A comparison between nickel and palladium precatalysts of 1,2,4-triazole based N-heterocyclic carbenes in hydroamination of activated olefins†

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A comparison is drawn between the nickel and palladium precatalysts of 1,2,4-triazole based N-heterocyclic carbenes in the hydroamination of activated olefins. Though all of the newly designed nickel and palladium precatalysts, *trans*-[1-*i*-propyl-4-R-1,2,4-triazol-5-ylidene]$_2$MBr$_2$ [R = Et, M = Ni (**1b**); R = Et, M = Pd (**1c**); R = $CH_2CH{=}CH_2$, M = Ni (**2b**) and R = $CH_2CH{=}CH_2$, M = Pd (**2c**)], are moderately active for hydroamination reaction of a variety of secondary amines *viz*. morpholine, piperidine, pyrrolidine and diethylamine with activated olefins like, acrylonitrile, methyl acrylate, ethyl acrylate and *t*-butyl acrylate at room temperature in 1 hour, the nickel complexes (**1b** and **2b**) exhibited superior activity compared to its palladium counterparts (**1c** and **2c**). The better performance of the nickel complexes has been correlated to the more electron deficient metal center in the nickel **1b** and **2b** complexes than in the palladium **1c** and **2c** analogs based on the density functional theory studies. The **1b-c** and **2b-c** complexes were synthesized by the reaction of 1-*i*-propyl-4-R-1,2,4-triazolium bromide [R = Et (**1a**) and R = $CH_2CH{=}CH_2$ (**2a**)] with MCl_2 [M = Ni, Pd] in presence of NEt_3 as a base.

Introduction

The hydroamination of olefins provides a convenient access to nitrogen based chemical feedstock that are of interests as pharmaceuticals as well as bulk, specialty and agrochemicals.[1] It offers an attractive 100% atom-economic route from cheap and readily available starting materials without generating any waste byproducts and hence the catalytic construction of C–N bond through hydroamination reaction remains of significant industrial interest even today. A foremost challenge arise from its thermodynamic characteristic as the hydroamination transformation is weakly exergonic or at most approximately thermoneutral while displaying a very high negative entropy of the reaction.[2] In this backdrop, the transition metal catalyzed hydroamination reaction assumes relevance as it provides a solution by not only facilitating the catalytic formation of a C–N bond but also do so by inducing a host of other important attributes like chemo-, regio- and stereoselectivity, functional group tolerance and also in allowing the reaction to happen under amenable conditions.[3] In this context notable are the *d*-[4] and *f*-block metals[5] that have been reported for the hydroamination reaction. For example, though the lanthanides as well as the early-transition metals yield highly active catalysts with high turnover numbers, a serious drawback to these metals arise from their highly oxophilic nature, which dictates stringent conditions for the reaction thereby limiting its applicability in large scale synthesis.[1a,6] Unlike the early-transition metals, the late-transition metals are less active, more tolerant toward functional groups and are also convenient to handle owing to their remarkable air and moisture stability.[7] Because of these aforementioned reasons, we became interested in designing late transition metal based precatalysts particularly of nickel and palladium for the hydroamination reaction.

With the primary objective of our research being on exploring the utility of N-heterocyclic carbenes[8] in biomedical applications[9] as well as in chemical catalysis, we have recently reported a series of N-heterocyclic carbene based precatalysts for a variety of transformations ranging from ring-opening polymerization (ROP) of L-lactide[10] to a host of C–C coupling reactions namely, the Suzuki-Miyaura,[11] Hiyama,[12] Sonogashira[12,13] and the base-free Michael addition reaction.[14] Eventually, extending beyond the C–C bond we focused on a C–N bond forming reaction particularly the hydroamination reaction with an ancillary objective of performing these reactions under amenable conditions using late-transition metals mainly the Ni and Pd based precatalysts of N-heterocyclic carbenes. Additionally, we intended to carry out a comparative study of the first row nickel and the second row palladium metals in order to find out which one of the two is better suited for the hydroamination reaction.

Here in this contribution, we report a series of nickel **1b** and **2b** and palladium **1c** and **2c** complexes of 1,2,4-triazole based N-heterocyclic carbenes as effective catalysts for the hydroamination reaction of secondary amines with activated olefins at room temperature (Fig. 1). The density functional theory studies showed that the 1,2,4-triazole based N-heterocyclic carbenes closely mirrored the imidazole based N-heterocyclic carbenes in being strongly σ-donating with very little π-back bonding tendencies.

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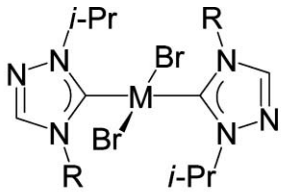
† Electronic supplementary information (ESI) available: The catalysis data of control and blank experiments, Ortep plots of **2b** and **2c**, the B3LYP coordinates of the optimized geometries for **1b**, **2b**, **1c** and **2c**, NBO tables and CDA table along with orbital interaction diagrams of **1b**, **2b**, **1c** and **2c**. CCDC reference numbers 678986 (**1b**), 719442 (**2b**), 680131 (**1c**) and 673137 (**2c**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917892a

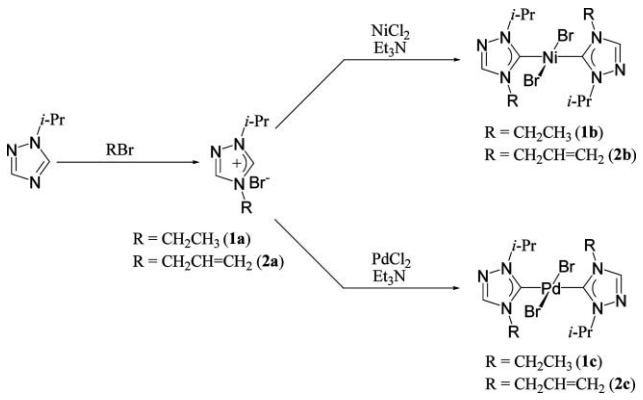


R = CH_2CH_3, M = Ni (**1b**)
R = CH_2CH_3, M = Pd (**1c**)
R = $CH_2CH{=}CH_2$, M = Ni (**2b**)
R = $CH_2CH{=}CH_2$, M = Pd (**2c**)

Fig. 1 Nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes of 1,2,4-triazole based N-heterocyclic carbenes.

Results and discussion

Two new 1,2,4-triazole based N-heterocyclic carbene ligand precursors **1a** and **2a** were synthesized by direct alkylation of 1-(*i*-propyl)-1,2,4-triazole with ethyl and allyl bromides in 54–78% yield (Scheme 1). The ^{1}H NMR spectrum of **1a** and **2a** showed the characteristic NC*H*N resonance appearing at *ca*. 11.5 ppm, at a region more downfield shifted than that of the imidazole based N-heterocyclic carbene systems (*ca*. 10.1 ppm) and is in concurrence with the highly acidic nature of the NC*H*N resonance of the 1,2,4-triazole ring containing three electronegative nitrogen atoms compared to that of the imidazole ring containing two electronegative nitrogen atoms. Similar downfield shift was observed in the corresponding ^{13}C{^{1}H} NMR spectrum as the N*C*HN resonance appeared at 143.6–144.1 ppm, again at a far more downfield region than its imidazole counterparts (*ca*. 135.8 ppm).[15]



Scheme 1

The nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes were prepared by directly reacting 1,2,4-triazolium bromide salts (**1a** and **2a**) with respective MCl_2 (M = Ni and Pd) in presence of NEt_3 as a base in 47–55% yield. In this regard it is noteworthy that the late-transition metal complexes of 1,2,4-triazole based N-heterocyclic carbenes in general are prepared by (*i*) the direct reaction of the 1,2,4-triazolium halide salts with the metal halides or acetates in presence of a base or a dative solvent[16] and (*ii*) from its silver analogs by transmetallation reaction with various metal salts.[17]

The formation of the metal complexes **1b-c** and **2b-c** was very much evident in the ^{1}H NMR spectrum as it showed the absence of NC*H*N resonance of the starting 1,2,4-triazolium bromide salts (**1a** or **2a**) while the ^{13}C{^{1}H} NMR spectrum showed the appearance of a highly downfield shifted metal bound N*C*N resonance at 170.5–171.9 ppm. Quite interestingly, ^{1}H and ^{13}C NMR of the nickel and palladium complexes **1b-c** and **2b-c** showed two sets of resonances indicating the presence of two rotamers, *trans–syn* and *trans–anti*, in solution along the lines of similar observation made earlier for related nickel and palladium complexes of triazole and imidazole based N-heterocyclic carbenes.[16b,18] Specifically, the rotamers were observed in *ca*. 1:1 ratio in the **1b-c** and **2b-c** complexes.

The molecular structures of the nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes revealed the monomeric nature of these complexes with its metal centers displaying the expected square planar geometry (Fig. 2-3 and Supporting Information Fig. S1-S2).† Quite interestingly, the *trans–anti* rotamer was seen in the crystal structure of all the **1b-c** and **2b-c** complexes. The two 1,2,4-triazol-5-ylidene ligands and the two bromide ligands were at *trans* disposition to each other around the metal center. The Ni–$C_{carbene}$ distance in **1b** [1.902(3) Å] and **2b** [1.925(8) Å and 1.931(7) Å] is not only comparable to the Ni–$C_{carbene}$ distance in another nickel 1,2,4-triazole based N-heterocyclic carbene complex, *trans*-[(1-(1-adamantyl)-3-phenyl-4-(2-oxyphenyl)-1,2,4-triazol-5-ylidene)]$_2$Ni [1.890(4) Å and 1.888(4) Å][19] but also to that in nickel imidazole based N-heterocyclic carbene complexes namely, *trans*-[1,3-diallylimidazolin-2-ylidene]$_2$NiI$_2$ [1.908(4) Å] and *trans*-[1-methyl-3-allylimidazolin-2-ylidene]$_2$NiI$_2$ [1.901(6) Å].[20] Similarly, the Pd–$C_{carbene}$ distances in **1c** [2.018(3) Å] and **2c** [2.030(8) Å and 2.010(8) Å] too are in good agreement with that in another palladium 1,2,4-triazole based N-heterocyclic carbene complex, *trans*-[(1-phenyl-4-(1-phenylethyl)-1,2,4-triazol-5-ylidene)]$_2$PdI$_2$ [2.020(8) Å and 2.041(8) Å],[21] and also with that in palladium imidazole based N-heterocyclic carbene complexes namely, *trans*-[1,3-diallylimidazolin-2-ylidene]$_2$PdBr$_2$ [2.018(3) Å and 2.024(3) Å][20] and *trans*-[1-ethyl-3-methylimidazolin-2-ylidene]PdCl$_2$ [2.030(2) Å].[22] Lastly, consistent with shorter covalent radii of Ni (1.154 Å) compared to Pd (1.283 Å),[23] the Ni–$C_{carbene}$ distance in **1b** [1.902(3) Å] and **2b** [1.925(8) Å and 1.931(7) Å] are

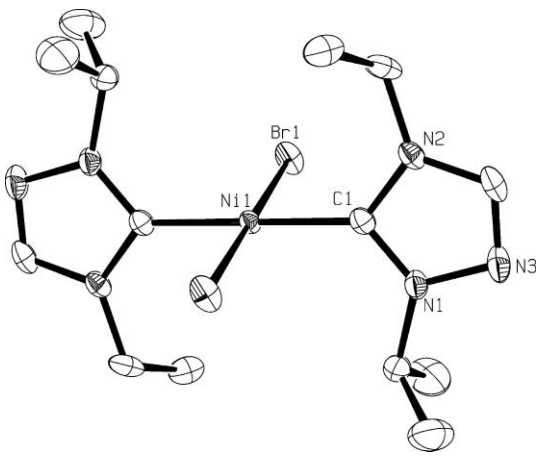


Fig. 2 ORTEP drawing of **1b** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Ni(1)-C(1) 1.902(3), Ni(1)-Br(1) 2.3162(3), C(1)-Ni(1)-Br(1) 89.02(7).

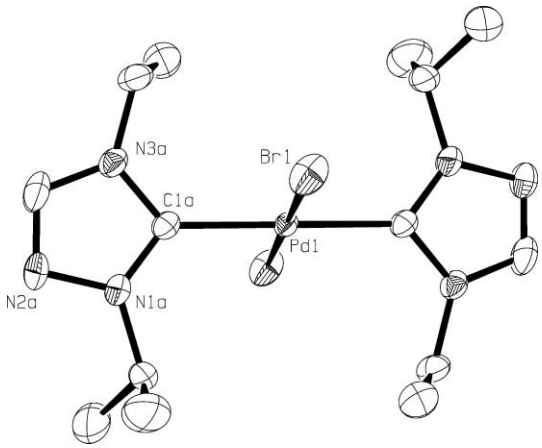


Fig. 3 ORTEP drawing of **1c** with thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)-C(1a) 2.018(3), Pd(1)-Br(1) 2.4178(6), C(1a)-Pd(1)-Br(1) 89.45(9).

shorter than the Pd–$C_{carbene}$ distance in **1c** [2.018(3) Å] and **2c** [2.030(8) Å and 2.010(8) Å].

Additional insights into the electronic structure of the **1b-c** and **2b-c** complexes could be obtained from the density functional theory (DFT) study. In this regard, the geometry optimized structures of the nickel (**1b** and **2b**) complexes were computed at B3LYP/LANL2DZ, 6-31G(d) level of the theory and the palladium (**1c** and **2c**) complexes at B3LYP/SDD, 6-31G(d) level of the theory using atomic coordinates adopted from the X-ray data (Supporting Information Tables S1-S4†). The single point calculations were subsequently performed at the same level of theory for the detailed prediction of the electronic properties.

The good σ-donating ability of the triazole based N-heterocyclic carbene ligand is all the more conspicuous in both the Mulliken and natural charge analysis that showed significant increase in electron density at the metal center of the nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes along with concomitant decrease in the electron density of the carbene carbon with respect to the free triazole fragment (Supporting Information Tables S5-S8†) arising from strong σ-donation of the ligand to the metal center. Further scrutiny of the electronic configuration as obtained by Natural Bond Orbital (NBO) analysis showed that the electron donation from the NHC fragments occur on to *3d* orbital of nickel (**1b** and **2b**) and to *5s* palladium (**1c** and **2c**) complexes (Supporting Information Tables S9-S10†). The NBO analysis further revealed that the Ni–$C_{carbene}$ bond in **1b** and **2b** as well as the Pd–$C_{carbene}$ bond in **1c** and **2c** is composed of an interaction of a C_{sp^2} orbital of the ligand with a *sd* orbital of the metal (Supporting Information Table S11). Lastly, the Charge Decomposition Analysis (CDA) studies, which estimate the relative extent of the $NHC \xrightarrow{\sigma} MBr_2 (M = Ni, Pd)$ donation (*d*) and the $NHC \xleftarrow{\pi} MBr_2 (M = Ni, Pd)$ donation (*b*) also suggested that the 1,2,4-triazole based N-heterocyclic carbenes are σ–donating ligands based on their high estimated *d*/*b* ratio values *e.g.* **1b** (1.86), **2b** (1.72), **1c** (3.64) and **2c** (3.26) (Supporting Information Table S12†).

Further insight into the strength of the 1,2,4-triazole NHC–M (M = Ni and Pd) interaction could be obtained by estimating the 1,2,4-triazole NHC–M (M = Ni and Pd) bond dissociation energy (D_e) for the nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes computed respectively at B3LYP/LANL2DZ, 6-31G(d) and B3LYP/SDD, 6-31G(d) levels of the theory. Quite interestingly, the 1,2,4-triazole NHC–Ni interaction [D_e: 68.8 kcal/mol (**1b**) and 68.9 kcal/mol (**2b**)] was estimated to be weaker than the 1,2,4-triazole NHC–Pd interaction [D_e: 74.7 kcal/mol (**1c**) and 74.8 kcal/mol (**2c**)] (Supporting Information Table S13†).

A better understanding of the 1,2,4-triazole NHC–M (M = Ni and Pd) interaction could be obtained by further constructing the molecular orbital (MO) correlation diagram from the fragment molecular orbitals (FMOs) of the 1,2,4-triazole NHC ligand fragment and the MBr_2 (M = Ni and Pd) fragment. Of primary interest is the σ-interaction between the 1,2,4-triazole NHC ligand and the MBr_2 (M = Ni and Pd) fragment represented by the following molecular orbitals, HOMO–27 (**1b**), HOMO–31 (**1c**), HOMO–29 (**2b**) and HOMO–33 (**2c**), that depict the interaction of the 1,2,4-triazole carbene lone pair with the fragment molecular orbital of the MBr_2 (M = Ni and Pd) fragment in these complexes (Fig. 4, 5 and Supporting Information Fig. S3-S8†).

Another notable feature of the 1,2,4-triazole NHC–M (M = Ni and Pd) σ-interaction is that these σ-bonding molecular orbitals are [HOMO–27 (**1b**), HOMO–31 (**1c**), HOMO–29 (**2b**) and HOMO–33 (**2c**)] deeply seated thereby indicating a stable interaction. In this regard it is worth noting that similar deeply buried σ-bonding molecular orbitals are also observed in the related imidazole NHC–M (M = Ni and Pd) complexes.[9b,11b,12,13,14b] In contrast to the both 1,2,4-triazole NHC–metal and imidazole NHC–metal interactions, whose molecular orbitals are low lying and hence generally inert to electrophiles or nucleophiles, the well-known Schrock and Fischer carbenes are very much susceptible to the electrophilic and nucleophilic attacks.[24]

Significantly enough, all the nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes are moderately active for hydroamination of activated olefins (Equation 1 and Table 1). In particular, when a variety of secondary amines namely, morpholine, piperidine, pyrrolidine and diethylamine were treated with activated olefins like, acrylonitrile, methyl acrylate, ethyl acrylate and *t*-butyl acrylate in presence of 5 mol% of catalyst (**1b** or **2b** or **1c** or **2c**) and 10 mol% AgOTf, poor to excellent conversions to the hydroaminated products were obtained at room temperature in 1 hour of the reaction time. Significant amplification in the product formation observed in comparison to the blank and the control experiments performed with MCl_2 (M = Ni and Pd) under identical conditions thus underscores the "ligand effect" on the metal center in the **1b-c** and the **2b-c** complexes. In particular, enhancement of the product yield of up to 62% for the nickel (**1b** and **2b**) complexes was observed relative to the control experiment performed with anhydrous $NiCl_2$ and $NiBr_2$ under the same conditions while that of up to 35% was observed for the palladium (**1c** and **2c**) complexes again relative to the control experiment performed with $PdCl_2$ and $PdBr_2$ under the same conditions (Supporting Information Table S14†). Also, significant enhancement of up to 67% were observed for the both the nickel and palladium (**1b-c** and **2b-c**) precatalysts in comparison to the control performed with AgOTf but in absence of the catalyst under identical conditions (Supporting Information Table S14†). Lastly, significantly amplification of up to 62% were also observed for the **1b-c** and the **2b-c** precatalysts with respect to the *in situ* generated free N-heterocyclic carbene ligand (Supporting Information Table S15†).

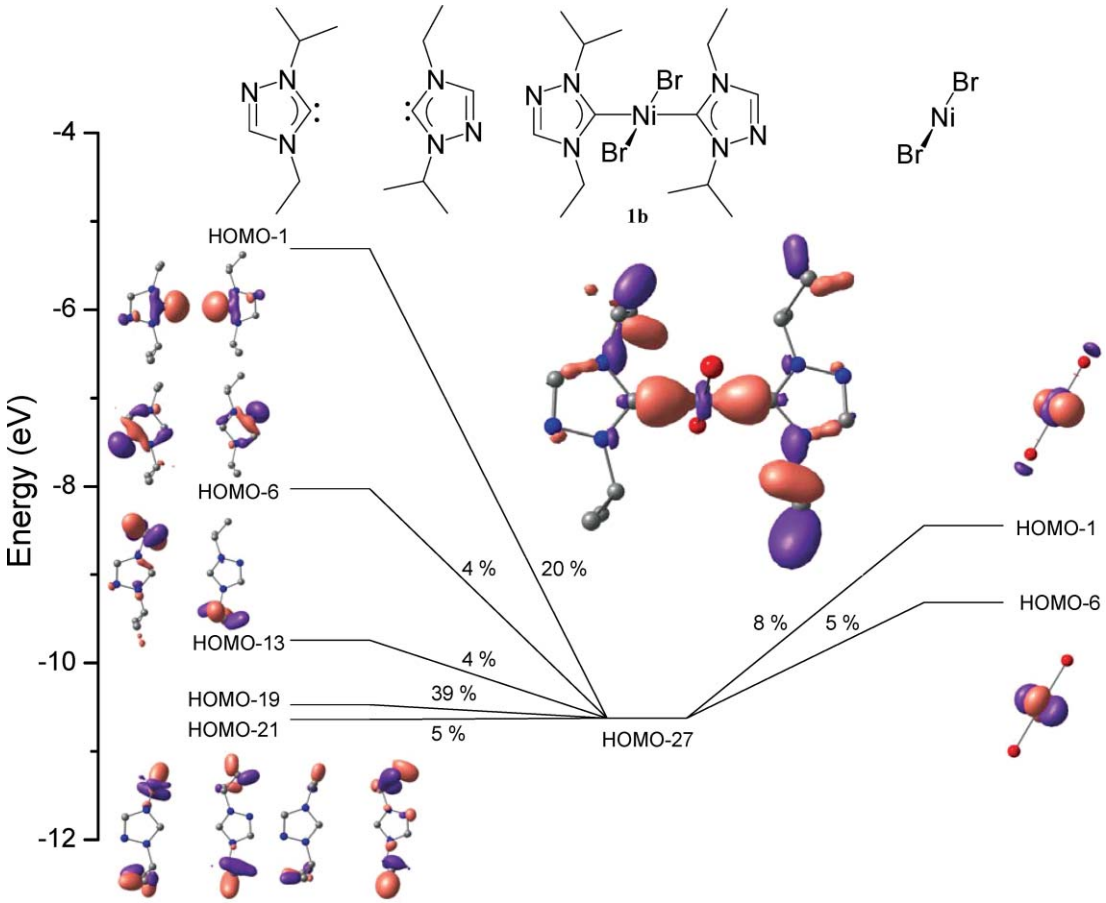
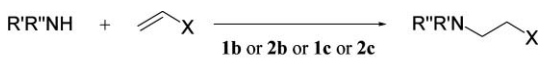


Fig. 4 Simplified orbital interaction diagram showing the major contributions of the NHC-nickel bond in **1b**.



(1)

X = CN, COOR (R = Me, Et, *t*Bu)

In order to establish the regiochemistry of the hydroamination reaction, the isolation and subsequent characterization of the final products of the addition reaction showed anti-Markovnikov type N–H addition across the activated olefinic substrates. The homogeneous nature of the hydroamination catalysis was confirmed by the classical mercury-poisoning experiment[25] performed on the representative morpholine and acrylonitrile substrates using the **1c** catalyst and that showed no significant reduction in activity under identical conditions.

More interestingly, the nickel (**1b** and **2b**) complexes exhibited superior activity than its palladium (**1c** and **2c**) counterparts owing to greater Lewis acidity of the former, the support of which comes from the density functional theory studies, as both the Mulliken as well as the natural charge analysis showed the palladium center in **1c** and **2c** to be more electron rich than the nickel center in the **1b** and **2b** complexes. Indeed, a recent report by Togni and co-workers suggests nickel to be a better catalyst than palladium or platinum for the catalytic hydroamination of alkenes.[26]

Important is the comparison of the performances of these nickel (**1b** and **2b**) and palladium (**1c** and **2c**) precatalysts with the other reported catalysts, particularly the N-heterocyclic carbene based ones for the hydroamination reaction. In this context it is worth noting that while no such reports of nickel based N-heterocyclic carbene catalysts for the hydroamination reaction exists, we are aware of only a handful of structurally characterized examples of the palladium complexes of imidazole based N-heterocyclic carbenes for the hydroamination reaction. For example, the [*trans*-(κ^2-^{tBu}*C*N(Bn)*C*^{tBu})Pd(MeCN)$_2$][BF$_4$]$_2$,[27] [*trans*-(κ^2-^{Mes}*C*N(H)*C*^{Mes})Pd(MeCN)$_2$][BF$_4$]$_2$,[27] [(κ^3-^{tBu}*CN*(H)*C*^{tBu})-Pd(MeCN)$_2$][BF$_4$]$_2$[27] and [(κ^3-*CNO*)Pd(MeCN)][BF$_4$][28] complexes displayed low to excellent conversions (9–>99%) for the hydroamination of only one substrate, methacrylonitrile, with a series of secondary amines namely, piperidine, pyrolidine, morpholine and N-methyl-piperazine at 2 mol% of the precatalyst loading at 40–90 °C in 24 hours of the reaction time. Additionally, Togni and co-workers[29] reported two palladium precatalysts namely, [(PCP)Pd(MeCN)](PF$_6$)$_2$ and [(3,5-Me-PCP)Pd(MeCN)](PF$_6$)$_2$ {PCP = [1,3-*bis*{(*R*)-1-[(*S*)-2-{[3,5-bis(trifluoromethyl)phenyl]phosphanyl}ferrocenyl]ethyl}imidazol-2-ylidene]} for the asymmetric hydroamination reaction of aliphatic amines also for the methacrylonitrile substrate by using 5 mol% of precatalysts loading at –80 °C to 20 °C in 24 hours to 3 days of the reaction time. Thus, quite significantly, the nickel (**1b** and **2b**) and the palladium (**1c** and **2c**) complexes represents the first examples of the use of well-defined 1,2,4-triazole derived N-heterocyclic carbene based precatalysts for the hydroamination reaction of a variety of secondary amines namely morpholine,

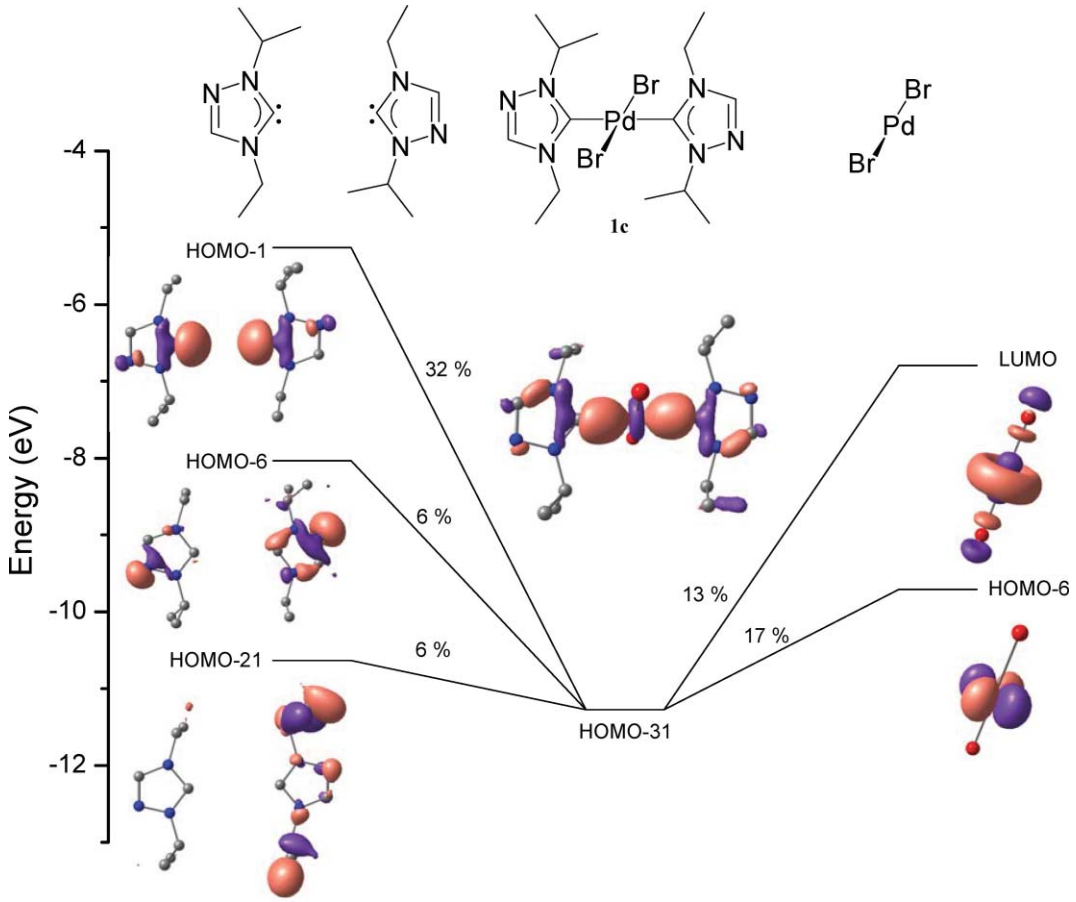


Fig. 5 Simplified orbital interaction diagram showing the major contributions of the NHC-palladium bond in **1c**.

piperidine, pyrrolidine and diethylamine with activated olefins like, acrylonitrile, methyl acrylate, ethyl acrylate and *t*-butyl acrylate at 5 mol% of the precatalyst loading at room temperature in 1 hour of the reaction time.

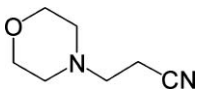
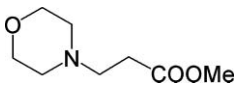
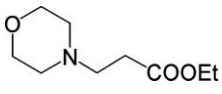
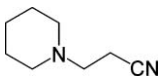
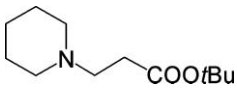
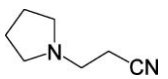
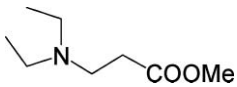
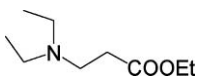
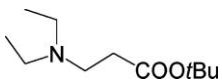
Of the several mechanisms proposed for the hydroamination of activated olefins, the two common ones are, (*i*) one involving N–H activation of amines and (*ii*) the other proceeding by the activation of olefins.[1b,30] Between these two mechanisms, the amine activation mechanism is less favored as the oxidative addition of N–H bond to a metal center is relatively rare owing to very low metal M–N (amido) bond energy, particularly for the late-transition metals *viz*. Ni and Pd, and hence, the other mechanism involving the olefin activation has been proposed for the hydroamination reaction by the nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes.

Specifically, the hydroamination reaction is proposed to proceed by the activation of olefin, in which step the olefin coordinates to the active species **A** yielding the olefin coordinated intermediate **B** (Scheme 2). Quite significantly, the evidence for the formation of the olefin adduct for a representative precatalyst **1c** (m/z = 586) was experimentally obtained from a mass spectrometric experiment, whose positive-ion LCMS–ESI mass spectrum showed the presence of the corresponding olefin adduct species (m/z = 586) when treated with acrylonitrile in $CHCl_3$ and the observed spectrum was in total concurrence with the simulated isotopic distribution pattern (See Fig. 6 and Supporting Information Fig. S9†). In this regard it is worth noting that the mild ionization technique likes electrospray ionization (ESI) has become an important tool in detecting the reaction intermediates in various catalytic processes.[31] Subsequent attack by a secondary amine at the less substituted olefinic-end of **B** results in the formation of a metal bound 2-aminoalkyl intermediate **C** *via* an anti-Markovnikov addition, as also corroborated by the ^{1}H NMR characterization of the isolated products. The last step involves the elimination of the hydroaminated product by protonolysis of the metal bound 2-aminoalkyl intermediate **C** in presence of an olefin alongside regenerating the olefin coordinated intermediate **B**.

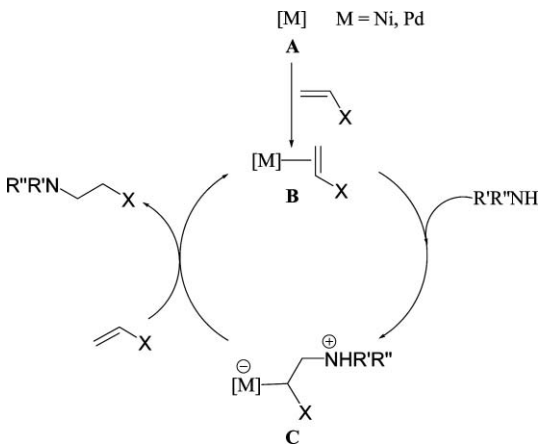
Conclusions

In summary, a series of nickel (**1b** and **2b**) and palladium (**1c** and **2c**) complexes supported over 1,2,4-triazole based N-heterocyclic carbene ligands that are moderately active for hydroamination reaction of secondary amines with activated olefins under ambient conditions have been designed. The nickel (**1b** and **2b**) complexes exhibited superior activity compared to the palladium (**1c** and **2c**) complexes due to more electron deficient nickel center, as observed from the density functional theory studies, in **1b** and **2b** than the palladium center in the **1c** and **2c** complexes. Lastly, the computational study further indicated that the 1,2,4-triazole based N-heterocyclic carbenes are good σ-donating ligands that form

Table 1 Selected results of hydroamination reaction with aliphatic amines catalyzed by **1b**, **2b**, **1c** and **2c**[a]

				Ni		Pd	
entry	reagent	reagent	product	Yield[b] **1b**	Yield[b] **2b**	Yield[b] **1c**	Yield[b] **2c**
1				70	55	46	24
2				39	39	25	27
3				60	47	25	19
4				83	77	78	72
5				89	>99	79	70
6				78	69	76	71
7				56	39	13	17
8				42	45	20	18
9				25	28	14	15

[a] Reaction conditions: 0.50 mmol of aliphatic amines, 1.00 mmol of activated olefin, 5 mol% of catalyst **1b** or **1c** or **2b** or **2c**, 10 mol% AgOTf and 5 mL of dry CH_3CN at room temperature under inert conditions (1 hour). [b] The yields (%) were determined by GC using diethylene glycol di-*n*-butyl ether as an internal standard.



Scheme 2

strong bonds with the metals very much like its related imidazole based counterpart.

Experimental section

General procedures

All manipulations were carried out using standard Schlenk techniques. Solvents were purified and degassed by standard procedures. 1-(*i*-propyl)-1,2,4-triazole was synthesized according to literature procedures.[32] ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on 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 on a Perkin Elmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were done on a Micromass Q-Tof spectrometer. GC spectra were obtained on a PerkinElmer Clarus 600 equipped with a FID. GC-MS spectra were obtained on a PerkinElmer Clarus 600 T equipped with EI source. Elemental Analysis was carried out on Thermo Quest FLASH 1112 SERIES (CHNS) Elemental Analyzer. ESI–MS experiments were performed with a Varian ProStar 500-LCMS instrument, with

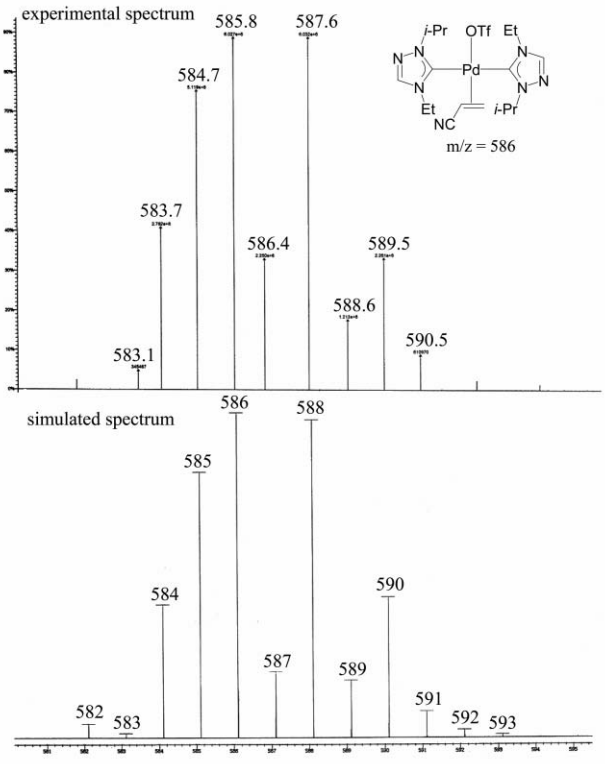


Fig. 6 Overlay of experimental and simulated LCMS–ESI mass spectrum in $CHCl_3$ showing isotopic distribution of olefin adduct species of **1c**.

upper mass limit of m/z 2000, through direct infusion *via* a syringe pump. Standard experimental conditions in the LCMS was at the given capillary voltage 80 V, needle voltage 5000 V, syringe pressure 10 psi, temperature 320 °C, flow rate 10 μL min^{-1}, RF loading 80%, nebulizing gas (helium) pressure 50 psi.

Synthesis of 1-(*i*-propyl)-4-(ethyl)-1,2,4-triazolium bromide (1a)

A mixture of 1-(*i*-propyl)-1,2,4-triazole (2.82 g, 25.4 mmol) and ethyl bromide (*ca.* 20 mL) was refluxed for 14 hours. The reaction mixture was cooled to room temperature, washed in hot hexane (*ca.* 2 × 20 mL) and dried under vacuum to obtain the product **1a** as an off white solid (3.02 g, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 11.5 (s, 1H, N-C(5)*H*-N), 9.61 (s, 1H, N-C(3)*H*-N), 5.01 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 4.70 (q, 2H, $^3J_{HH}$ = 7 Hz, C*H*$_2$CH$_3$), 1.73 (t, 3H, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*$_3$), 1.68 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 144.1 (N-*C*(5)H-N), 140.9 (N-*C*(3)H-N), 56.1 (*C*H$(CH_3)_2$), 43.8 (*C*H$_2$CH$_3$), 21.6 (CH(*C*H$_3)_2$), 15.4 (CH$_2$*C*H$_3$). IR Data (KBr pellet cm^{-1}): 2985(s), 1636(m), 1574(s), 1518(w), 1466(m), 1444(s), 1393(w), 1236(w), 1181(s), 1154(s), 993(m), 888(w), 643(m). HRMS (ES): m/z 140.1186 $[NHC+H]^+$, Calculated 140.1188.

Synthesis of *trans*-[1-(*i*-propyl)-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$NiBr$_2$ (1b)

A mixture of 1-(*i*-propyl)-4-(ethyl)-1,2,4-triazolium bromide (**1a**) (0.405 g, 1.84 mmol), $NiCl_2$ (0.119 g, 0.920 mmol) and Et_3N (0.557 g, 5.52 mmol) in dry acetonitrile (*ca.* 30 mL) was refluxed for 6 hours. The reaction mixture was filtered, the filtrate was collected and was dried under vacuum to give the product as a pink colored solid. The product was further purified by column chromatography on a silica gel column by eluting with neat $CHCl_3$ to obtain the product **1b** as a pink colored solid (0.219 g, 48%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.82 (7.81) (s, 2H, N-C(3)*H*-N), 6.41 (6.39) (sept, 2H, $^3J_{HH}$ = 8 Hz, C*H*$(CH_3)_2$), 4.94 (4.92) (q, 4H, $^3J_{HH}$ = 8 Hz, C*H*$_2$CH$_3$), 1.91 (1.89) (t, 6H, $^3J_{HH}$ = 8 Hz, CH$_2$C*H*$_3$), 1.73 (1.71) (d, 12H, $^3J_{HH}$ = 8 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 171.5 (171.5$_{overlap}$) (N-*C*(5)-N), 141.5 (141.5$_{overlap}$) (N-*C*(3)H-N), 55.0 (54.9) (*C*H$(CH_3)_2$), 43.7 (43.6) (*C*H$_2$CH$_3$), 22.2 (22.2$_{overlap}$) (CH(*C*H$_3)_2$), 15.9 (15.9$_{overlap}$) (CH$_2$*C*H$_3$). IR Data (KBr pellet cm^{-1}): 3120(m), 3052(w), 2975(s), 2936(m), 1702(w), 1539(m), 1444(s), 1368(m), 1272(m), 1205(m), 1119(w), 983(m), 855(m), 721(w), 665(w). Anal. Calcd. for $C_{14}H_{26}N_6Br_2Ni$: C, 33.84; H, 5.27; N, 16.91 Found: C, 34.23; H, 5.52; N, 17.32%.

Synthesis of *trans*-[1-(*i*-propyl)-4-(ethyl)-1,2,4-triazol-5-ylidene]$_2$PdBr$_2$ (1c)

A mixture of 1-(*i*-propyl)-4-(ethyl)-1,2,4-triazolium bromide (**1a**) (0.576 g, 2.62 mmol), $PdCl_2$ (0.232 g, 1.31 mmol) and Et_3N (0.794 g, 7.86 mmol) in acetonitrile (*ca.* 30 mL) was refluxed for 8 hours. The reaction mixture was filtered and dried under vacuum to obtain the product as a yellow colored solid. The product was further purified by column chromatography on a silica gel column by eluting with neat $CHCl_3$ to obtain the product **1c** as a yellow colored solid (0.392 g, 55%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.94 (7.93) (s, 2H, N-C(3)*H*-N), 5.58 (5.58$_{overlap}$) (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 4.55 (4.54) (q, 4H, $^3J_{HH}$ = 8 Hz, C*H*$_2$CH$_3$), 1.73 (1.72) (t, 6H, $^3J_{HH}$ = 8 Hz, CH$_2$C*H*$_3$), 1.64 (1.62) (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 170.5 (170.4) (N-*C*(5)-N), 141.6 (141.6$_{overlap}$) (N-*C*(3)H-N), 55.2 (55.1) (*C*H$(CH_3)_2$), 43.9 (43.8) (*C*H$_2$CH$_3$), 22.3 (22.2) (CH(*C*H$_3)_2$), 16.0 (15.9) (CH$_2$*C*H$_3$). IR Data (KBr pellet cm^{-1}): 3118(m), 2975(s), 1539(m), 1445(s), 1371(m), 1272(m), 1207(m), 1121(w), 988(m), 858(m), 720(m), 667(w). Anal. Calcd. for $C_{14}H_{26}N_6Br_2Pd$: C, 30.87; H, 4.81; N, 15.43 Found: C, 31.08; H, 5.27; N, 14.71%.

Synthesis of 1-(*i*-propyl)-4-(allyl)-1,2,4-triazolium bromide (2a)

A mixture of 1-(*i*-propyl)-1,2,4-triazole (1.65 g, 14.8 mmol) and allyl bromide (8.95 g, 74.0 mmol) was refluxed for 12 hours. The reaction mixture was cooled to room temperature, washed in hot hexane (*ca.* 2 × 10 mL) and dried under vacuum to obtain the product **2a** as a brownish solid (2.69 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 11.5 (s, 1H, N-C(5)*H*-N), 8.79 (s, 1H, N-C(3)*H*-N), 6.22-6.12 (m, 1H, CH$_2$-C*H*=CH$_2$), 5.65 (d, 1H, $^3J_{HH}$ = 17 Hz, CH$_2$-CH=C*H*$_2$), 5.53 (d, 1H, $^3J_{HH}$ = 10 Hz, CH$_2$-CH=C*H*$_2$), 5.30 (d, 2H, $^3J_{HH}$ = 7 Hz, C*H*$_2$-CH=CH$_2$), 5.01 (sept, 1H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 1.69 (d, 6H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 143.6 (N-*C*(5)H-N), 140.6 (N-*C*(3)H-N), 129.0 (CH$_2$-*C*H=CH$_2$), 123.0 (CH$_2$-CH=*C*H$_2$), 55.8 (*C*H$_2$), 49.9 (*C*H$(CH_3)_2$), 21.2 (CH(*C*H$_3)_2$). IR Data (KBr pellet cm^{-1}): 3113(w), 2985(w), 1646(m), 1571(s), 1518(w), 1457(w), 1425(w), 1375(w), 1340(w), 1232(m), 1180(m), 1152(m), 992(s), 950(m), 766(m), 628(m). HRMS (ES): m/z 152.1182 $[NHC+H]^+$, Calculated 152.1188.

Synthesis of *trans*-[1-(*i*-propyl)-4-(allyl)-1,2,4-triazol-5-ylidene]$_2$NiBr$_2$ (2b)

A mixture of 1-(*i*-propyl)-4-(allyl)-1,2,4-triazolium bromide (**2a**) (1.33 g, 5.72 mmol), $NiCl_2$ (0.372 g, 2.86 mmol) and Et_3N (0.866 g, 8.58 mmol) in dry acetonitrile (*ca.* 30 mL) was refluxed for 4 hours after which it was filtered and the filtrate was dried under reduced pressure to obtain a pink residue. The residue was purified by column chromatography on a silica gel column by eluting with neat $CHCl_3$ to obtain the product **2b** as a pink colored solid (0.728 g, 49%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.80 (7.79) (s, 2H, N-C(3)*H*-N), 6.45-6.34 (6.45-6.34$_{overlap}$) (m, 4H, CH_2=C*H*-CH_2 and C*H*$_2$=CH-CH_2), 5.60-5.48 (5.60-5.48$_{overlap}$) (m, 8H, CH_2=CH-CH_2 and C*H*$(CH_3)_2$), 1.73 (1.69) (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 171.9 (171.9$_{overlap}$) (N-*C*(5)-N), 141.8 (141.7) (N-*C*(3)H-N), 132.1 (132.0) (CH_2-*C*H=CH_2), 120.9 (120.8) (CH_2-CH=*C*H$_2$), 55.1 (55.0) (*C*H$_2$), 51.3 (51.3$_{overlap}$) (*C*H$(CH_3)_2$), 22.3 (22.2) (CH(*C*H$_3)_2$). IR Data (KBr pellet cm^{-1}): 3111(m), 2980(m), 1538(m), 1443(s), 1368(w), 1255(m), 1185(w), 984(m), 930(m), 858(w), 785(m), 664(w). Anal. Calcd. for $C_{16}H_{26}N_6Br_2Ni$: C, 36.89; H, 5.03; N, 16.13. Found: C, 37.33; H, 4.63; N, 16.27%.

Synthesis of *trans*-[1-(*i*-propyl)-4-(allyl)-1,2,4-triazol-5-ylidene]$_2$PdBr$_2$ (2c)

A mixture of 1-(*i*-propyl)-4-(allyl)-1,2,4-triazolium bromide (**2a**) (0.639 g, 2.75 mmol), $PdCl_2$ (0.243 g, 1.38 mmol) and Et_3N (0.417 g, 4.12 mmol) in acetonitrile (*ca.* 30 mL) was refluxed for 10 hours. The reaction mixture was filtered and solvent was removed under vacuum to obtain the product as a yellow colored solid. The product was further purified by column chromatography on a silica gel column by eluting with neat $CHCl_3$ to obtain the product **2c** as a yellow colored solid (0.368 g, 47%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.92 (7.91) (s, 2H, N-C(3)*H*-N), 6.30-6.19 (6.27-6.17$_{overlap}$) (m, 2H, CH_2=C*H*-CH_2), 5.58 (5.57) (sept, 2H, $^3J_{HH}$ = 7 Hz, C*H*$(CH_3)_2$), 5.51-5.40 (5.51-5.40$_{overlap}$) (m, 4H, C*H*$_2$=CH-CH_2), 5.14-5.10 (5.14-5.10$_{overlap}$) (m, 4H, CH_2=CH-C*H*$_2$), 1.64 (1.60) (d, 12H, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C): δ 170.7 (170.7$_{overlap}$) (N-*C*(5)-N), 141.9 (141.8) (N-*C*(3)H-N), 131.9 (131.9$_{overlap}$) (CH_2-*C*H=CH_2), 120.7 (120.7$_{overlap}$) (CH_2-CH=*C*H$_2$), 55.2 (55.1) (*C*H$_2$), 51.4 (51.4$_{overlap}$) (*C*H$(CH_3)_2$), 22.3 (22.2) (CH(*C*H$_3)_2$). IR Data (KBr pellet cm^{-1}): 3112(m), 2979(m), 1538(m), 1444(s), 1369(m), 1253(m), 1226(w), 1188(w), 1134(w), 985(m), 930(m), 858(w), 784(m), 665(m). HRMS (ES): m/z 487.0445 [(NHC)PdBr]$^+$, Calculated 487.0437. Anal. Calcd. for $C_{16}H_{26}N_6Br_2Pd$: C, 33.79; H, 4.61; N, 14.78 Found: C, 32.86; H, 4.62; N, 14.31%.

Computational methods

The density functional theory calculations were performed on the following nickel(II) and palladium(II) $(NHC)_2MBr_2$ (M = Ni, Pd) type species, **1b**, **2b**, **1c** and **2c** using GAUSSIAN 03[33] suite of quantum chemical programs. The Becke three parameter exchange functional in conjunction with Lee-Yang-Parr correlation functional (B3LYP) has been employed in this study.[34,35] Stuttgart-Dresden effective core potential (ECP), representing 19 core electrons, along with valence basis set, SDD is used for palladium[36] and LANL2DZ basis set for nickel.[37] All other atoms are treated with 6-31G(d) basis set.[38] All stationary points are characterized as minima by evaluating Hessian indices on the respective potential energy surfaces. Tight SCF convergence (10^{-8} a.u.) was used for all calculations. Natural bond orbital (NBO) analysis[39] was performed using the NBO 3.1 program implemented in the GAUSSIAN 03 package.

Inspection of the metal-ligand donor-acceptor interactions was carried out using the charge decomposition analysis (CDA).[40] CDA is a valuable tool in analyzing the interactions between molecular fragments on a quantitative basis, with an emphasis on the electron donation.[41] The orbital contributions in the geometry optimized nickel(II) and palladium(II) $(NHC)_2MBr_2$ (M = Ni, Pd) type species, **1b**, **2b**, **1c** and **2c** can be divided into three parts:

(i) σ-donation from the [NHC→MBr_2], M = Ni, Pd fragment

(ii) π-back donation from [NHC←MBr_2], M = Ni, Pd fragment and

(iii) repulsive polarization (r)

The CDA calculations are performed using the program *AOMix*,[42] using the B3LYP/LANL2DZ, 6-31G(d) wave function for **1b** and **2b** and B3LYP/SDD, 6-31G(d) wave function for **1c** and **2c**. 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, the charge decomposition analysis (CDA) was performed using the *AOMix-CDA*.[43]

General procedure for the hydroamination reaction

In a typical run, a Schlenk was charged with a mixture of complexes **1b** or **2b** or **1c** or **2c** (5 mol%, 0.025 mmol), AgOTf (10 mol%, 0.050 mmol) and dry acetonitrile (*ca.* 5 mL) and to this was added the mixture of aliphatic secondary amines, activated olefin and diethyleneglycol-di-*n*-butyl ether (internal standard) in a molar ratio of 1:2:1 (Table 1). The reaction mixture was stirred at room temperature for 1 hour under inert conditions, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di-*n*-butyl ether as an internal standard.

General procedure of control experiments for the hydroamination reaction

In a typical run, a Schlenk was charged with a mixture of $NiBr_2$ (5 mol%)/AgOTf (10 mol%) or $NiCl_2$ (5 mol%)/AgOTf (10 mol%) or $PdBr_2$(5 mol%)/AgOTf (10 mol%) or $PdCl_2$ (5 mol%)/AgOTf (10 mol%) or AgOTf (10 mol%) and dry acetonitrile (*ca.* 5 mL) and to this was added the mixture of aliphatic secondary amines, activated olefin and diethyleneglycol-di-*n*-butyl ether (internal standard) in a molar ratio of 1:2:1 (See Supporting Information Table S14). The reaction mixture was stirred at room temperature for 1 hour under inert conditions, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di-*n*-butyl ether as an internal standard.

General procedure of blank experiments

In a typical run, a Schlenk was charged with a mixture of aliphatic secondary amines, activated olefin and diethyleneglycol-di-*n*-butyl ether (internal standard) in a molar ratio of 1:2:1 in dry acetonitrile (*ca.* 5 mL) (See Supporting Information Table S14†). The reaction

Table 2 X-ray crystallographic data for **1b**, **2b**, **1c** and **2c**

compound	**1b**	**2b**	**1c**	**2c**
lattice	Triclinic	Monoclinic	Monoclinic	Monoclinic
formula	$C_{14}H_{26}Br_2N_6Ni$	$C_{16}H_{26}Br_2N_6Ni$	$C_{14}H_{26}Br_2N_6Pd$	$C_{16}H_{26}Br_2N_6Pd$
formula weight	496.90	520.92	544.63	568.65
space group	*P-1*	$P2_1/n$	$P2_1/m$	$P2_1/n$
a/Å	11.1745(4)	11.5509(13)	11.101(2)	13.9545(15)
b/Å	11.4189(4)	16.5181(16)	16.730(3)	16.9015(18)
c/Å	13.8592(5)	22.475(2)	11.513(2)	18.118(2)
α/°	102.131(3)	90.00	90.00	90.00
β/°	109.498(3)	104.068(11)	104.63(3)	90.197(9)
γ/°	105.581(3)	90.00	90.00	90.00
V/Å^3	1515.71(9)	4159.5(7)	2068.9(7)	4273.2(8)
Z	2	8	4	8
temperature (K)	150(2)	150(2)	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd.), g cm^{-3}	1.633	1.664	1.748	1.768
μ(Mo Kα), mm^{-1}	4.921	4.787	4.767	4.620
θ max, deg.	25.00	25.00	25.00	25.00
no. of data	5282	7296	6886	7516
no. of parameters	322	469	252	459
R(int)	0.0175	0.1909	0.0256	0.0590
R_1	0.0245	0.0642	0.0354	0.0589
wR_2	0.0617	0.1646	0.0793	0.1517
GOF	1.022	0.939	0.902	1.028

mixture was stirred at room temperature for 1 hour under inert conditions, after which it was filtered and the product was analyzed by gas chromatography using diethyleneglycol-di-*n*-butyl ether as an internal standard.

Mercury-poisoning experiment

A Schlenk was charged with a mixture of complex **1c** (5 mol%, 0.025 mmol), AgOTf (10 mol%, 0.050 mmol), excess Hg(0) (0.628 g, 125 equiv with respect to the catalyst loading) and dry acetonitrile (*ca.* 5 mL) and to this was added the mixture of morpholine, acrylonitrile and diethyleneglycol-di-*n*-butyl ether (internal standard) in a molar ratio of 1:2:1. The reaction mixture was stirred at room temperature for 1 hour under inert conditions, after which it was filtered and the gas chromatography analysis showed 43% of the product formation with respect to diethyleneglycol-di-*n*-butyl ether as an internal standard. Note that the exact same experiment preformed in absence of Hg-drop yielded 46% of the product (See entry 1 Table 1).

X-ray structure determination†

X-ray diffraction data for compounds **1b, 1c**, **2b** and **2c** were collected on an Oxford Diffraction XCALIBUR-S diffractometer and crystal data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).[44]

ESI-MS experiment for detection of the olefin adduct

The ESI-MS experiment was performed in a positive ion mode to detect the proposed olefin adduct of the hydroamination of activated olefin catalytic cycle by a representative precatalyst **1c**. In a typical experiment, a mixture of the precatalyst **1c** (1 eqv.), AgOTf (2 eqv.) and acrylonitrile (excess) in chloroform was injected in the LCMS-ESI instrument and spectrum was collected in positive ion mode. Specifically, the positive ion mode spectrum of **1c** showed a peak at m/z 586 corresponding to the desired olefin adduct (see Fig. 6 and Supporting Information Fig. S9†).

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