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Organonickel complexes encumbering bis-imidazolylidene carbene ligands: Synthesis, X-ray structure and catalytic insights on Buchwald-Hartwig amination reactions

Muthukumaran Nirmala [a], Gandhi Saranya [a], Periasamy Viswanathamurthi [a, *], Roberta Bertani [b], Paolo Sgarbossa [b], Jan Grzegorz Malecki [c]

[a] Department of Chemistry, Periyar University, Salem 636 011, India
[b] Department of Industrial Engineering, University of Padova, Via Marzolo 9, 35131 Padova, Italy
[c] Department of Crystallography, Silesian University, Szkolna 9, 40-006 Katowice, Poland

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ABSTRACT

New four coordinated homoleptic bis(diimidazolylidene)nickel(II) complexes (**C1 & C2**) were synthesized and characterized by elemental analysis, NMR (^{1}H and ^{13}C) as well as ESI-Mass spectrometry. The molecular structure of the complex **C1** was identified by means of single-crystal X-ray diffraction analysis, which revealed that the complexes possess a distorted square planar geometry with chelating bis(diimidazolylidene) NHC ligands and two non coordinating bromide counter ions in tetradentate C_4 fashion. A survey of their catalytic activity in Buchwald–Hartwig amination has been performed. The newly synthesized complexes also catalyzed the amination of aryl chlorides in the presence of KO^{t}Bu. Various aryl chlorides and amines can react smoothly to give the corresponding aminated products in moderate to high yields. The scope of the reaction encompasses electronically varied aryl chlorides and nitrogen-containing heteroaryl chlorides, including pyridine and quinoline derivatives. Both secondary and primary amines are well tolerated under the optimal reaction conditions.

1. Introduction

Aryl amines are very important compounds in organic synthesis because of their potential applications in chemistry, pharmaceuticals, materials sciences and polymers and thus are very important intermediates in the chemical industry [1]. Transition metal catalyzed C–N bond formation has become a prevailing and reliable method for the synthesis of a variety of aromatic amines under mild and convenient conditions [2]. Besides the abundant traditional methods for the synthesis of such compounds [3], the C–N cross-coupling reactions catalyzed by palladium have become one of the most powerful methods due to their high efficiency of diverse substrates under mild conditions [4]. Compared to palladium, much less research has been devoted to the first-row counterpart nickel. Nevertheless, nickel has proven to be a cost-effective and viable alternative for most of the achievable transformations using palladium [5]. Nickel's time in catalysis, however, has returned with a reprisal. Driven by moribund natural reserves of precious metals and their consequent tremendous price increases, the development of catalytic reactions based on economical earth abundant materials has become a key strategic issue, as highlighted by a recent report from the European Commission [6]. More importantly, nickel presents a number of characteristics that makes it much more than just “ersatz palladium” [7]. For instance, it is more nucleophilic than palladium and thus favors the oxidative addition of electrophiles less common than aryl halides, such as phenol derivatives [8] and aryl fluorides [9]. Many Ni based systems have been developed for C–C and C–N bond formation and other coupling reactions [10]. Among the organic electrophiles involved, aryl chlorides seem to be the most desirable ones due to their lower cost, easy availability and higher stability compared to their iodide and bromide counterparts in spite of their lower reactivity [11]. To achieve efficient coupling of aryl chlorides, kinds of tertiary phosphine ligands, which are usually air and thermal-sensitive, have been synthesized to date [12]. On the other hand, during the past years, *N*-heterocyclic carbenes (NHCs) have been in the focus of academia and industry in many fields of chemistry [9]. Rivalling

* Corresponding author.
E-mail address: viswanathamurthi72@gmail.com (P. Viswanathamurthi).

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more reputable phosphine ligands, these carbon-based donors have become ubiquitous in organometallic chemistry and, building on pioneer work by Herrmann in the late 90s, transformed homogeneous transition metal catalysis [13,14]. NHC's behave like typical strong σ-donor ligands with non-negligible π-acceptor abilities in comparison to alkyl phosphines, although enhancing their plead as ancillary ligands and a wide range of donor properties can be accessed within the broader ligand class and also they show similar abilities to stabilize the various oxidation states and coordinative unsaturated intermediates that appear in catalytic reactions [15]. The steric uniqueness of NHC ligands further distinguish them from their phosphine counterparts; the combination of shorter metal–ligand bonds and flanking substituents that are directed towards the bound metal, permit NHC ligands to encroach deep into the metal coordination sphere [16]. In addition, NHCs exhibit superior qualities regarding ligand dissociation and degradative cleavage [17]. Both properties lead to higher complex stability. Underpinning these hallmarks, the ability to tune the electronic and steric environment of the metal coordination sphere using NHC ligands have shown unprecedented catalytic activity under homogeneous conditions in many important organic reactions [15]. As a result, the olefin metathesis, carbon-carbon and carbon-heteroatom bond forming reactions have benefited greatly from the development of NHCs complexes of ruthenium [18] and palladium [19], respectively. However, the development of a general, robust and operationally simple catalytic system of transition metal catalyze coupling reactions has remained significantly challenging.

In recent years, some of the nickel(II)-based NHC complexes exhibit higher catalytic activity than palladium-based NHC complexes in various coupling reactions have led to more active catalysts and mild reaction conditions [20]. Many groups have expanded Ni-catalyzed C–N cross coupling to wide array of electrophiles to achieve good results [21,27,28]. The first NHC complexes of the type $(Ph_3P)_2Ni(1\text{-nap})Cl$ used in C–N coupling reactions with excellent results were reported in 2007 by Yang [22]. All of these methods have their own merits; however, these methods are associated with certain demerits like instability of catalyst, high catalytic loading and requirement of severe conditions etc. Hence, the development of stable catalytic system with NHC–Ni(II) catalysts those can be performed under mild conditions has received much attention.

Even though, many Ni based systems have been developed for C–N bond formation reactions, the use of well-defined [Ni(NHC)] precatalysts has been explored to a lesser extent despite the interesting activity of such systems [14c]. Supplementing the earlier commentaries and our previous success using dianionic bis(aryloxy–NHC) as a supporting ligand in Ni-based catalysis [23], we sought to investigate the use of a *cis*-chelating bidentate *N*-heterocyclic carbenes ligated Ni(II)-complexes as precatalyst in C–N bond forming reactions.

2. Results and discussion

2.1. Synthetic strategy

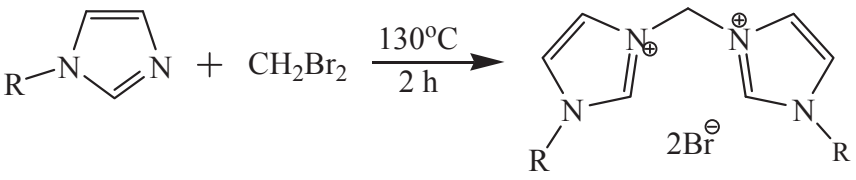
The diimidazolium NHC ligands (**L1 & L2**) were selected as potential ligand platforms of different wingtip substituents on imidazole ring, and were synthesized according to known methods [23,24] by the reaction of corresponding substituted imidazole, and an excess of dibromomethane. The reaction mixture was stirred at 130 °C for 2 h then cooled to room temperature to give a white precipitate of corresponding diimidazolium NHC ligands (**L1 & L2**) in good yield (~83%) after washing with acetone (Scheme 1). The new ligands **L1 & L2** obtained are highly air and moisture stable. They are not soluble in acetone, hexane, diethyl ether, but dissolves readily in $CHCl_3$, CH_2Cl_2, EtOH, MeOH, DMF and DMSO.

Nickel complexes (**C1 & C2**) with corresponding NHC ligands (**L1 & L2**) were typically prepared from the mixture of diimidazolium NHC ligands (**L1 & L2**) and $Ni(OAc)_2.4H_2O$ in ethanol in the presence of Et_4NBr and Et_3N at 80 °C in air as depicted in Scheme 2 that afforded the homoleptic $[(diNHC)_2Ni]^{2+}$ complexes with chelating diNHC and two non coordinating bromide counterions as the only isolated products in quantitative yield (~82%). The complexes were insoluble in chloroform, acetone, hexane, and diethyl ether, but dissolve readily in EtOH, MeOH, DMF and DMSO, which may be due to higher degree of organization in the solid state. They are also thermally stable and will not melt over 300 °C. The compounds were characterized by ^1H, ^{13}C NMR, ESI-MS and single-crystal X-ray diffraction. Their purity was confirmed by elemental analysis. The analytical data (C, H, N) of the compounds diimidazolium NHC ligands (**L1 & L2**) and their nickel complexes (**C1 & C2**) are in good agreement with the proposed molecular formulae.

2.2. Spectroscopic description

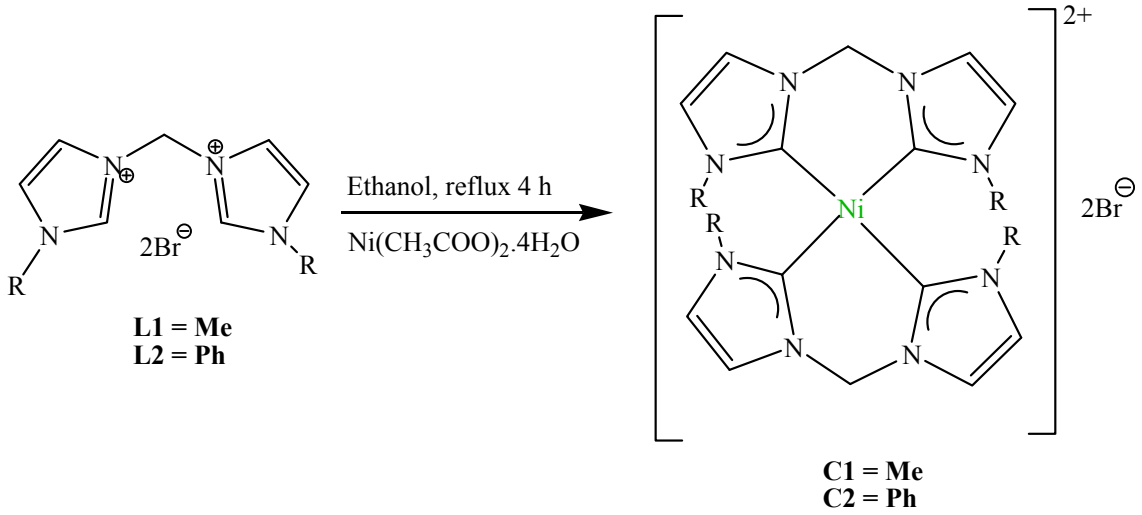
IR spectra of free ligands were compared with those of the corresponding complexes in order to confirm the coordination of ligand to nickel metal. The ligand showed a strong band in the region 1347–1395 cm^{-1} due to $\nu_{N\text{-}C\text{-}N}$. This band has been shifted to higher frequency 1423–1456 cm^{-1} in the metal complex, indicating the coordination of ligand to metal through carbene carbon. A strong vibration was observed at 1593–1577 cm^{-1} in the spectra of complexes corresponding to C=C stretching. In addition, vibrations corresponding to the presence of C–C also appeared in the expected region.

The ^1H NMR spectra of the ligands (**L1 & L2**) and complexes (**C1 & C2**) showed the signals in the expected region (Fig. S1-S3, ESI†). As expected the NHC hydrogen atom of the azolium salts gives rise to a singlet at 9.70–9.54 ppm in the ligands. The generation of free carbene and subsequent formation of the [Ni–NHC] complexes were unambiguously confirmed by the absence of the ^1H NMR resonances of imidazolium (NCHN) protons. In addition, a singlet



L1 = Me
L2 = Ph

Scheme 1. Synthesis of diimidazolium NHC ligands.



Scheme 2. General synthesis of [Ni–NHC] complexes (**C1** & **C2**).

appeared around 3.91–3.16 ppm for compounds **L1** and **C1** corresponding to terminal $-CH_3$ group protons. Furthermore, the spectra of all the complexes showed a series of signals for aromatic protons in the region 7.35–7.17 ppm. In addition, a clear singlet appeared around 6.15–7.12 ppm for all the compounds (**L1, L2, C1 & C2**) corresponding to the methylene bridge protons [25].

The ^{13}C NMR spectra show the expected signals in the appropriate regions (Fig. S4-S7, ESI†). The spectra of ligands show the carbenic carbon signal in the region 138.0–137.85 ppm. For the uncoordinated ligand the imi–C appeared in the region 124.25–122.12 ppm. The disappearance of the ^1H NMR signals of NC*H*C, and the downfield ^{13}C NMR signals of NCN carbene carbon at *ca.* 173.46–172.01 ppm in the ^1H and ^{13}C NMR spectra of [Ni–NHC] complexes are indicative of the Ni-$C_{carbene}$ bond formation [26]. It is worth of noting that only one singlet was observed for the carbene carbon in ^{13}C NMR spectrum of this complex. The signals observed in the region 136.29–123.26 ppm in the spectra of ligands and the complexes are assigned to aromatic carbons. For the **C1** complex, the signal appeared at 36.99 ppm is attributed to the methyl carbon attached to the ring nitrogen.

The ESI-Mass analysis of diimidazolium NHC ligands (**L1 & L2**) showed that the base peaks at *m/z* 177.1 and 301.1, respectively, were originated by the $[M\text{-}2Br\text{-}H]^+$ ionic species. As for the complexes (**C1 & C2)** abundant peaks at 491.0 and 775.1, respectively, corresponding to the ionic species containing the ligands coordinated to Ni, were observed (Fig. S8-S11, ESI†). The isotopic patterns were in agreement with the simulated ones.

2.3. X-ray crystal structure description of complex C1

Even though the analytical and spectral data gave some idea about the molecular formulae of the complexes, they do not indicate the exact coordination of bis(carbene) units in them. To gain additional insight into the coordination chemistry and the structural parameters of the complexes, single crystals of one of the complexes (**C1**) were grown by slow evaporation of the concentrated ethanolic solution of complex and characterized by X-ray diffraction analysis. The crystal data and structure refinement parameters for complex **1** are collected in Table 1 and the selected bond lengths and bond angels are depicted in Table 2. The ORTEP view and packing arrangement of atoms in unit cell are given in Figs. 1 and 2. The structure is solved in the space group *P*-1 with a water molecule, presumably from the wet crystallization solvent, incorporated in the asymmetry unit. As depicted in the figure, the ligand **L1** is coordinated in a bidentate fashion and showed a distorted square planar geometry around the metal centre. The two C–Ni–C planes defined by the two chelating diNHC ligands are exactly coplanar with an average Ni–C bond length of 1.902(4) Å and a C–Ni–C bite angle of C(1)–Ni(1)–C(7) = 94.02(17) & C(1)–Ni(1)–C(7) = 85.98(17) for the fine and six membered chelate rings. The C–C and C–N bond distances within the imidazoline-2-ylidene based ring systems and the Ni–C bond distances are

Table 1
Crystal data and structure refinement parameters for complex **C1**.

	C1
CCDC number	1469201
Empirical formula	$C_{18}\ H_{28}Br_2N_8NiO_2$
Formula weight	607.01
T (K)	295
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a (Å)	7.7788(8)
b (Å)	8.7807(10)
c (Å)	10.0922(12)
α (°)	115.087(11)
β (°)	94.562(9)
γ(°)	102.13(1)
Volume (Å^3)	599.19 (13)
Z	1
Density (calculated) Mg m^{-3}	1.682
Absorption coefficient mm^{-1}	4.175
F(000)	306
Scan range for data collection (deg)	3.86 to 26.80
Index ranges	$-9 <= h <= 10$ $-10 <= k <= 11$ $-13 <= l <= 13$
Reflections collected/unique, R_{int}	5359/2791,0.0531
Completeness to $theta_{max}$	0.996
Data/restraints/parameters	2791/0/152
Goodness-of-fit on F^2	1.018
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0531$ $wR_2 = 0.1095$
R indices (all data)	$R_1 = 0.0905$ $wR_2 = 0.1306$

[a] Structures were refined on F_o^2: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2
Selected geometrical parameters for complex **C1**.

Interatomic distances (Å)	
Ni(1)–C(1)	1.901(4)
Ni(1)–C(1)	1.901(4)
Ni(1)–C(7)	1.903(4)
Ni(1)–C(7)	1.903(4)
Bond angles(°)	
C(1)–Ni(1)–C(1)	180.0
C(1)–Ni(1)–C(7)	94.02(17)
C(1)–Ni(1)–C(7)	85.98(17)
C(1)–Ni(1)–C(7)	94.02(17)
C(1)–Ni(1)–C(7)	85.98(17)
C(7)–Ni(1)–C(7)	180.0
N(1)–C(1)–Ni(1)	134.2(3)
N(2)–C(1)–Ni(1)	121.8(3)
N(3)–C(7)–Ni(1)	121.8(3)
N(4)–C(7)–Ni(1)	134.2(3)

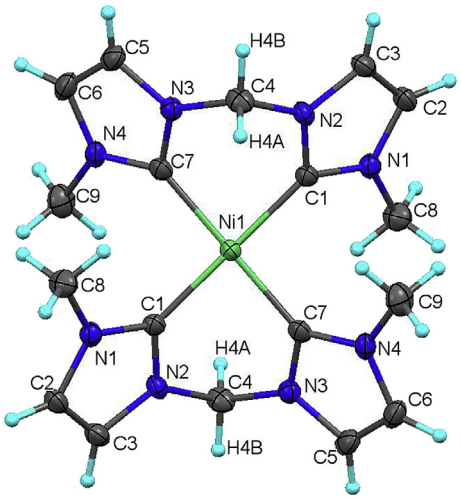


Fig. 1. ORTEP representation of the X-ray crystal structure of [Ni–NHC] complex **C1**. The two non coordinating bromide ions and water molecules have been omitted for clarity. Thermal ellipsoids are shown at 30% probability.

consistent with both contributions from σ and π-donation to the metal centre and π-stabilization of the carbene onto the adjacent nitrogens. These parameters indicate that the Ni atom takes distorted square planar coordination geometry.

3. Catalytic studies

3.1. Carbon-nitrogen bond formation

The newly synthesized Ni–NHC complexes were evaluated as precatalysts for C–N bond formation reaction.

3.1.1. Evaluation of conditions for the Ni–NHC complex (C1) catalyzed amination reaction

The optimization process was lead toward the determination of the best reaction conditions to analyze the substrate scope. Initial studies were performed using chlorobenzene with aniline as building blocks, and it was found that satisfactory yields were obtained with 1 mol % of C_1 in the presence of KO^{t}Bu as a base and dioxane as solvent and the outcome was depicted in Table 3. The choice of bases was also crucial for the reaction. Of the various base explored: NaO^{t}Bu, KOH, NaOH, K_2CO_3, Na_2CO_3, $KHCO_3$ and KO^{t}Bu, the catalyst was active only in the presence of KO^{t}Bu in 97% yield (Table 3, **entry 7**). In the presence of other bases such as K_2CO_3 (Table 3, **entry 4**) and $KHCO_3$ (Table 3, **entry 6**), almost no desired product can be detected. To this end, we noticed that a strong base was required to promote the reaction. In the presence of KO^{t}Bu, some common solvents were tested and the moderate yield was obtained in toluene (Table 3, **entry 12**). Out of different solvents tested during the course of optimization, the solvent such as DMF, CH_3CN, DMSO and *i*PrOH were found to be ineffective (Table 3, **entry 9, 10, 11, 13**). Solvents such as THF and Et_2O could bring about only little conversion. However, dioxane was found as the best solvent for the C – N coupling reaction resulting in 97% isolated yield at the temperature of 90 °C (Table 3, **entry 7**). Moreover, in the absence of catalyst and base the C–N coupling reaction was not observed (Table 3, **entry 15, 16, 17[d]**). Since the temperature is also crucial for the success of a coupling process, we have carried out the

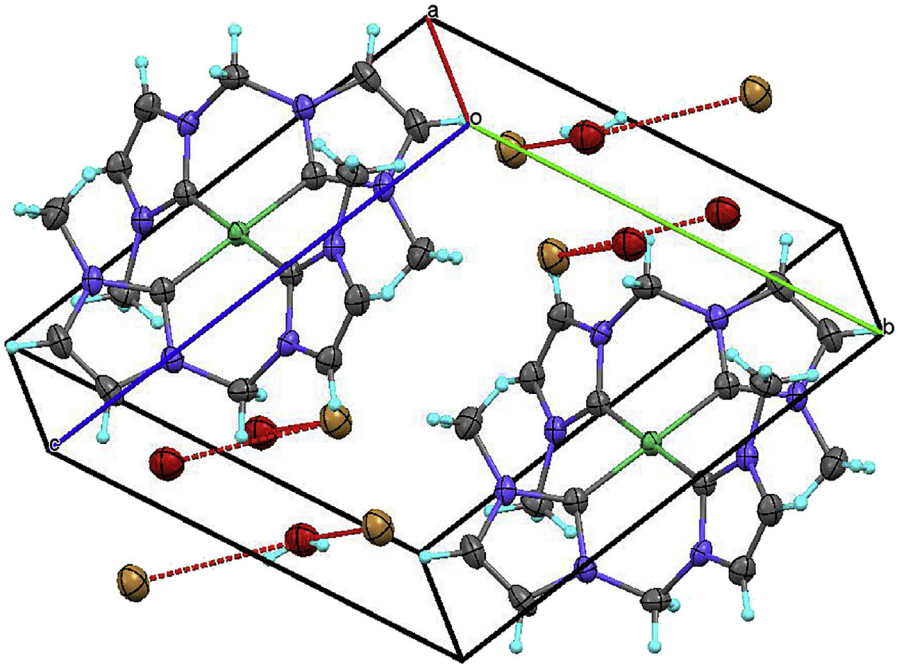
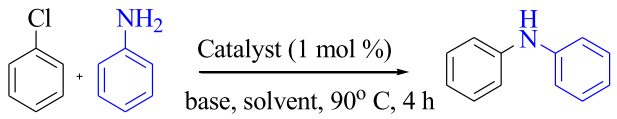


Fig. 2. Packing diagram of complex **C1**.

Table 3
Evaluation of conditions for model C – N coupling reaction using complex **C1**[a].



Entry	Base	Solvent	Temp (°C)	Yield (%)[b]
1	NaO^{t}Bu	Dioxane	90 °C	21
2	KOH	Dioxane	90 °C	17
3	NaOH	Dioxane	90 °C	36
4	K_2CO_3	Dioxane	90 °C	n. r
5	Na_2CO_3	Dioxane	90 °C	52
6	$KHCO_3$	Dioxane	90 °C	n. r
7	**KO^{t}Bu**	**Dioxane**	**90°C**	**97**
8	KO^{t}Bu	THF	65 °C	42
9	KO^{t}Bu	DMF	153 °C	n. r
10	KO^{t}Bu	CH_3CN	85 °C	n. r
11	KO^{t}Bu	DMSO	190 °C	n. r
12	KO^{t}Bu	Toluene	110 °C	76
13	KO^{t}Bu	*i*PrOH	83 °C	n. r
14	KO^{t}Bu	Et_2O	35 °C	43
15	KO^{t}Bu[c]	Dioxane	90 °C	n. r
16	KO^{t}Bu[c]	DMF	90 °C	n. r
17[d]	–	Dioxane	90 °C	n. r
18	KO^{t}Bu	DMF	90 °C	n. r
19	KO^{t}Bu	DMSO	90 °C	n. r
20	KO^{t}Bu	Toluene	90 °C	62

[a] All reactions were carried out using chlorobenzene (1 mmol), aniline (1.3 mmol), base (1.3 mmol), catalyst (1 mol %), solvent (2 mL) at 90 °C for 4 h.
[b] Isolated yield after column chromatography.
[c] No catalyst was used; n.r: no reaction.
[d] The reaction was carried out using chlorobenzene (1 mmol), aniline (1.3 mmol), without base, catalyst (1 mol %), solvent (2 ml) at 90 °C for 12 h.

reaction in DMF, DMSO, and toluene at 90 °C to nullify the advantage of high temperature and to compare the conversion yield with other solvents without the influence of temperature. No conversion took place in DMF and DMSO at 90 °C (Table 3, **entry 18, 19**) due to lack of minimum thermal energy that should be supplied to cross the energy barrier. In the case of toluene as the solvent (Table 3, **entry 20**), the conversion yield diminished to 62% at 90 °C.

3.1.2. Catalyst screening

We continued the C–N bond formation reaction optimization process after finding the need for a base to activate the catalyst (**C1**) in the amination reaction. The following step was done to study the influence of the substituents and catalyst loading on the catalytic activity of Ni–NHC complexes (**C1 & C2**). The results are shown in Fig. 3. Catalyst screening in the model reaction revealed that all the Ni–NHC complexes triggered the reaction. The results also indicate that the higher catalyst loadings lead to higher yields. Conversely, a decrease in the catalyst (mol %) led to diminish the yield of the product considerably. Further, the Ni–NHC catalyst with methyl as a wingtip substituent exhibit slightly higher activity than those containing phenyl as a wingtip substituent. This behavior indicates that the influence of steric effects is only slightly significant (even no significance in some conversions) in the catalytic activity.

The optimization process was led toward the determination of the best reaction conditions to evaluate the substrate scope. The newly synthesized Ni–NHC complexes were effectively catalyzed C–N bond formation reaction between aryl chlorides and a range of amines with 1.3 mmol of KO*t*Bu as a base and 1 mol % of catalyst in presence of dioxane at 90 °C for 4 h.

3.1.3. Amination of aryl chlorides with aniline derivatives

Under the optimal conditions identified, to expand the scope of

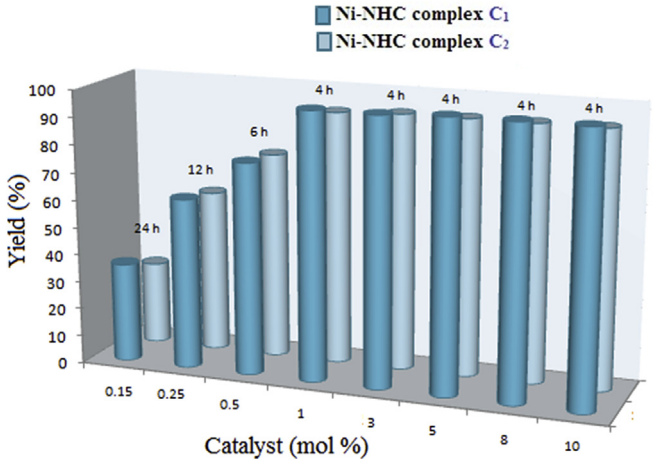


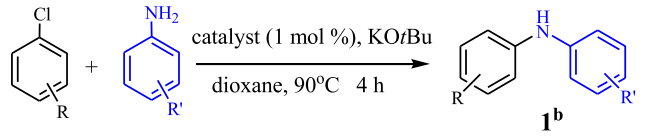
Fig. 3. Effect of catalyst (mol %) with respect to time on amination of aryl chlorides.

the present homogeneous catalyst system, the amination reaction has been extended to the copious aryl chlorides with anilines consisting of diverse functional groups. Table 4 summarizes the catalytic activity of **C1 & C2** under the dioxane/KO^{t}Bu recipe for this coupling reaction. Various anilines having both electron rich, poor and sterically hindered groups underwent the reaction smoothly and gave rise to good to excellent yields (Table 4, **entry 1–16**). The sterically-encumbered substrates seem to be a challenge in the previously reported methods, especially at low catalyst loadings. However, to our delight the anilines bearing sterically-hindered substituents such as 2-methyl aniline (Table 4, **entry 5**), 2,4-dimethylaniline (Table 4, **entry 8**), 2,4,6-trimethyl aniline (Table 4, **entry 9**), 2,6-dimethylaniline (Table 4, **entry 10**), 2,6-diisopropylaniline (Table 4, **entry 11**) are reacted well with corresponding aryl chlorides to furnish excellent yield of coupling products under optimized conditions. The sterically hindered aryl chlorides such as 2-methylphenylchloride (Table 4, **entry 5**), 3-chlorophenyldimethylamine (Table 4, **entry 13**), 2,6-dimethylphenylchloride (Table 4, **entry 12**) are all compatible for coupling reactions. The reaction of 2-chloroquinoline was carried out with *p*-toluidine to obtain *N*-*p*-tolylquinolin-2-amine (Table 4, **entry 14**) in 89–94% yield. In addition, unsubstituted aryl chlorides afforded the products in higher yields (Table 4, **entry 1, 3, 4**). The reaction of *N*-methylaniline with 4-chloropyridylchloride could also be coupled, revealing the formation of solely *N*-methyl-*N*-phenylpyridin-4-amine (Table 4, **entry 15**) in 92–96% isolated yield after 4 h of reaction time. Also, by changing the substitution on the nitrogen atom from methyl to simple ethyl group provided the diarylamine in a modest yield 58–62% (Table 4, **entry 16**).

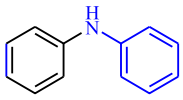
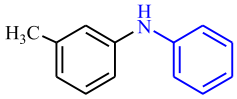
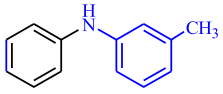
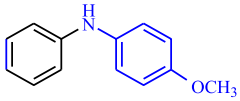
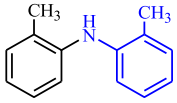
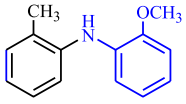
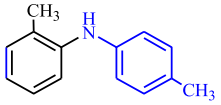
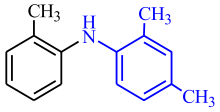
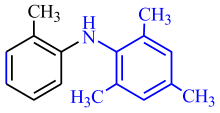
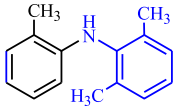
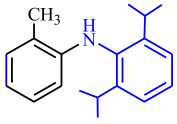
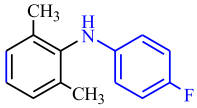
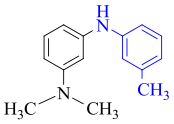
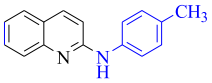
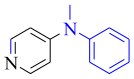
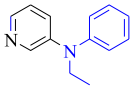
3.1.4. Amination of aryl chlorides with secondary amines

To expand the scope of the present homogeneous catalyst system, the C–N coupling reaction has been extended to the copious aryl chlorides consisting of diverse functional groups with secondary amines. Table 5 summarizes the catalytic activity of Ni–NHC catalysts **C1 & C2** under the dioxane/KO^{t}Bu recipe for this coupling reaction. All the reactions proceed smoothly to give the corresponding aminated products in good to high yield (Table 5, **entry 1–13**). Electron poor aryl chlorides generally gave the amination product in good to excellent yields (Table 5, **entry 5–10, 12**). Surprisingly, while pyrolidine, morpholine, piperidine, and piperazine were effectively coupled with chlorobenzene to give rise a moderate to excellent product yield (Table 5, **entry 1, 2, 4, 11**).

Table 4
[Ni–NHC] catalyzed coupling of aryl chlorides with aniline derivatives[a].



1[b]

Entry	Products	TOF[c]		Yield (%)[b]	
		C1	C2	C1	C2
1		24	24	**97**	**92**
2		23	23	**92**	**93**
3		25	24	**98**	**97**
4		25	24	**99**	**96**
5		25	24	**98**	**94**
6		24	23	**96**	**92**
7		23	24	**93**	**94**
8		24	23	**98**	**93**
9		24	25	**97**	**98**
10		24	23	**96**	**92**
11		22	21	**89**	**84**
12		20	19	**80**	**76**
13		25	24	**98**	**96**
14		22	24	**89**	**94**
15		24	23	**96**	**92**
16		15	16	**58**	**62**

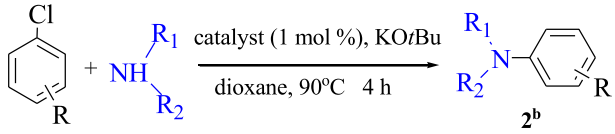
[a] All reactions carried out using aryl chlorides (1 mmol), anilines (1.3 mmol), KO^{t}Bu (1.3 mmol), catalyst (1 mol %), and dioxane (2 mL) at 90 °C for 4 h.
[b] Isolated yield after column chromatography.
[c] TOF = TON/times.

Moreover, the reaction of 2-chloropyridine was carried out with morpholine to obtain 4-(pyridin-2-yl)morpholine (Table 5, **entry 13**) in 87–91% yield.

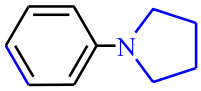
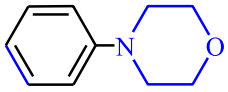
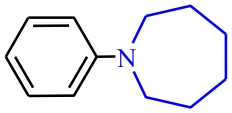
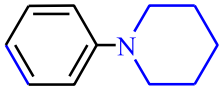
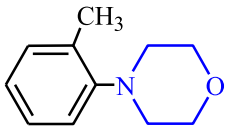
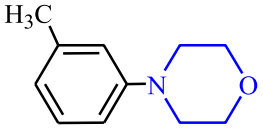
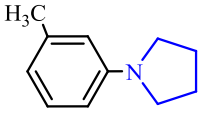
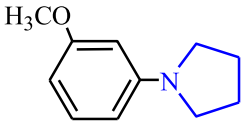
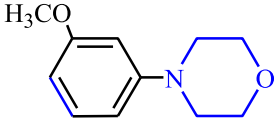
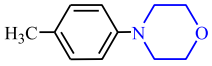
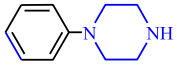
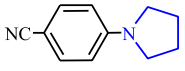
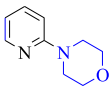
3.1.5. Amination of aryl chlorides with primary amines

In order to ensure the generality of this finding, a variety of primary aliphatic amines underwent this amination process in good to excellent isolated yields using the above optimized protocol. The results of this study are summarized in Table 6. The range of electron rich (Table 6, **entry 2, 4**) and electron neutral (Table 6, **entry 3**) aryl chlorides coupled with cyclopentyl, cyclohexylamines in high yields. To our pleasure, the sterically hindered aryl chlorides such as 2,6-dimethyl phenylchloride and 2,6-diisopropylphenylchloride were coupled with primary aliphatic amines provided the desired products in excellent yield (Table 6, **entry 5, 6, 7, 8**). Reaction of sterically hindered chloroarene such as (3-chloro-phenyldimethylamine) successfully furnished respective coupled products with cyclohexylamine in 91–93% yield (Table 6, **entry 9**). As nitrogen-containing heterocycles possessing amino substituents often are of particular pharmaceutical interest. Inspired by the above interesting result, we have extended the scope of the present Ni–NHC catalytic system to the amination of heteroaryl chlorides. However, the C – N coupling reactions between nitrogen containing heteroaryl electrophiles and primary amines are exigent, presumably because of the coordinating properties of both pyridines and primary amines. Such reactions proceed smoothly to give the corresponding aminated products in good yields using the previously developed conditions. An array of heteroaryl chlorides that underwent this amination reaction sheltered a range of 2-pyridyl (Table 6, **entry 11, 12, 16, 17**), 3-pyridyl (Table 6, **entry 13, 14, 15, 18**) chlorides containing electron donating groups (OMe) and electron withdrawing groups (CN & CF_3). In general, these reactions afforded the corresponding heteroaryl alkylamines in good to excellent yields of 67–99%. Even the sterically hindered dibenzylamine reacted with 3-chloropyridine to give the coupled product in 62–67% yield (Table 6, **entry 19**). The reaction of 2-chloropyridine was carried out with octylamine to obtain *N*-octyl-3-aminopyridine (Table 6, **entry 10**) in 96–94% yield. Interestingly (4-methoxyphenyl)methanamine reacted well with 1-chloro-3-methoxybenzene and 1-chloro-3-methylbenzene

Table 5
[Ni–NHC] catalyzed coupling of aryl chlorides with secondary amines[a].



2[b]

Entry	Products	TOF[c]		Yield (%)[b]	
		C1	C2	C1	C2
1		24	25	**96**	**98**
2		24	25	**97**	**99**
3		19	20	**74**	**79**
4		17	18	**67**	**72**
5		19	20	**74**	**79**
6		23	24	**93**	**96**
7		25	25	**98**	**99**
8		16	17	**65**	**69**
9		25	25	**98**	**99**
10		17	17	**67**	**69**
11		21	22	**84**	**88**
12		20	21	**80**	**83**
13		22	23	**87**	**91**

[a] All reactions carried out using aryl chlorides (1 mmol), secondary amines (1.3 mmol), KO^{t}Bu (1.3 mmol), catalyst (1 mol %), and dioxane (2 mL) at 90 °C for 4 h.
[b] Isolated yield after column chromatography.
[c] TOF = TON/time.

to furnish excellent yield of coupling products in 88–97% yields under optimized conditions (Table 6, **entry 20, 21**).

In addition to the limitations on the scope of the coupling of aryl halides with amines, the mechanism of the coupling of aryl halides with amines catalyzed by nickel complexes has not been studied. Many papers cite the potential of Ni(I) intermediates [29], either as part of a one-electron redox event or as part of a mechanism involving Ni(I) and Ni(III) intermediates. In contrast, the mechanism for the palladium-catalyzed amination of aryl electrophiles has been studied in detail, including the kinetic behavior of the catalytic reaction and stoichiometric reactions of isolated intermediates [30–33]. Such studies have not been conducted on nickel-catalyzed couplings to form C–N bonds, but are particularly important to determine how to create catalysts of nickel that are as long-lived as those of palladium and that react with similarly broad scope. The mechanism of the Buchwald-Hartwig aminations of aryl chloride with primary alkyl amines, using a Ni precatalyst, has been recently studied, in detail, by Hartwig and co-workers [34]. Based on previous literature reports [35], it appears to us that both steric and electronic effect combines to mediate the coupling process. Initially, the electron donor properties of the carbene facilitate the activation of aryl chlorides. The present protocol provides an extremely convenient, highly efficient and less expensive alternative for the synthesis of aryl amines. Efforts are currently underway in our laboratory to elucidate the mechanistic details of these C–N bond forming reactions.

4. Conclusions

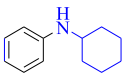
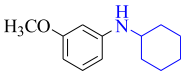
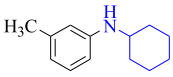
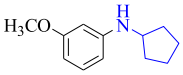
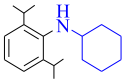
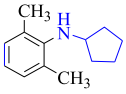
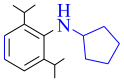
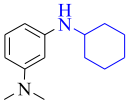
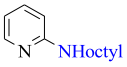
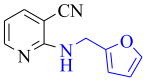
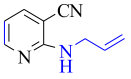
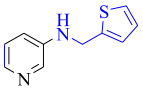
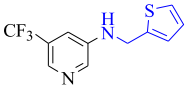
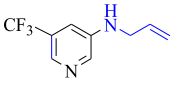
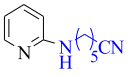
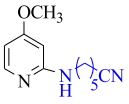
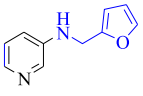
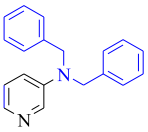
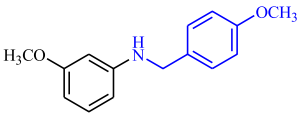
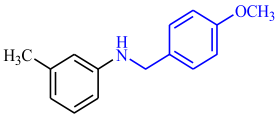
In summary, we have developed a practical protocol for the preparation of two new nickel complexes bearing diimidazolium NHC ligands with different wingtip substituents (**C1** (R = Me) and **C2** (R = Ph)) in the imidazole ring. These complexes were fully characterized by NMR, and single crystal X-ray diffraction studies. A survey of their catalytic properties in Buchwald–Hartwig amination was presented. The reaction has a broad scope and could be applied to a variety of electron poor aryl chlorides as well as nitrogen-containing heteroaryl chlorides, including pyridine and quinoline derivatives. Electron rich and sterically hindered aryl chlorides could be coupled with various amines. Good to excellent yields were obtained with the vast majority of substrates. The use of the dioxane solvent system proved to be the most beneficial. The nickel diimidazolium NHC complexes are usually decomposes in the presence of trace amount of water. In our case, the exceptional stability of our NHC complexes may be due to steric factor [36]. Efforts are currently underway in our research group to expand the scope of this method to a library of different functionalized substrates, to elucidate mechanistic principles underlying these C–N bond formation reactions with even greater activity and to investigate the outstanding stability of our NHC complexes.

5. Experimental section

5.1. General considerations

Unless otherwise noted, all experiments with metal complex and the NHC ligand were carried out without taking precautions to exclude air and moisture. All catalytic reactions were carried out under an atmosphere of dry Ar or N_2 using standard Schlenk techniques. All solvents were reagent grade or better. All reagents were purchased from Aldrich chemical Co. and used as received without further purification. Thin-layer chromatography (TLC) was performed on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications

Table 6
[Ni–NHC] catalyzed coupling of aryl chlorides with primary amines.[a].

Entry	Products	TOF[c]		Yield (%)[b]	
		C1	C2	C1	C2
1		23	24	**90**	**94**
2		21	21	**85**	**82**
3		22	23	**89**	**92**
4		23	22	**90**	**86**
5		21	22	**82**	**87**
6		20	21	**79**	**82**
7		22	22	**86**	**89**
8		21	22	**84**	**89**
9		23	23	**91**	**93**
10		24	24	**94**	**96**
11		22	23	**89**	**93**
12		19	20	**75**	**79**
13		23	24	**92**	**96**
14		25	24	**99**	**95**
15		23	24	**90**	**94**
16		21	22	**84**	**88**
17		17	18	**67**	**72**
18		24	25	**96**	**99**
19		16	17	**62**	**67**
20		24	24	**97**	**94**
21		23	22	**92**	**88**

[a] All reactions carried out using aryl chlorides (1 mmol), primary amines (1.3 mmol), KO^{t}Bu (1.3 mmol), catalyst (1 mol %), and dioxane (2 mL) at 90 °C for 4 h.
[b] Isolated yield after column chromatography.
[c] TOF = TON/time.

were performed by Merck silica gel 60 (0.063–0.200 mm). Microanalyses of carbon, hydrogen and nitrogen were carried out using a Vario EL III elemental analyzer. Infrared spectra of the ligands and the metal complexes were recorded as KBr discs in the range of 4000–400 cm^{-1} using a Nicolet Avatar model FT-IR spectrophotometer. ^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were taken in DMSO-d_6 or $CDCl_3$ at room temperature with a Bruker AV400 instrument with chemical shifts relative to tetramethylsilane. ESI MS analyses were performed using a Finningan LCQ-Duo ion-trap instrument, operating in positive ion mode (sheath gas flow N2 30 au, source voltage 4.0 kV, capillary voltage 21 V, capillary temperature 200 °C). The He pressure inside the trap was kept constant. The pressure, directly read by an ion gauge (in the absence of the N_2 stream), was 1.33 × 10^{-5} Torr. Sample solutions were prepared by dissolving the compounds (3 mg) in CH_3CN (5 ml) or MeOH (5 mL) immediately before analysis. Melting points were determined in open capillary tubes on a Technico micro heating table and are uncorrected.

5.2. Synthesis of diimidazolium NHC ligands

The diazolium NHC ligands were prepared according to previous literature reports [37,38]. Typically, mixture of dibromomethane (5.0 mL, 1 mmol) and 1-substituted imidazole (2 mmol) was added in a round bottom flask and stirred at 130 °C for 2 h, and then stored at room temperature. The resultant white precipitate were collected and washed with acetone.

5.2.1. Compound ***L1*** (*R* = *Me*)

The synthetic procedure of this compound was the same as that of above representative procedure, using 1-methylimidazole to give a white solid **L1**. Yield: 80%. M.Pt: 123 °C. Anal.Calc.for.$C_9H_{14}N_4Br_2$: C, 31.98; H, 4.17; N, 16.57%. Found: C, 31.66; H, 4.38; N, 16.21%. IR (KBr disks, cm^{-1}); 1570 (C=C), 1553 (N–C–N). ^{1}H NMR (300.13 MHz, DMSO-d_6, δ): 9.54 (s, 2H, NCHN), 8.08 (s, 2H, CH_{imi}), 7.82 (s, 2H, CH_{imi}), 6.76 (s, 2H, NCH_2N), 3.91 (s, 6H, CH_3). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ): 138.0 (NCHN), 124.25 (CH_{imi}), 121.86 (CH_{imi}), 57.76 (NCH_2N), 36.23 (CH_3). ESI-MS (*rel.ab.%*): [M-Br]$^+$, *m/z* 257 (22%), [M-2Br–H]$^+$, *m/z* 177 (100%).

*5.2.2. Compound **L2** (R = Ph)*

The synthetic procedure of this compound was the same as that of above representative procedure, using 1-phenylimidazole to give a white solid **L2**. Yield: 83%. M.Pt: 119 °C. Anal.Calc.for.$C_{19}H_{18}N_4Br_2$: C, 49.38; H, 3.93; N, 12.12%. Found: C, 49.63; H, 3.54; N, 12.22%. IR (KBr disks, cm^{-1}); 1558 (C═C), 1534 (N—C—N), 1437 (C—C). ^1H NMR (300.13 MHz, DMSO-d_6, δ): 10.37 (s, 2H, NCHN), 8.49 (s, 2H, CH_{imi}), 7.88 (s, 2H, CH_{imi}), 7.84–7.68 (m, 10H, ArH), 6.94 (s, 2H, NCH_2N). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ): 137.85 (NCHN); 134.97, 130.84, 130.76 & 123.56 (ArC), 122.46 (CH_{imi}), 122.12 (CH_{imi}), 58.98 (NCH_2N).). ESI-MS (*rel.ab.%*): $[M\text{-}2Br\text{—}H]^+$, *m/z* 301 (100%).

5.3. Synthesis of diimidazolium nickel(II) complexes (C1 & C2)

To an ethanol (20 mL) solution of corresponding diimidazolium salt (1.00 mmol) was added nickel(II) acetate tetrahydrate (44.8 mg, 0.183 mmol), Et_4NBr (165 mg, 0.785 mmol), and Et_3N (3 drops). The mixture was stirred at 80 °C for 4 h. The precipitated green solid of [Ni—NHC] complex was collected and washed with small amount of EtOH (6 ml).

*5.3.1. Compound **C1***

Yield: 83%. M.P.: 289 °C (decomp.). Anal.Calc.for.$C_{18}H_{24}N_8Br_2Ni$: C, 37.60; H, 4.91; N, 19.49%. Found: C, 37.83; H, 4.65; N, 19.81%. IR (KBr disks, cm^{-1}); 1575 (C═C), 1563 (N—C—N). ^1H NMR (300.13 MHz, DMSO-d_6, δ): 7.32 (s, 4H, CH_{imi}), 7.18 (s, 4H, CH_{imi}), 6.15 (s, 4H, NCH_2N), 3.16 (s, 12H, CH_3). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ): 173.46 ($C_{carbene}$), 124.66 (CH_{imi}), 122.27 (CH_{imi}), 51.93 (NCH_2N), 36.99 (CH_3). Single crystals suitable for X-ray determination was grown in ethanolic solution of **C1** at room temperature. ESI-MS (*rel.ab.%*): $[M\text{-}Br\text{-}2H]^+$, *m/z* 491 (45%); $[C_7H_7N_4Ni]^+$, *m/z* 205 (100%).

*5.3.2. Compound **C2***

Yield: 81%. M.pt: 277 °C (decomp.). Anal.Calc.for.$C_{38}H_{32}N_8Br_2Ni$: C, 55.71; H, 3.94; N, 13.68%. Found: C, 55.47; H, 3.69; N, 13.45%. IR (KBr disks, cm^{-1}); 1562 (C═C), 1531 (N—C—N), 1440 (C—C). ^1H NMR (300.13 MHz, DMSO-d_6, δ): 7.38 (s, 4H, CH_{imi}), 7.37 (s, 8H, CH_{imi}), 7.35–7.33 (m, 10H, ArH), 7.26–7.17 (m, 10H, ArH), 7.12 (s, 4H, NCH_2N). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ): 172.01 ($C_{carbene}$), 136.29, 130.55, 130.28, 129.17, 126.56 and 123.26 (ArC), 122.28 (CH_{imi}), 121.98 (CH_{imi}), 52.03 (NCH_2N). ESI-MS (*rel.ab.%*): $[C_{38}H_{39}N_8O_2BrNiK]^+$, *m/z* 815 (25%), $[M\text{-}Br\text{-}2H{+}2H_2O]^+$, *m/z* 775 (50%); $[C_{19}H_{16}N_4Na]^+$, *m/z* 323 (45%), $[C_{19}H_{18}N_4K]^+$, *m/z* 341 (100%).

5.4. Catalysis

5.4.1. General procedure for the Buchwald-Hartwig reaction

Under an N_2 atmosphere, KO^{t}Bu (1.3 mmol), [Ni—NHC] catalyst (1 mol %), dioxane (2 mL), amines (1.3 mmol) and aryl chlorides (1.0 mmol) were successively added into a Schlenk tube. The mixture was stirred vigorously at 90 °C for 4 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: PE/EA = 15:1) to give the pure products. The reported yields are the average of two runs. The catalytic reactions have been given in Tables 3–6. The resulting amines were identified by comparison of the ^1H & ^{13}C NMR data with those previously reported (ESI†).

5.5. X-ray crystallography

Crystal of complex **C1** was mounted on glass fibers used for data collection. Crystal data were collected at 295 K using a Gemini An Ultra Oxford Diffraction automatic diffractometer. Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The absorption corrections were performed by the multi-scan method. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods using the program SHELXS [39]. Refinement and all further calculations were carried out using SHELXL [39]. The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-hydrogen atoms were refined anisotropically using weighted full-matrix least squares on F^2. Atomic scattering factors were incorporated into the computer programs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.12.029.

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