

In this regard a series of new amido-functionalized N-heterocyclic carbene precursors namely, 1-(R^1-aminocarbonylmethyl)-3-R^2-imidazolium chloride [R^1 = 2-C_6H_4-(OMe); R^2 = Me (**1a**), *i*Pr (**2a**), CH_2Ph (**3a**) and R^1 = 2-$CH_2C_4H_3O$; R^2 = Me (**4a**), CH_2Ph (**5a**)] were synthesized from the respective substituted imidazoles by the direct reaction with 2-chloro-*N*-(2-methoxyphenyl)acetamide or 2-chloro-*N*-(2-furanylmethyl)acetamide in 65–76% yields (Scheme 1). The formations of **1a**–**5a** were verified by the appearance of the diagnostic imidazolium (NC*H*N) resonance in the highly downfield region of the ^1H NMR (9.25–10.34 ppm) and ^{13}C NMR (135.3–138.0 ppm) spectra.

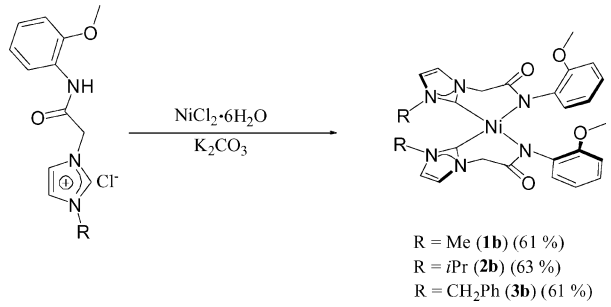


R^1 = 2-C_6H_4(OMe), R^2 = Me (**1a**) (70 %)
R^1 = 2-C_6H_4(OMe), R^2 = *i*Pr (**2a**) (72 %)
R^1 = 2-C_6H_4(OMe), R^2 = CH_2Ph (**3a**) (65 %)
R^1 = 2-$CH_2C_4H_3O$, R^2 = Me (**4a**) (71 %)
R^1 = 2-$CH_2C_4H_3O$, R^2 = CH_2Ph (**5a**) (76 %)

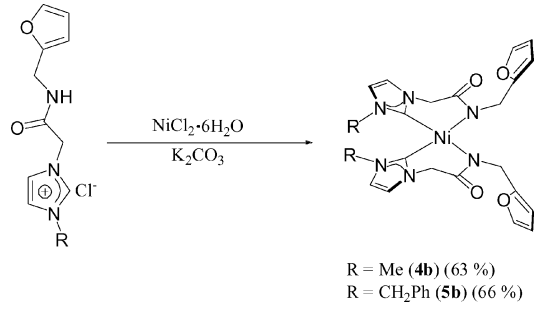
Scheme 1.

The nickel complexes **1b**–**5b** were synthesized from the corresponding imidazolium chloride salts **1a**–**5a** by the treatment with $NiCl_2{\cdot}6H_2O$ in CH_3CN in the presence of K_2CO_3 as a base in 61–66% yields (Scheme 2 and Scheme 3). With regard to this it is worth mentioning that there broadly exists two methods of preparation of the nickel complexes of N-heterocyclic carbenes viz. (*i*) the one involving the reaction of the N-heterocyclic carbene with Ni^0 precursors like $Ni(COD)_2$[20] and (*ii*) the other involving the direct reaction of the imidazolium salts with various Ni^{II} precursors like, $Ni(acac)_2$,[21] $NiBr_2(DME)$,[22] $Ni(PPh_3)_2X_2$ (X = Cl, Br),[23] and anhydrous $NiCl_2$ in the presence of any base.[24] All of the **1b**–**5b** complexes were found to be diamagnetic from the ^1H NMR and ^{13}C NMR spectra suggesting the square-planar nature of the metal center in these complexes. The ^{13}C NMR spectra of **1b**–**5b** showed the characteristic highly downfield shifted nickel bound carbene (Ni–$C_{carbene}$) resonance at 168.7–169.8 ppm, in keeping with the formation of these complexes. Furthermore, the ^1H NMR spectrum of **1b**–**5b** revealed the absence of the amido-N*H* resonance of the amido-functionalized sidearm of the N-heterocyclic carbene ligand, and thereby suggesting its deprotonation under the basic reaction conditions followed by chelation to the nickel center.

Indeed, in the molecular structures of **1b**–**5b**, the amido-functionalized N-heterocyclic carbene ligand was seen chelating to the nickel center through its carbene-C and amido-N donor atoms (Figure 2 and Figure 3 and Supporting Information Figures S1–S3 and Table S1). More interestingly, the two amido-functionalized N-heterocyclic carbene ligands in **1b**–**5b** were found to bind to the metal center in a *cis* fashion with two amido-N atoms occupying two adjacent sites of the square-planar geometry around the nickel atom while the two carbene-C atoms reside on the remaining two adjacent sites. The Ni–$C_{carbene}$ distances in **1b** [1.742(2) Å, 1.959(3) Å], **2b** [1.863(2) Å, 1.857(2) Å], **3b**



Scheme 2.



Scheme 3.

[1.865(4) Å, 1.867(5) Å], **4b** [1.852(4) Å, 1.859(4) Å], and **5b** [1.851(4) Å, 1.861(4) Å] are comparable to that observed in other structurally characterized nickel N-heterocyclic carbene complexes namely, [1-benzyl-3-(phenylaminocarbonylmethyl)imidazol-2-ylidene]$_2$Ni [1.860(2) Å and 1.853(3) Å],[24] [1-(4-fluorobenzyl)-3-(phenylaminocarbonylmethyl)imidazol-2-ylidene]$_2$Ni [1.858(3) Å],[24] [1-(4-methoxybenzyl)-3-(phenylaminocarbonylmethyl)imidazol-2-ylidene]$_2$Ni [1.864(3) Å and 1.866(3) Å],[24] and [1,3-bis(phenylaminocarbonylmethyl)imidazol-2-ylidene]$_2$Ni [1.843(5) Å and 1.846(5) Å].[24] The Ni–N (amido) distances are as follows, **1b** [1.8564(19) Å, 2.052(2) Å], **2b** [1.962(2) Å, 1.9636(19) Å], **3b** [1.982(4) Å, 1.966(4) Å], **4b** [1.921(3) Å, 1.938(3) Å], and **5b** [1.922(3) Å, 1.922(4) Å].

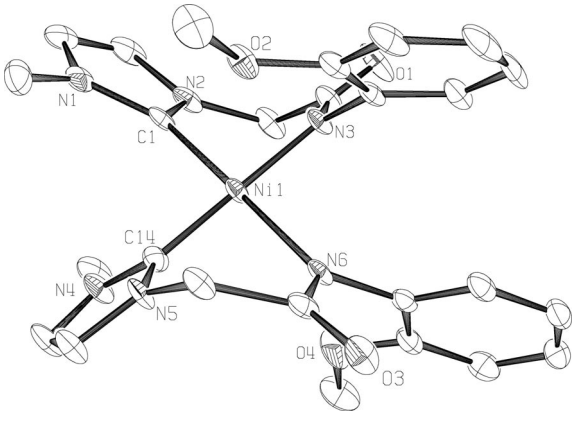


Figure 2. ORTEP diagram of **1b**. Selected bond lengths (Å) and angles (°): Ni1–C1 1.959(3), Ni1–C14 1.742(2), Ni1–N3 1.8564(19), Ni1–N6 2.052(2), C1–Ni1–N3 86.49(9), C14–Ni1–N6 86.42(10), C1–Ni1–C14 93.01(11), N3–Ni1–N6 94.07(9).

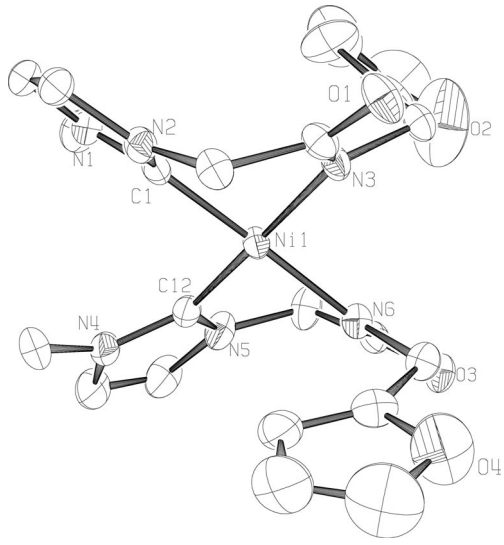


Figure 3. ORTEP diagram of **4b**. Selected bond lengths (Å) and angles (°): Ni1–C1 1.852(4), Ni1–C12 1.859(4), Ni1–N3 1.921(3), Ni1–N6 1.938(3), C1–Ni1–C12 93.68(16), C1–Ni1–N3 86.59(14), C12–Ni1–N6 87.35(14), N3–Ni1–N6 92.56(13).

Despite striking similarities among the **1b**–**5b** structures, an important feature, which sets the isopropyl derivative **2b** apart from the rest, is the observation of a strong π–π interaction in the former (Figure 4). Specifically, the two aryl rings in **2b** were found stacked parallel to each other displaying a centroid($C_0$1)-to-centroid($C_0$2) distance of 3.926 Å and thereby exhibiting an intramolecular offset or slipped-type π–π interaction.[25]

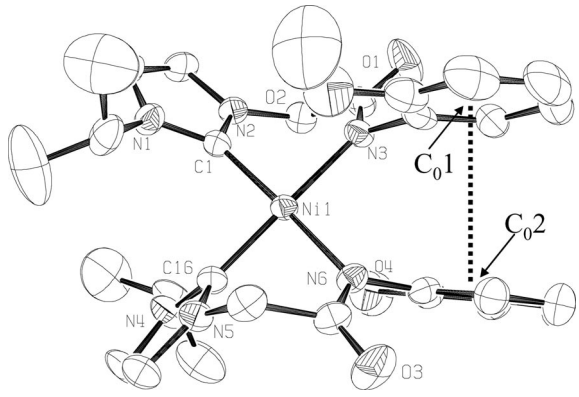


Figure 4. Offset or slipped π–π interaction observed in **2b** displaying a centroid($C_0$1)-to-centroid($C_0$2) distance of 3.926 Å.

In order to get a better insight into the nature of the NHC–Ni interaction, detailed density functional theory (DFT) studies were undertaken. In particular, geometry optimized structures were computed at the B3LYP/LANL2DZ, 6-31G(d) level of theory using the atomic coordinates adopted from an X-ray analysis and subsequently the single-point calculations along with the post-wave function analysis using the natural bond order (NBO) method

were done at the same level of theory for the detailed understanding of the electronic properties of these complexes. The geometric parameters observed from the X-ray structures were in strong agreement with those obtained from the optimized geometries of **1b**–**5b**. (Supporting Information, Tables S7–S11). The strong electron-donating ability of the anionic amido-functionalized N-heterocyclic carbene (NHC) ligand to the nickel center was evident from both natural and Mulliken charge analyses that showed a significant increase in the electron density at the nickel center in **1b**–**5b** as a consequence of binding of the free NHC ligand fragment relative to the bare Ni^{II} ion (see Supporting Information, Tables S12–S16). Indeed, scrutiny of the electronic configuration of the nickel center in **1b**–**5b** revealed that electron donation from the carbene lone pair occurred onto the 3d and 4s orbitals of the nickel center in these complexes (Supporting Information, Table S17). Further scrutiny of the hybridization of the $C_{carbene}$ and Ni atoms in the **1b**–**5b** complexes showed that while the $C_{carbene}$ atoms were sp^2, the Ni atoms had sd character (Supporting Information, Table S18).

Using charge decomposition analysis (CDA), an estimate of the NHC-ligand-to-metal σ donation, denoted by *d*, and the metal-to-NHC-ligand π back-donation, denoted by *b*, occurring in **1b**–**5b** was made (Supporting Information, Table S19). The *d*/*b* ratio for **1b** (10.77), **2b** (11.11), **3b** (10.66), **4b** (11.36), and **5b** (11.10) showed that the N-heterocyclic carbene ligands were strongly electron donating in nature. It is worth noting that the σ donation (*d*) and π back-donation (*b*) values obtained in **1b**–**5b** represent the donations (forward σ and backward π) between the metal center and the functionalized NHC-ligand fragment, which is a composite of two interactions, a carbene–nickel interaction along with an amido-N–nickel interaction. It is noteworthy that owing to the amido-functionalized nature of the NHC ligand, the chelation to the metal center through the carbene-C and amido-N was seen to occur in these complexes resulting in a composite NHC-ligand-to-metal interaction.

A better understanding of the NHC–Ni interaction in **1b**–**5b** could be obtained from the molecular orbital (MO) correlation diagram constructed from the interaction of two free NHC-ligand fragments with the free Ni^{II} ion in these complexes. Of importance is the NHC–nickel σ interaction that is comprised of the interaction of the carbene lone pair with the nickel-based orbital, as depicted by the following orbitals, **1b** (HOMO-31), **2b** (HOMO-30), **3b** (HOMO-36), **4b** (HOMO-25), and **5b** (HOMO-33) (see Figures 5–6 and Figures S4–S12 in the Supporting Information). A careful look at these NHC–nickel σ-bonding molecular orbitals reveals that the carbene lone pairs along with the amido groups of the free NHC ligand fragments interact with the unfilled 4s orbital of the nickel center (see Figures 5–6 and Figures S4–S12 in the Supporting Information). These deeply buried NHC–nickel σ-bonding molecular orbitals are the reason behind the inert nature of the NHC–nickel interaction, which in turn contribute towards the exceptional stability of these complexes. With regard to this it is worth mentioning that contrary to the NHC–Ni interaction, the other metal–carbene interactions like those in Fischer carbene and Schrock carbene complexes are highly susceptible to both electrophilic and nucleophilic attack.[26]

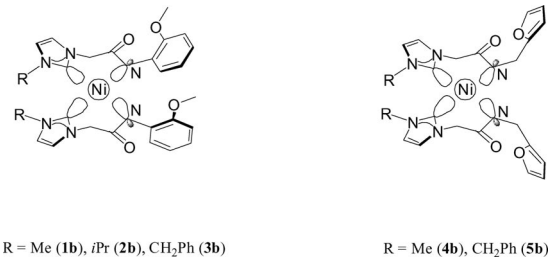
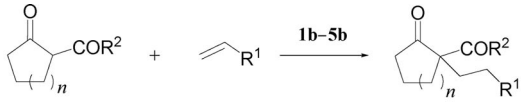


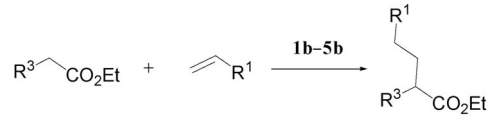
Figure 5. Interaction of the filled carbene lone pairs and the amido groups of the free NHC ligand fragments with the unfilled 4s orbital of nickel in **1b**–**5b**.

More significantly, the **1b**–**5b** complexes successfully catalyzed the base-free Michael reaction of a wide variety of substrates ranging from cyclic ethyl 2-oxocyclopentane carboxylate, ethyl 2-cyclohexanone carboxylate and 2-acetylcyclopentanone, to acyclic ethyl cyanoacetate and diethyl malonate compounds with α,β-unsaturated carbonyl compounds in air at ambient temperature [Equation (1) and Equation (2)]. It is quite interesting that significantly higher conversions were observed for the cyclic five-membered ethyl 2-oxocyclopentane carboxylate and 2-acetylcyclopentanone and the six-membered ethyl 2-cyclohexanone carboxylate substrates than the acyclic ethyl cyanoacetate and diethyl malonate substrates. Furthermore, for the acyclic substrates, the (2-methoxyphenyl)aminocarbonylmethyl-substituted **1b**–**3b** precatalysts were found to be consistently more active than the (2-furanylmethyl)aminocarbonylmethyl-substituted **4b** and **5b** precatalysts. It is worth nothing that base-free conditions are very much desirable for the Michael reactions since often these reactions are performed in basic conditions, which also facilitate a variety of unwanted side reactions, namely the aldol-cyclization, retro-Claisen type decomposition, Knoevenagel reaction, etc. Specifically the β-dicarbonyl compounds, when treated with α,β-unsaturated carbonyl compounds in the presence of 5 mol-% of the precatalysts **1b**–**5b** in chloroform, underwent a clean conversion to the Michael reaction products



(1)

R^1 = COMe, CO_2Me, CO_2Et, CO_2tBu
R^2 = Me, OEt
n = 1, 2



(2)

R^1 = COMe, CO_2Me, CO_2Et, CO_2tBu
R^3 = CN, CO_2Et

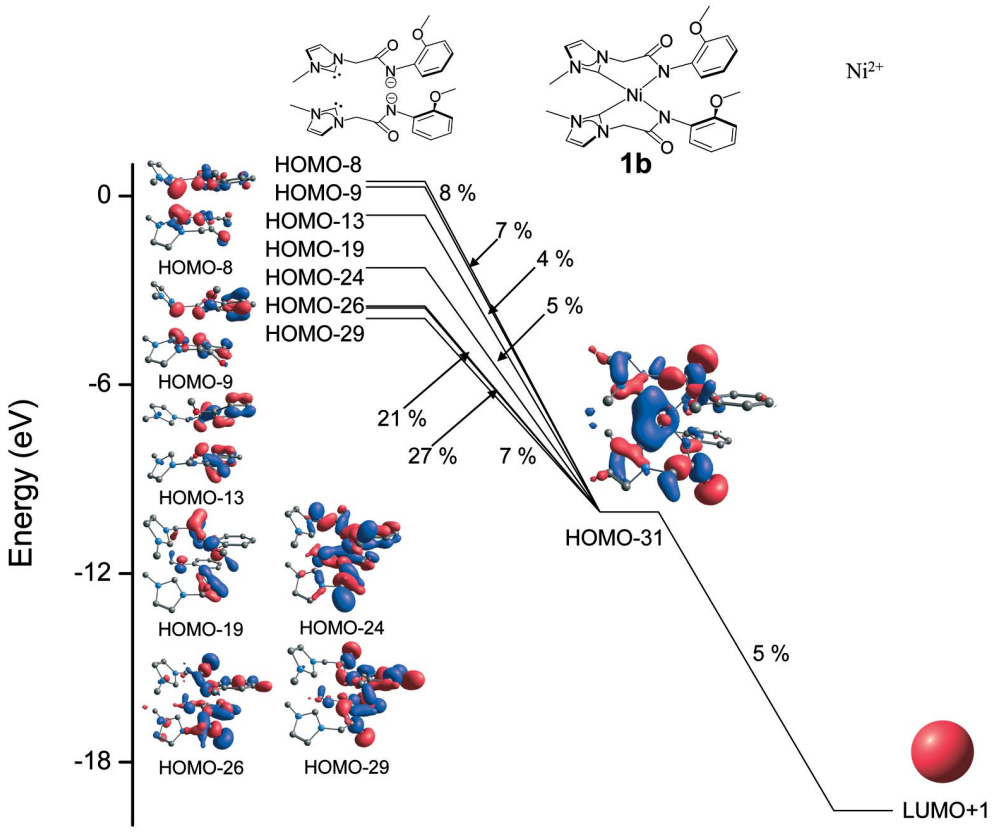


Figure 6. Simplified orbital interaction diagram showing the major contributions of the NHC–nickel bond in **1b**.

in good to excellent yields at room temperature (Table 1 and Table 2). All of the control experiments carried out with $NiCl_2·6H_2O$ and $Ni(acac)_2$ as well as the blank experiments performed for each of the individual substrates showed no or negligible formation of the desired Michael addition products (Supporting Information, Tables S20 and S21). Quite interestingly, for both the ethyl 2-oxocyclopentane carboxylate and 2-acetylcyclopentanone substrates the reaction yields were lowest for the bulkiest *tert*-butyl acrylate presumably due to steric reasons.

The significance of the N-heterocyclic carbene-based **1b**–**5b** precatalysts for the base-free Michael reaction becomes prominent when considering that there exists only one prior report of the use of N-heterocyclic carbene under organocatalytic conditions i.e. in the absence of any metal for the enantioselective intramolecular Michael reaction.[27]

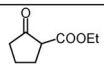
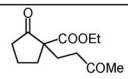
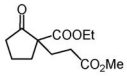
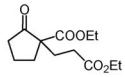
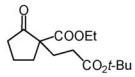
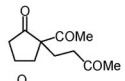
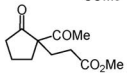
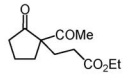
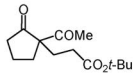
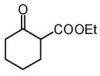
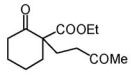
The most impressive features of the **1b**–**5b** precatalysts are their ability to carry out the Michael reaction under base-free conditions and in air at room temperature. Also worth noting is that the **1b**–**5b** complexes represent well-defined precatalysts for the base-free Michael reactions since most of the known reports commonly use non-N-heterocyclic carbene ligands under LAC conditions, in which the catalytically active species is generated in situ and hence the active species is poorly characterized.[28] It is quite interesting that the comparison with a few prior reports that exist of simple nickel precursors, like $Ni(acac)_2$,[29] show that the reactions were carried out at much higher temperatures, 80–100 °C, compared with room temperature as is the case with our base-free Michael addition reaction by the precatalysts **1b**–**5b**.

A proposed mechanism for the base-free Michael reaction involves the reaction of the nickel catalyst **1b**–**5b** with a representative β-dicarbonyl compound to give an intermediate **A** containing an anionic β-dicarbonyl moiety bound to the metal and a non-chelated protonated amido moiety (Scheme 4). The intermediate **A** then reacts with the α,β-unsaturated carbonyl compound to give the intermediate **C**, having the anionic Michael addition product bound to the metal by a transition-state **B**. The last step involves protonation and subsequent release of the Michael addition product concomitant with the deprotonation and chelation of the amido moiety to give back the nickel precatalyst **1b**–**5b**.

Conclusions

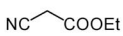
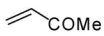
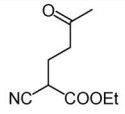
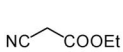
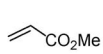
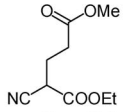
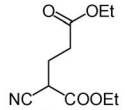
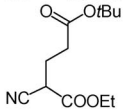
In summary, a series of nickel precatalysts **1b**–**5b** that efficiently carried out Michael reactions of β-dicarbonyl, β-keto ester, β-diester, and α-cyano ester compounds with α,β-unsaturated carbonyl compounds in air and at ambient temperature under the much preferred base-free conditions have been designed. The air and moisture stability of these precatalysts has been attributed to the deeply buried NHC–Ni σ-bonding orbitals as seen from the density functional theory studies.

Table 1. Selected results of 1,4-Michael type activated C–H addition across α,β-unsaturated substrates catalyzed by **1b**–**5b**.

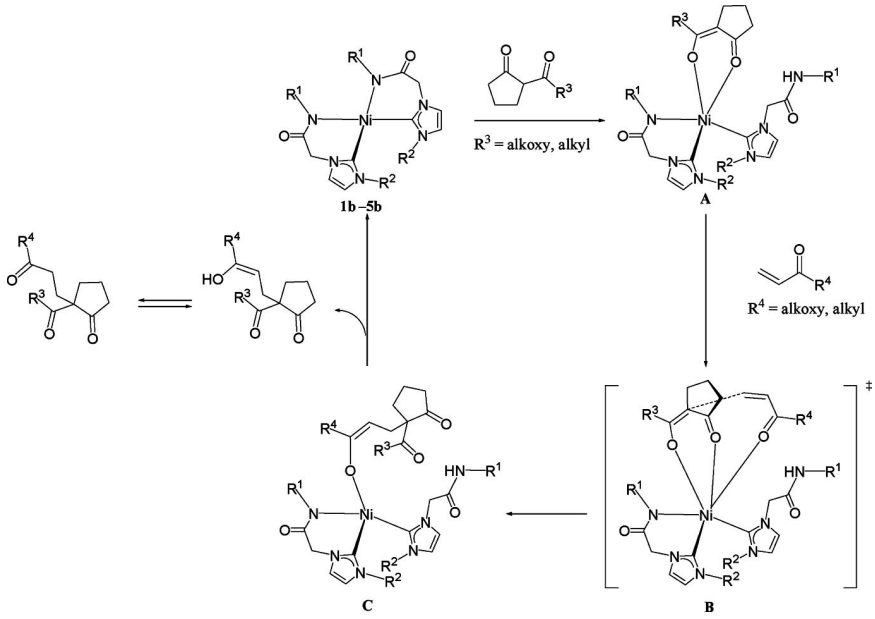
Entry	Reagent[a]	Reagent[a]	Product	**1b** Yield[b] (%)	**2b** Yield[b] (%)	**3b** Yield[b] (%)	**4b** Yield[b] (%)	**5b** Yield[b] (%)
1				85	77	98	87	78
2				78	21	26	59	54
3				52	15	55	49	57
4				11	2	13	11	11
5				59	30	67	71	87
6				73	33	86	83	83
7				77	24	90	85	69
8				50	12	22	21	31
9				65	7	50	15	21

[a] Reaction conditions: 0.50 mmol of cyclic β-dicarbonyl or β-keto ester compounds, 0.60 mmol of α,β-unsaturated substrates, 2.50×10^{-2} mmol of catalyst **1b**–**5b** and 2 mL of $CHCl_3$ were taken for each run at room temperature for 17 h. [b] GC yields were recorded using diethyleneglycol di-*n*-butyl ether as an internal standard.

Table 2. Selected results of 1,4-Michael type activated C–H addition across α,β-unsaturated substrates catalyzed by **1b**–**5b**.

Entry	Reagent[a]	Reagent[a]	Product	**1b** Yield[b] (%)	**2b** Yield[b] (%)	**3b** Yield[b] (%)	**4b** Yield[b] (%)	**5b** Yield[b] (%)
1				21	23	26	12	14
2				26	16	41	6	9
3				19	10	43	3	10
4				11	4	13	2	2
5				38	31	50	13	15

[a] Reaction conditions: 0.50 mmol of acyclic β-diester or α-cyano ester compounds, 0.60 mmol of α,β-unsaturated substrates, 2.50×10^{-2} mmol of catalyst **1b**–**5b** and 2 mL of $CHCl_3$ were taken for each run at room temperature for 17 h. [b] GC yields using diethyleneglycol di-*n*-butyl ether as an internal standard.



Scheme 4.

Experimental Section

General Procedures: All manipulations were carried out using a combination of a glovebox and standard Schlenk techniques. Solvents were purified and degassed by standard procedures. $NiCl_2·6H_2O$ was purchased from SD-fine Chemicals (India) and 1-methylimidazole was purchased from Spectrochem Pvt. Ltd. (Mumbai, India) and were used without further purification. The 1-isopropylimidazole[30] and 1-benzylimidazole[31] were prepared according to the literature procedures. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Varian 400 MHz NMR spectrometer. ^1H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), multiplet (m), and septet (sept). Infrared spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done with a Micromass Q-Tof spectrometer. GC spectra were obtained with a PerkinElmer Clarus 600 equipped with a FID. GC–MS spectra were obtained with a Perkin–Elmer Clarus 600 T equipped with an EI source. Elemental Analysis was carried out with a Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. X-ray diffraction data for **1b**–**5b** were collected with an Oxford Diffraction Excaliber-S diffractometer. The crystal data collection and refinement parameters are summarized in Table S1. The structures were solved by direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).[32]

CCDC-678648 (for **1b**), CCDC-645977 (for **2b**), CCDC-700839 (for **3b**), CCDC-675231 (for **4b**), and CCDC-657169 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 1-[(2-Methoxyphenyl)aminocarbonylmethyl]-3-methylimidazolium Chloride (1a): 2-Chloro-*N*-(2-methoxyphenyl)acetamide (2.00 g, 10.0 mmol) and 1-methylimidazole (0.821 g, 10.0 mmol) were added to toluene (ca. 10 mL) and refluxed overnight to obtain a light brown precipitate, which was isolated by decanting off the solvent. The residue was washed with hot hexane (ca. 15 mL) and dried under vacuum to obtain the product **1a** as a light brown powder (1.97 g, 70%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 10.17 (s, 1 H, NC*H*N), 9.72 (s, 1 H, N*H*), 8.01 (d, $^3J_{HH}$ = 8 Hz, 1 H, C_6H_4), 7.65 (s, 1 H, NC*H*CHN), 7.16 (s, 1 H, NCHC*H*N), 7.07 (t, $^3J_{HH}$ = 8 Hz, 1 H, C_6H_4), 6.90–6.85 (m, 2 H, C_6H_4), 5.68 (s, 2 H, CH_2), 3.96 (s, 3 H, OCH_3), 3.87 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 100 MHz, 25 °C): δ = 164.2 (*C*=O), 150.1 (C_6H_4), 138.0 (N*C*HN), 126.5 (C_6H_4), 125.5 (C_6H_4), 123.9 (N*C*HCHN), 123.2 (NCH*C*HN), 122.3 (C_6H_4), 120.4 (C_6H_4), 111.6 (C_6H_4), 55.9 (OCH_3), 51.4 (CH_2), 36.0 (CH_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3436 (m), 1693 (s), 1601 (m), 1540 (s), 1491 (w), 1462 (m), 1259 (w), 1177 (m), 1117 (w), 1023 (m), 756 (s), 624 (w) cm^{-1}. HRMS (ES): *m*/*z* 246.1248 [(NHC) + H]$^+$, calcd. 246.1243.

Synthesis of {1-[(2-Methoxyphenyl)aminocarbonylmethyl]-3-methylimidazol-2-ylidene}$_2$Ni (1b): 1-[(2-Methoxyphenyl)aminocarbonylmethyl]-3-methylimidazolium chloride (0.500 g, 1.78 mmol), $NiCl_2·6H_2O$ (0.420 g, 1.77 mmol), and K_2CO_3 (0.735, 5.32 mmol) were added to CH_3CN (ca. 30 mL). The reaction mixture was refluxed for 24 h, after which it was filtered and the solvent removed. The residue was extracted in CH_2Cl_2 (ca. 20 mL) and dried under vacuum to obtain the product **1b** as a yellow solid (0.297 g, 61%). Single crystals for X-ray diffraction studies were grown in a minimum volume of CH_3CN (ca. 2 mL). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 7.04 (br., 1 H, NC*H*CHN), 6.84 (br., 2 H, C_6H_4), 6.76 (br., 1 H, NCHC*H*N), 6.54 (s, 1 H, C_6H_4), 6.42 (s, 1 H, C_6H_4), 5.78 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 4.38 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 3.90 (s, 3 H, OCH_3), 3.22 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 169.3 (N*C*N), 167.6 (*C*=O), 152.8 (C_6H_4), 135.3 (C_6H_4), 130.7 (C_6H_4), 123.3 (N*C*HCHN), 122.1 (C_6H_4), 121.3 (C_6H_4), 119.7 (NCH*C*HN), 111.4 (C_6H_4), 57.5 (OCH_3), 56.6 (CH_2), 35.6 (CH_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 2938 (w), 1670 (w), 1599 (m), 1574 (s), 1492 (m), 1370 (m), 1238 (s), 1177 (w), 1117 (w), 1027 (w), 748 (m) cm^{-1}. HRMS (ES): *m*/*z* 547.1587 [(NHC)$_2$Ni + H]$^{+\cdot}$, calcd. 547.1604. $C_{26}H_{28}N_6NiO_4·0.5CH_2Cl_2$ (589.7): calcd. C 53.97, H 4.96, N 14.25; found C 53.81, H 4.77, N 13.60.

Synthesis of 1-Isopropyl-3-[(2-methoxyphenyl)aminocarbonylmethyl]-imidazolium Chloride (2a): 2-Chloro-*N*-(2-methoxyphenyl)acetamide (2.00 g, 10.0 mmol) and 1-isopropylimidazole (1.11 g, 10.1 mmol) were added to toluene (ca. 10 mL) and refluxed overnight to obtain a light brown precipitate, which was isolated by decanting off the

solvent. The residue was washed with hot hexane (ca. 15 mL) and dried under vacuum to obtain the product **2a** as a light brown powder (2.23 g, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 10.22 (s, 1 H, NC*H*N), 9.77 (s, 1 H, N*H*), 7.98 (d, $^3J_{HH}$ = 7 Hz, 1 H, C_6H_4), 7.67 (s, 1 H, NC*H*CHN), 7.26 (s, 1 H, NCHC*H*N), 7.05 (t, $^3J_{HH}$ = 7 Hz, 1 H, C_6H_4), 6.85 (t, $^3J_{HH}$ = 7 Hz, 1 H, C_6H_4), 6.83 (d, $^3J_{HH}$ = 7 Hz, 1 H, C_6H_4), 5.72 (s, 2 H, CH_2), 4.66 [sept, $^3J_{HH}$ = 7 Hz, 1 H, C*H*$(CH_3)_2$], 3.83 (s, 3 H, OCH_3), 1.55 [d, $^3J_{HH}$ = 7 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 162.8 (*C*=O), 149.3 (C_6H_4), 135.3 (N*C*HN), 125.6 (C_6H_4), 124.6 (C_6H_4), 123.0 (N*C*HCHN), 121.2 (C_6H_4), 119.5 (NCH*C*HN), 118.8 (C_6H_4), 110.2 (C_6H_4), 55.1 (O*C*H_3), 52.2 (*C*H_2), 51.2 [*C*H$(CH_3)_2$], 21.9 [CH(*C*H_3)$_2$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 3124 (w), 2972 (m), 1694 (s), 1601 (s), 1574 (s), 1491 (m), 1460 (m), 1370 (m), 1289 (m), 1239 (s), 1178 (w), 1115 (m), 1024 (m), 747 (s) cm^{-1}. HRMS (ES): *m*/*z* 274.1563 [(NHC) + H]$^+$, calcd. 274.1556.

Synthesis of {1-Isopropyl-3-[(2-methoxyphenyl)aminocarbonylmethyl]-imidazol-2-ylidene}$_2$Ni (2b): 1-Isopropyl-3-[(2-methoxyphenyl)-aminocarbonylmethyl]imidazolium chloride (0.310 g, 1.00 mmol), $NiCl_2$·$6H_2O$ (0.237 g, 1.00 mmol), and K_2CO_3 (0.417, 3.02 mmol) were added to CH_3CN (ca. 30 mL). The reaction mixture was refluxed for 24 h, after which it was filtered and the solvent removed. The residue was extracted in CH_2Cl_2 (ca. 20 mL) and dried under vacuum to obtain the product **2b** as a yellow solid (0.190 g, 63%). Single crystals for X-ray diffraction studies were grown in a minimum volume of CH_3CN (ca. 2 mL). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 7.09 (br., 1 H, NC*H*CHN), 6.79 (br., 1 H, NCHC*H*N), 6.78–6.77 (m, 2 H, C_6H_4), 6.44–6.42 (m, 1 H, C_6H_4), 6.39–6.37 (m, 1 H, C_6H_4), 5.89 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 4.47 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 4.41 [sept, $^3J_{HH}$ = 7 Hz, 1 H, C*H*$(CH_3)_2$], 4.05 (s, 3 H, OCH_3), 1.53 [d, $^3J_{HH}$ = 7 Hz, 3 H, CH(CH_3)$_2$], 0.91 [d, $^3J_{HH}$ = 7 Hz, 3 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 168.7 (N*C*N), 167.6 (*C*=O), 152.0 (C_6H_4), 135.1 (C_6H_4), 129.6 (N*C*HCHN), 122.7 (C_6H_4), 122.6 (C_6H_4), 119.6 (NCH*C*HN), 116.2 (C_6H_4), 109.7 (C_6H_4), 58.0 (O*C*H_3), 55.6 (*C*H_2), 51.7 [*C*H$(CH_3)_2$], 25.2 [CH(*C*H_3)$_2$], 21.6 [CH(*C*H_3)$_2$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 3428 (s), 2981 (w), 1627 (s), 1541 (m), 1462 (m), 1380 (s), 1257 (m), 1181 (m), 1116 (w), 1025 (m), 755 (s), 656 (w) cm^{-1}. $C_{30}H_{36}N_6NiO_4$·H_2O (621.35): calcd. C 57.99, H 6.16, N 13.53; found C 58.41, H 6.37, N 13.87.

Synthesis of 1-Benzyl-3-[(2-methoxyphenyl)aminocarbonylmethyl]imidazolium Chloride (3a): 2-Chloro-*N*-(2-methoxyphenyl)acetamide (2.00 g, 10.0 mmol) and 1-benzylimidazole (1.58 g, 10.0 mmol) were added to toluene (ca. 10 mL) and refluxed overnight to obtain a light brown solid precipitate, which was isolated by decanting off the solvent. The residue was washed with hot hexane (ca. 15 mL) and dried under vacuum to obtain the product **3a** as a light brown powder (2.33 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 10.34 (s, 1 H, NC*H*N), 9.86 (s, 1 H, N*H*), 7.99 (d, $^3J_{HH}$ = 8 Hz, 1 H, C_6H_4), 7.62 (br., 1 H, NC*H*CHN), 7.36 (br., 5 H, C_6H_5), 7.04 (br., 1 H, NCHC*H*N), 7.02 (d, $^3J_{HH}$ = 8 Hz, 1 H, C_6H_4), 6.85 (t, $^3J_{HH}$ = 8 Hz, 1 H, C_6H_4), 6.83 (t, $^3J_{HH}$ = 8 Hz, 1 H, C_6H_4), 5.70 (s, 2 H, CH_2), 5.41 (s, 2 H, CH_2), 3.83 (s, 3 H, OCH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 163.3 (*C*=O), 150.0 (C_6H_4), 138.2 (C_6H_5), 137.6 (N*C*HN), 132.6 (C_6H_4), 129.4 (C_6H_5), 128.7 (C_6H_5), 126.4 (C_6H_5), 125.3 (C_6H_4), 124.0 (N*C*HCHN), 121.8 (C_6H_4), 120.8 (C_6H_4), 120.4 (NCH*C*HN), 110.8 (C_6H_4), 55.8 (O*C*H_3), 53.4 (*C*H_2), 52.2 (*C*H_2) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3395 (m), 3262 (m), 3063 (w), 1661 (s), 1601 (m), 1537 (s), 1497 (w), 1462 (m), 1270 (m), 1155 (m), 1024 (m), 761 (m), 633 (m) cm^{-1}. HRMS (ES): *m*/*z* 322.1554 [(NHC) + H]$^+$, calcd. 322.1556.

Synthesis of {1-Benzyl-3-[(2-methoxyphenyl)aminocarbonylmethyl]-imidazol-2-ylidene}$_2$Ni (3b): 1-Benzyl-3-[(2-methoxyphenyl)aminocarbonylmethyl]imidazolium chloride (0.358 g, 1.00 mmol), $NiCl_2$·$6H_2O$ (0.237 g, 1.00 mmol), and K_2CO_3 (0.417, 3.00 mmol) were added to CH_3CN (ca. 30 mL). The reaction mixture was refluxed for 24 h, after which it was filtered and the solvent removed. The residue was extracted in CH_2Cl_2 (ca. 20 mL) and dried under vacuum to obtain the product **3b** as a yellow solid (0.214 g, 61%). Single crystals for X-ray diffraction studies were grown in a minimum volume of CH_3CN (ca. 2 mL). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 7.33 (br., 5 H, C_6H_5), 7.03 (br., 1 H, NC*H*CHN), 7.02 (br., 1 H, NCHC*H*N), 6.82–6.77 (m, 2 H, C_6H_4), 6.49–6.47 (m, 2 H, C_6H_4), 5.78 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 4.95 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 4.41 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 4.35 (d, $^2J_{HH}$ = 14 Hz, 1 H, CH_2), 3.78 (s, 3 H, OCH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 169.8 (N*C*N), 167.2 (*C*=O), 152.3 (C_6H_4), 134.7 (C_6H_5), 134.6 (C_6H_4), 130.2 (C_6H_5), 129.1 (C_6H_5), 128.7 (C_6H_4), 127.6 (C_6H_5), 122.8 (N*C*HCHN), 122.4 (C_6H_4), 120.1 (NCH*C*HN), 119.4 (C_6H_4), 109.9 (C_6H_4), 57.7 (O*C*H_3), 55.8 (*C*H_2), 52.7 (*C*H_2) ppm. IR (KBr pellet): $\tilde{\nu}$ = 2933 (w), 3368 (m), 1742 (w), 1599 (s), 1566 (s), 1494 (m), 1455 (m), 1369 (m), 1240 (s), 1117 (w), 1024 (m), 742 (m) cm^{-1}. HRMS (ES): *m*/*z* 699.2202 [(NHC)$_2$Ni + H]$^{+\cdot}$, calcd. 699.2230. $C_{38}H_{36}N_6NiO_4$·CH_2Cl_2 (784.36): calcd. C 59.72, H 4.88, N 10.71; found C 60.12, H 5.55, N 11.16.

Synthesis of 1-[(2-Furanylmethyl)aminocarbonylmethyl]-3-methylimidazolium Chloride (4a): 2-Chloro-*N*-(2-furanylmethyl)acetamide (1.74 g, 10.0 mmol) and 1-methylimidazole (0.821 g, 10.0 mmol) were added to toluene (ca. 10 mL) and refluxed overnight to obtain a light brown precipitate, which was isolated by decanting off the solvent. The residue was washed with hot hexane (ca. 15 mL) and dried under vacuum to obtain the product **4a** as a light brown powder (1.80 g, 71%). ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): δ = 9.25 (br., 1 H, NC*H*N), 9.24 (br., 1 H, N*H*), 7.74 (br., 2 H, NC*H*CHN), 7.58 (s, 1 H, C_4H_3O), 6.38 (s, 1 H, C_4H_3O), 6.31 (s, 1 H, C_4H_3O), 5.10 (s, 2 H, CH_2), 4.30 (d, $^3J_{HH}$ = 6 Hz, 2 H, CH_2), 3.89 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100 MHz, 25 °C): δ = 165.0 (*C*=O), 151.4 (C_4H_3O), 142.3 (C_4H_3O), 137.9 (N*C*HN), 123.6 (N*C*HCHN), 123.1 (NCH*C*HN), 110.5 (C_4H_3O), 107.3 (C_4H_3O), 50.5 (*C*H_2), 35.8 (*C*H_3), 35.7 (*C*H_2) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3473 (s), 1683 (s), 1565 (m), 1428 (w), 1346 (w), 1265 (m), 1178 (m), 1080 (w), 1017 (m), 753 (s), 622 (m) cm^{-1}. HRMS (ES): *m*/*z* 220.1082 [(NHC) + H]$^+$, calcd. 220.1086.

Synthesis of {1-[(2-Furanylmethyl)aminocarbonylmethyl]-3-methylimidazol-2-ylidene}$_2$Ni (4b): 1-[(2-Furanylmethyl)aminocarbonylmethyl]-3-methylimidazolium chloride (0.500 g, 1.95 mmol), $NiCl_2$·$6H_2O$ (0.463 g, 1.95 mmol), and K_2CO_3 (0.810, 5.86 mmol) were added to CH_3CN (ca. 30 mL). The reaction mixture was refluxed for 24 h, after which it was filtered and the solvent removed. The residue was extracted in CH_2Cl_2 (ca. 20 mL) and dried under vacuum to obtain the product **4b** as a yellow solid (0.304 g, 63%). Single crystals for X-ray diffraction studies were grown in a minimum volume of CH_3CN (ca. 2 mL). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 7.31 (s, 1 H, C_4H_3O), 6.93 (br., 1 H, NC*H*CHN), 6.66 (br., 1 H, NCHC*H*N), 6.32 (s, 1 H, C_4H_3O), 6.07 (s, 1 H, C_4H_3O), 5.08 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 4.81 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 4.27 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 3.62 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 2.93 (s, 3 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ = 169.3 (N*C*N), 168.6 (*C*=O), 156.7 (C_4H_3O), 140.6 (C_4H_3O), 122.0 (N*C*HCHN), 121.2 (NCH*C*HN), 110.2 (C_4H_3O), 105.2 (C_4H_3O), 56.2 (*C*H_3), 41.5 (*C*H_2), 35.4 (*C*H_2) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3413 (s), 1672 (m), 1578 (s), 1468 (w), 1392 (m), 1300 (w), 1240 (w), 1179 (w), 1146 (w), 1077 (w), 1006 (m), 809 (w), 744 (s) cm^{-1}. $C_{22}H_{24}N_6NiO_4$·CH_2Cl_2 (580.09): calcd. C 47.62, H 4.52, N 14.49; found C 46.90, H 4.98, N 15.22.

Synthesis of 1-Benzyl-3-[(2-furanylmethyl)aminocarbonylmethyl]imidazolium Chloride (5a): 2-Chloro-*N*-(2-furanylmethyl)acetamide (1.74 g, 10.0 mmol) and 1-benzylimidazole (1.58 g, 10.0 mmol) were added to toluene (ca. 10 mL) and refluxed overnight to obtain a light brown solid precipitate, which was isolated by decanting off the solvent. The residue was washed with hot hexane (ca. 15 mL) and dried under vacuum to obtain the product **5a** as a light brown powder (2.52 g, 76%). ^{1}H NMR ([D$_6$]DMSO, 400 MHz, 25 °C): δ = 9.44 (br., 1 H, NC*H*N), 9.26 (br., 1 H, N*H*), 7.87 (br., 1 H, NC*H*CHN), 7.77 (br., 1 H, NCHC*H*N), 7.59 (s, 1 H, C$_4H_3$O), 7.44–7.38 (m, 5 H, C$_6H_5$), 6.39 (s, 1 H, C$_4H_3$O), 6.31 (s, 1 H, C$_4H_3$O), 5.52 (s, 2 H, CH_2), 5.12 (s, 2 H, CH_2), 4.31 (s, 2 H, CH_2) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100 MHz, 25 °C): δ = 164.8 (*C*=O), 151.4 (*C*$_4$H$_3$O), 142.1 (*C*$_4$H$_3$O), 137.4 (N*C*HN), 134.8 (*C*$_6$H$_5$), 128.8 (*C*$_6$H$_5$), 128.6 (*C*$_6$H$_5$), 128.2 (*C*$_6$H$_5$), 124.0 (N*C*HCHN), 121.8 (NCH*C*HN), 110.3 (*C*$_4$H$_3$O), 107.2 (*C*$_4$H$_3$O), 51.7 (*C*H$_2$), 50.6 (*C*H$_2$), 35.7 (*C*H$_2$) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3450 (w), 3064 (w), 1685 (s), 1560 (m), 1456 (w), 1261 (m), 1161 (m), 1080 (w), 1021 (w), 804 (w), 714 (m), 625 (w) cm^{-1}. HRMS (ES): *m*/*z* 296.1393 [(NHC) + H]$^+$, calcd. 296.1399.

Synthesis of {1-Benzyl-3-[(2-furanylmethyl)aminocarbonylmethyl]-imidazol-2-ylidene}$_2$Ni (5b): 1-Benzyl-3-[(2-furanylmethyl)aminocarbonylmethyl]imidazolium chloride (0.332 g, 1.00 mmol), NiCl$_2$·6H$_2$O (0.237 g, 1.00 mmol), and K$_2$CO$_3$ (0.417, 3.00 mmol) were added to CH$_3$CN (ca. 30 mL). The reaction mixture was refluxed for 24 hours, after which it was filtered and the solvent removed. The residue was extracted in CH$_2$Cl$_2$ (ca. 20 mL) and dried under vacuum to obtain the product **5b** as a yellow solid (0.214 g, 66%). Single crystals for X-ray diffraction studies were grown in a minimum volume of CH$_3$CN (ca. 2 mL). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ = 7.31 (br., 2 H, C$_6H_5$), 7.29 (s, 1 H, C$_4H_3$O), 7.18 (br., 1 H, NC*H*CHN), 6.96–6.94 (m, 3 H, C$_6H_5$), 6.50 (br., 1 H, NCHC*H*N), 6.27 (s, 1 H, C$_4H_3$O), 6.06 (s, 1 H, C$_4H_3$O), 5.08 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 4.81 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 4.40 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 4.28 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 4.16 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2), 3.64 (d, $^2J_{HH}$ = 15 Hz, 1 H, CH_2) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz, 25 °C): δ = 169.3 (N*C*N), 169.1 (*C*=O), 156.4 (*C*$_4$H$_3$O), 140.7 (*C*$_4$H$_3$O), 134.4 (*C*$_6$H$_5$), 129.1 (*C*$_6$H$_5$), 128.6 (*C*$_6$H$_5$), 127.5 (*C*$_6$H$_4$), 122.7 (N*C*HCHN), 120.2 (NCH*C*HN), 110.4 (*C*$_4$H$_3$O), 105.9 (*C*$_4$H$_3$O), 56.5 (*C*H$_2$), 52.8 (*C*H$_2$), 42.0 (*C*H$_2$) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3378 (m), 3125 (w), 2925 (w), 1595 (s), 1392 (w), 1328 (w), 1298 (w), 1238 (w), 1145 (w), 998 (w), 930 (w), 807 (w), 730 (w), 699 (w) cm^{-1}. C$_{34}$H$_{32}$N$_6$NiO$_4$·CH$_2$Cl$_2$ (732.28): calcd. C 57.41, H 4.68, N 11.48; found C 57.05, H 5.36, N 11.00.

Computational Methods: Density functional theory calculations were performed on the five nickel complexes **1b**–**5b** using the GAUSSIAN 03[33] suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with the Lee–Yang–Parr correlation functional (B3LYP) has been employed in this study.[34,35] The LANL2DZ basis set was used for the Ni atom,[36] while all other atoms were treated with the 6-31G(d) basis set.[37] All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces. A tight SCF convergence (10^{-8} a.u.) was used for all calculations.

Inspection of the metal–ligand donor–acceptor interactions was carried out using the charge decomposition analysis (CDA).[38] CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.[39] The orbital contributions in the NHC–Ni complexes, **1b**–**5b**, can be divided into two parts:

(i) σ donation from the NHC→Ni fragment and

(ii) π back-donation from the NHC←Ni fragment

The CDA calculations were performed using the program *AOMix*,[40] using the B3LYP/LANL2DZ, 6-31G(d) wave function. Molecular orbital (MO) compositions and the overlap populations were calculated using the *AOMix* program. The analysis of the MO compositions in terms of occupied and unoccupied fragment orbitals (OFOs and UFOs, respectively), construction of orbital interaction diagrams, and the charge decomposition analysis (CDA) were performed using the *AOMix-CDA*.[41]

General Procedure for the Michael Reaction: In a typical run, performed in air, a 25 mL vial was charged with a mixture of the β-dicarbonyl, β-keto ester, β-diester, or α-cyano ester compound (0.50 mmol) and diethyleneglycol di-*n*-butyl ether (0.50 mmol) (internal standard). The precatalyst **1b**–**5b** (5 mol-%) (Table 1) and then CHCl$_3$ (2 mL) were added to the reaction mixture and stirred at room temperature for 1 h. The α,β-unsaturated carbonyl compound (0.60 mmol) was then added to the reaction mixture and stirred for another 16 h at room temperature after which the solution was analyzed by quantitative GC analysis using diethyleneglycol di-*n*-butyl ether as an internal standard.

Supporting Information (see also the footnote on the first page of this article): X-ray crystallographic data, B3LYP coordinates of the optimized geometries of **1b**–**5b**, computational data, and control experimental data.

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