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Bifunctional nickel precatalysts of amido-functionalized N-heterocyclic carbenes for base-free Michael reaction under ambient conditions☆

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ABSTRACT

A series of new bifunctional nickel precatalysts, [1-(R)-3-*N*-(benzylacetamido)imidazol-2-ylidene]$_2$ Ni [R = Me (**1b**), *i*-Pr (**2b**), and CH_2Ph (**3b**)], containing a Lewis acidic metal site and a Lewis basic amido-N site in a pendent ligand sidearm, have been successfully designed for base-free Michael addition reaction. Specifically, the nickel (**1**–**3**)**b** complexes catalyzed the highly desired base-free Michael addition reactions of representative cyclic 5-membered β-dicarbonyl and β-ketoester substrates with a variety of activated olefinic compounds in air at ambient temperature in good to excellent yield. The nickel (**1**–**3**)**b** complexes were synthesized from the reactions of the corresponding imidazolium chloride salts, (**1**–**3**)**a**, with $NiCl_2$•$6H_2O$ in presence of K_2CO_3 as a base in 55–73% yield. The density functional theory (DFT) studies performed on the nickel complexes suggested the presence of a strong Ni–NHC σ-interaction in these complexes.

1. Introduction

The Michael addition involves the addition of a nucleophile, called a Michael Donor, to an activated electrophilic olefin, known as a Michael acceptor [1–3]; the reaction, being atom economic, is largely popular for its simplicity in constructing quaternary stereocenters with great efficiency and enantioselectivity [4–9]. It has thus evolved into a powerful carbon–carbon bond forming tool for synthesizing enantio-enriched, highly functionalized and intricate carbon skeletons in natural products, biologically active compounds and heterocyclic compounds etc.

The widespread applicability of Michael addition arises from its mild reaction conditions, high functional group tolerance and from its versatility in bond constructions that extend beyond the conventional C–C bonds to a variety of C–X (X = N, O, P, S) bonds. There exist several variations of the parent reaction mainly in the forms of oxa-Michael [10], involving oxygen nucleophiles like alcohols, phospha-Michael [11,12], involving phosphorus nucleophiles *eg.* triphenylphosphine, thia-Michael [13], involving thiol nucleophiles and finally the aza-Michael [14,15], involving nitrogen nucleophiles like amines. All of these variants rightfully occupy key positions in the synthesis of many a heteroatom compounds of interests for their applications as dyes and fine chemicals and for their biological activity [16,17].

An important prerequisite of Michael reaction is the use of a Brønsted base, which many a times affects the reaction in terms of yielding a host of unwanted side-products that cut into the overall reaction yield [1–3]. Specifically, the presence of a base in the reaction medium promotes a wide variety of side reactions like, ester solvolyses, hetero Diels–Alder dimerization, aldol cyclization, retro-Claisen C–C bond cleavage etc. Hence, against this backdrop, performing base-free Michael addition is of considerable interest to both industry and academia alike. It is thus anticipated that the absence of a base would suppress all of the undesired secondary reactions that unfavorably affects the reaction yield. In this regard two different strategies have been employed in achieving base-free Michael addition, the one taking recourse to organocatalysis [18] while the other employing transition metals [19–21]. A common premise that runs beneath both these approaches involves the use of bifunctional catalysts possessing both acidic and basic sites [22–25]. The organocatalysis provides a better alternative to traditional metal based catalysis by avoiding the use of metals that usually have various toxicity issues associated with it.

With one of the ongoing theme of our research being in exploring the biomedical [26,27] and catalytic [28–41] potentials of N-heterocyclic carbene [42–47] complexes of transition metals, we became interested in constructing a variety of C–X (X = C, heteroatom) bonds catalytically, including the base-free Michael reactions using bifunctional catalysts [48,49]. We rationalized that

☆ Dedicated to Professor Christian Bruneau on his 60th birthday.

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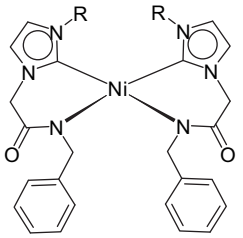


R = Me (**1b**), *i*-Pr (**2b**), CH_2Ph (**3b**)

Fig. 1. Nickel complexes of amido-functionalized N-heterocyclic carbenes are shown.

a basic functionality attached to an N-heterocyclic carbene ligand skeleton of the catalyst would make it bifunctional by virtue of its simultaneous presence with an acidic metal center in the same catalyst. The N-heterocyclic carbene, as such as a ligand, offers conducive electronic and steric environments amenable to easy tunability of the ligand topology, which is often achieved through incorporation of a variety of electron withdrawing, electron donating and sterically demanding functional groups. As far as the choice of the catalyst was concerned, we intended to employ nickel owing to a report of the use of $Ni(acac)_2$ in the Michael addition reaction [50] and because of our prior reports of the use of bifunctional nickel N-heterocyclic carbene complexes for its base-free version [48,49].

Here in this contribution, we report a series of bifunctional nickel precatalysts, [1-(R)-3-*N*-(benzylacetamido)imidazol-2-ylidene]$_2$Ni [R = Me (**1b**), *i*-Pr (**2b**), and CH_2Ph (**3b**)] (Fig. 1) that carried out the base-free Michael reaction of representative cyclic 5-membered β-dicarbonyl and β-ketoester substrates with a variety of activated olefinic compounds in air at ambient temperature in good to excellent yield. The Ni–NHC interaction in the nickel (**1**–**3**)**b** complexes have been studied using density functional theory (DFT) studies.

2. Results and discussions

A series of bifunctional nickel (**1**–**3**)**b** catalysts, possessing a Lewis acidic metal site and a Lewis basic amido-N site, built in a functionalized sidearm of a chelating N-heterocyclic carbene ligand, was specifically designed for carrying out base-free Michael addition reaction under ambient conditions. In particular, amido-functionalized N-heterocyclic carbenes namely, 1-(R)-3-*N*-(benzylacetamido)imidazol-2-ylidines (R = Me, *i*-Pr, CH_2Ph) were employed in stabilizing the targeted bifunctional (**1**–**3**)**b** catalysts that were obtained from the reaction of the respective (**1**–**3**)**a** imidazolium chloride salts and $NiCl_2{\bullet}6H_2O$ in CH_3CN in presence of

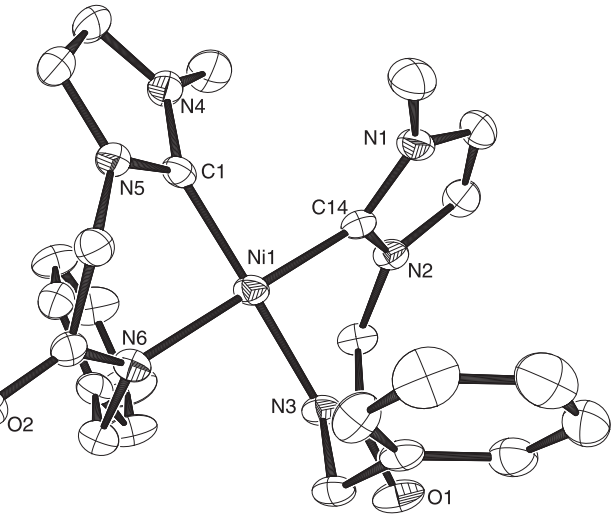
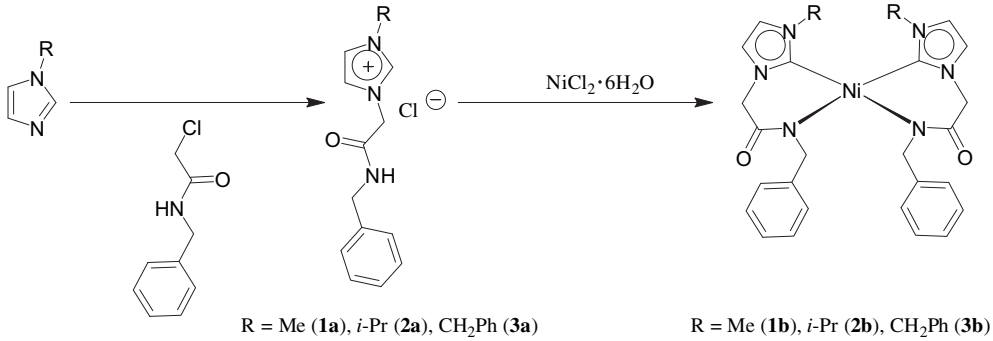


Fig. 2. ORTEP diagram of **1b** with thermal ellipsoids drawn at 50% probability level.

K_2CO_3 as a base in 55–73% yield (Scheme 1). The diamagnetic nature of the nickel (**1**–**3**)**b** complexes were evident from the ^1H and $^{13}C\{^1H\}$ NMR study, which showed the disappearance of a characteristic (NC*H*N) (**1**–**3**)**a** ligand resonance in its ^1H NMR spectrum while the appearance of a new diagnostic Ni–$C_{carbene}$ peak at a highly downfield region at ca. 169.2–169.9 ppm in its corresponding $^{13}C\{^1H\}$ NMR spectrum. More interestingly, the methylene (CH_2) moiety of the chelating N-heterocyclic carbene ligand in the nickel (**1**–**3**)**b** complexes appeared to be diastereotopic in nature as it exhibited two sets of doublets each displaying two-bond geminal coupling ($^2J_{HH}$) of 14 Hz in the ^1H NMR spectrum. The N-heterocyclic carbene precursors, *i.e.* the (**1**–**3**)**a** imidazolium chloride salts, were synthesized from the corresponding 1-(R)imidazoles (R = Me, *i*-Pr, CH_2Ph) by the treatment with *N*-benzyl-2-chloro-acetamide.

The X-ray diffraction studies revealed that the molecular structures of the nickel (**1**–**3**)**b** complexes are monomeric and isostructural, with each exhibiting a square planar geometry at the metal center, and which is in concurrence with the diamagnetic nature of the (**1**–**3**)**b** complexes as ascertained earlier from the NMR experiments (Fig. 2 and see supporting information Figs. S1 and S2 and Table S2). Another interesting features of the (**1**–**3**)**b** structures is that the amido-functionalized N-heterocyclic carbene ligands were found chelated to the metal center in a *cis*-disposition to each other.

The Ni–$C_{carbene}$ bond distances in **1b** [1.843(2) Å and 1.861(2) Å], **2b** [1.860(3) Å and 1.859(3) Å] and **3b** [1.841(4) Å and 1.858(4) Å], are



R = Me (**1a**), *i*-Pr (**2a**), CH_2Ph (**3a**)

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

Scheme 1.