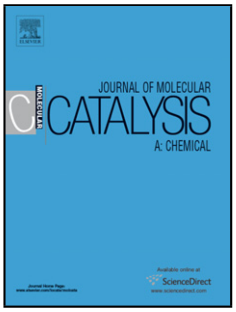

Title: Nickel(II) complex incorporating methylene bridged tetradentate dicarbene ligand as an efficient catalyst towards C-C and C-N bond formation reactions

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Nickel(II) complex incorporating methylene bridged tetradentate dicarbene ligand as an efficient catalyst towards C-C and C-N bond formation reactions

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Abstract

For the evaluation of binding and catalytic nature of N-heterocyclic carbenes (NHCs) and their complexes, a new methylene bridged bis(aryloxy-NHC) ligand has been prepared. A novel air-stable Ni(II) complex bearing the new NHC ligand has been synthesized and characterized by elemental analysis, NMR (^{1}H and ^{13}C) as well as ESI-Mass spectrometry. The molecular structure of the complex was identified by means of single crystal X-ray diffraction analysis which revealed that the Ni(II) complex possesses a square planar geometry with the ligand coordinating with bi-negative tetradentate C_2O_2 fashion and the complex showed efficient catalytic activity towards the Suzuki-Miyaura cross-coupling reaction between aryl halides and arylboronic acids under phosphine free conditions. The new complex 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. Both secondary and primary amines are well tolerated under the optimal reaction conditions.

Key words:

Dianionic bis(aryloxy-NHC) ligand

Ni-NHC complex

X-ray diffraction

Suzuki-Miyaura

C-N coupling reaction

1. Introduction

The first stable N-heterocyclic carbene reported by Arduengo et al [1] triggered the development of stable singlet carbenes from laboratory interests to key compounds for manifold applications, particularly in catalysis [2]. N-heterocyclic carbenes (NHCs) have been embraced as spectator ligands in catalyst design with a remarkable speed [3] in past few decades. Due to the strong metal carbon bond, carbene complexes give robust catalytic systems and so, a number of transition metal complexes of multidentate NHCs containing phosphorous [4], oxygen [5], and nitrogen [6] functionalities have been reported. Such ligands may significantly improve catalyst stability and their potential hemilability provide ease of generation of vacant coordination site and catalytically active species. The first catalytic application of NHCs in transition-metal catalysis was reported by Herrmann et al, who realized the great potential of NHCs as ancillary ligands in palladium mediated cross-coupling reactions [7] and in ruthenium mediated olefin metathesis [8]. Nowadays, NHC-metal complexes have found wide applications in hydrogen transfer reactions [9] and hydrosilylation reactions [10], especially C-C and C-N coupling reactions [11, 12]. Especially, the NHC ligands bearing hemilabile donor functionalities like nitrogen, oxygen or sulfur allow efficient stabilization of the catalytic species, while rapidly opening the free coordination sites for incoming substrates.

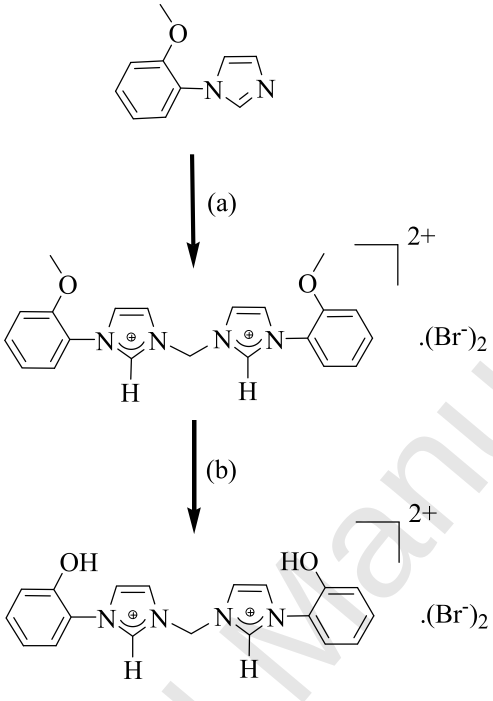
Carbon–carbon bond formation is an essential process within the realm of organic synthesis and of utmost importance for the generation of structural complexity and diversity [13]. Over the 30 years of research history on Suzuki-Miyaura cross-coupling, the palladium based catalysts have been the most frequently investigated one for C-C coupling. To the uninitiated, nickel might look like just the impoverished younger sibling of palladium in the field of transition metal catalysis [14]. After all, the use of nickel-NHC-catalyzed cross-coupling has skyrocketed and is currently experiencing a period of intensified interest [15]. In particular, some of the Ni(II)-based NHC complexes exhibit higher catalytic activity than palladium based NHC complexes [16]. Despite the aforementioned progresses, most of the established procedures required high catalyst loading (usually ≥ 5 mol%) and excess usage of phosphine supporting ligands [16b,17]. These results highlight the importance of performing control experiments while investigating the catalytic C-C coupling activity of any potential nickel catalyst. Unfortunately, such highly active NHC-Ni(II) based catalysts for C-C coupling reactions remain scarce [18-20].

Further, the transition-metal-catalyzed amination of aryl halides has become one of the most powerful methods to construct arylamines [21]. Most studies have focused on palladium and copper complexes as catalysts [22, 23]. However, the development of a general, robust and operationally simple catalytic system of Ni catalyzed C−N cross-coupling reactions has remained significantly challenging [24]. Many groups have expanded Ni-catalyzed C−N cross-coupling to include new electrophiles such as aryl tosylates, carbamates, sulfamates, methyl ethers, phosphates, pivalates, and nitriles [25-27]. In 2007, Yang reported the first use of NHC complexes of the type $(Ph_3P)_2Ni(1\text{-nap})Cl$ used in C-N coupling reactions [28-30]. All of these methods have their own advantages; however they suffer from 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.

As part of our effort to develop a better catalytic system using metal NHC catalyst, here we have reported a new air and moisture stable [31, 32] dianionic bis(aryloxy-NHC) ligand and its Ni(II) complex as a promising catalyst for Suzuki-Miyaura C-C coupling as well as C-N coupling.

2. Results and discussion

2.1 Synthesis of ligand precursors and metal complex: We prepared a ligand precursor 1-(2’-methoxy phenyl) imidazole, with 62 % yield by CuI/K_3PO_4 mediated coupling reaction between 2-iodoanisole and imidazole. The reaction between 1-(2’-methoxy phenyl) imidazole, and an excess of dibromomethane was stirred at 100 ºC for 48 h then cooled to room temperature. The resultant white precipitate was collected, washed with acetone to afforded 1,1’-Di(2-methoxy-phenyl)-3,3’-methylene diimidazolium dibromide as white solid. It was dissolved in 47 % HBr and CH_3COOH (1/1 v/v) and refluxed at 110 ºC for 48 h. The mixture was cooled to room temperature to give a white precipitate of 1,1’-di(2-hydroxy-phenyl)-3,3’-methylene diimidazolium dibromide ligand H_4LBr_2 in good yield (87%) after washing with acetone **(Scheme 1)**. The new ligand H_4LBr_2 obtained is highly air and moisture stable. It is not soluble in acetone, hexane, diethyl ether, but dissolves readily in $CHCl_3$, CH_2Cl_2, EtOH, MeOH, DMF and DMSO.

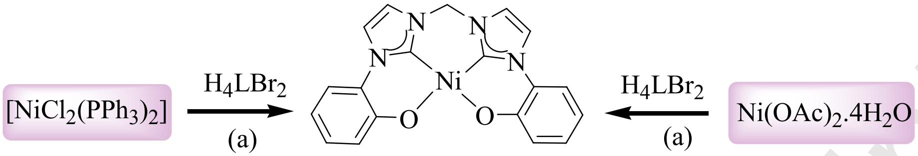


H_4LBr_2

Scheme 1. Synthesis of NHC ligand. Reagents and conditions: (a) CH_2Br_2, 100 °C, 48 h; (b) 47 % HBr, CH_3COOH, 110 °C, 48 h.

Nickel complex (**1**) with NHC ligand were typically prepared from the mixture of dianionic bis(aryloxy-NHC) ligand H_4LBr_2 and $Ni(OAc)_2.4H_2O$ in ethanol was allowed to react in the presence of Et_4NBr and Et_3N at 80 °C in air as depicted in **Scheme 2** that afforded the corresponding nickel complex in quantitative yield (82%) [31,32]. The complex **1** was also obtained by the reaction of $[NiCl_2(PPh_3)_2]$ with H_4LBr_2 in ethanol in the presence of few drops of Et_3N and Et_4NBr (**Scheme 2**). The complex was insoluble in chloroform, acetone, hexane, and diethyl ether, but dissolve readily in DMF and DMSO, which may be due to higher degree of organization in the solid state. The complex was stable not only in the solid phase for months under air but also in DMSO and DMF solution for several months. They are also thermally stable and will not melt over 300 °C. The compounds were fully characterized by ^1H & ^{13}C NMR, mass spectra and elemental analysis. The analytical data (C, H, N) of the compounds 1,1'-Di(2-

methoxy-phenyl)-3,3'-methylene diimidazolium dibromide, H_4LBr_2 and the nickel complex are in good agreement with the proposed molecular formulae.



1

Scheme 2. : Reaction conditions: (a) Et_4NBr, Et_3N, EtOH, 80 °C, 6 h

2.2 Spectroscopic studies

IR spectra of free ligand were compared with new complex in order to confirm the coordination of ligand to nickel metal. The ligand showed a strong band in the region 1545-1562 cm^{-1} due to $\nu_{N\text{-}C\text{-}N}$. This band has been shifted to higher frequency 1561-1573 cm^{-1} in the metal complex, indicating the coordination of ligand to metal through carbene carbon. In the spectra of free ligand, a strong band obtained around 1333 cm^{-1} was assigned to phenolic C □ O stretching, which has been shifted to a higher frequency 1393 cm^{-1} in complex indicating the participation of phenolic oxygen in bonding. This has been further confirmed by the disappearance of the broad $\square_{OH}$ band around 3383 cm^{-1} in complex due to the bonding of phenolic-OH group with nickel metal via deprotonation. The electronic spectrum of complex **1** has been recorded in dichloromethane and it displayed five bands in the region around 250-450 nm. The complex exhibit intense absorption bands at energy below 300 nm which can be attributed to ligand centered π-π* transitions. The absorption band around 350 nm has been assigned to transition involving phenolate-based HOMO and NHC based LUMO with small contribution from metal d-orbitals. The transition can be described to have mainly LLCT character. The band at ~400 nm is likely to involve transition of ligand based orbitals, and the absorption tail beyond 430 nm is attributed to d-d transition.

The ^1H NMR spectra of ligand H_4LBr_2 and its complex **1** show the signals in the expected region (Fig S1 – S2, ESI†). The carbenic proton of the ligand exhibited a signal in the region 10.01 ppm. The imidazole ring backbone signals (H_4LBr_2, 8.07/8.24 ppm; **1**, 7.89/7.94 ppm) appear as singlet due to low coupling constant. Further, the spectra of ligand and the complex showed a series of signals for aromatic protons at 7.21-8.50 ppm. In addition, a clear singlet appeared around 6.37 ppm for compounds H_4LBr_2 and **1** corresponding to the methylene bridge protons [33].

The ^{13}C NMR spectra show the expected signals in the appropriate regions (Fig. S3–S4, ESI†). The spectrum of ligand in DMSO-d_6 shows the carbenic carbon signal in the region 138.02 ppm. For the uncoordinated ligand the imi-C and aryloxy carbon signals appeared in the region 124.99-123.28 and 149.83 ppm respectively. Upon coordination and formation of new nickel(II) complex a downfield shift is observed for the signals of imi-C (around 5 ppm), in addition, the presence of peak in the region 148.76 ppm is assigned to aryloxy carbon respectively. The nickel complex shows its carbenic carbon (Ni-$C_{carbene}$) resonance at *ca.* 152.23 ppm, characteristic of the carbenic carbon bound to nickel [34]. 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 at 133.28-118.2 ppm in the spectra of ligand and complex is assigned to aromatic carbons. The ESI mass spectrum of complex **1** showed a peak at *m/z* 389.09 corresponding to $[M]^+$ (Fig. S6, ESI†).

2.3 Structural studies

Even though the analytical and spectral data gave some idea about the molecular formulae of the complex, they do not indicate the exact coordination of carbene-aryl oxygen units in them. Hence, there is a need to prove this structure by X-ray crystallography. Single crystals suitable for X-ray analysis were obtained from DMSO solution. The crystal data and structure refinement parameters for complex **1** are summarized in Table S1 and is displayed in supporting information (ESI†) and the selected bond length and bond angels are depicted in **Table 1**. The ORTEP view and side view of the complex **1** along with atom numbering scheme and packing arrangement of atoms in unit cell are given in **fig 1-3**. The single crystal X-ray studies revealed that the complex was crystallized in a monoclinic system with space group $P2_{1/n}$. As the coordination plane around Ni(II) ion in crystal adopts a square planar geometry, in which two carbene atoms and two oxygen atoms occupy the basal plane. The nickel-$C_{carbene}$ bond lengths [(1.835 (3), 1.846 (5) Å)] are analogous to those of other Ni(II)-NHC complexes [15d]. The Ni−O (phenolate) and Ni-$C_{carbene}$ bond distances of ~ 1.85 and ~1.84 Å are slightly smaller than those found in [Pt(II)salphen] (1.98 Å/ 2.03 Å) and [Mn(III)salphen] (1.91 Å/ 1.91 Å) complexes, probably due to the less trans-effect of the NHC moieties which induce the strong Ni-O bonds. Quite interestingly the solid-state molecular packing of complex **1** adopts a highly planar structure [31-33]. While, the other previously reported complexes with aryloxide modified biscarbene tetradentate NHC ligands generally showed bent framework due to the non-conjugated C(10) methylene linker between two NHC moieties [31-33]. The stability of complex in air is probably caused by the rigid structure of the tetradentate NHC ligand. These findings indicate the character of the aryl oxygen coordinating to Ni(II) is similar to that of the salen ligand [35]. The chelate bite angle of C(11)−Ni(1)−C(1) (91.51 (11)) is comparable to those of various metal complexes with six membered chelate rings consisting of two imidazolylidene rings and a bridged methylene group [36]. It is larger than the ideal angle and is probably due to the less constraint of the six membered chelate rings. The angles of C(11)−Ni(1)−O(1), C(1)−Ni(1)−O(1), C(11)−Ni(1)−O(2), C(1)−Ni(1)−O(2), O(1)−Ni(1)−O(2) are 175.60(9), 92.33(10), 92.28(9), 171.28(9) and 84.21(8) respectively. These parameters indicate that the Ni atom takes square planar coordination geometry.

Table 1. Selected geometrical parameters for complex **1**

Interatomic distances (Å)	
Ni(1)−C(11)	1.835(3)
Ni(1)−C(1)	1.846(2)
Ni(1)−O(1)	1.8597(18)
Ni(1)-O(2)	1.8651(17)
Bond angles(□)	
C(11)−Ni(1)−C(1)	91.51(11)
C(11)−Ni(1)−O(1)	175.60(9)
C(1)−Ni(1)−O(1)	92.33(10)
C(11)−Ni(1)−O(2)	92.28(9)
C(1)−Ni(1)−O(2)	171.28(9)
O(1)−Ni(1)−O(2)	84.21(8)

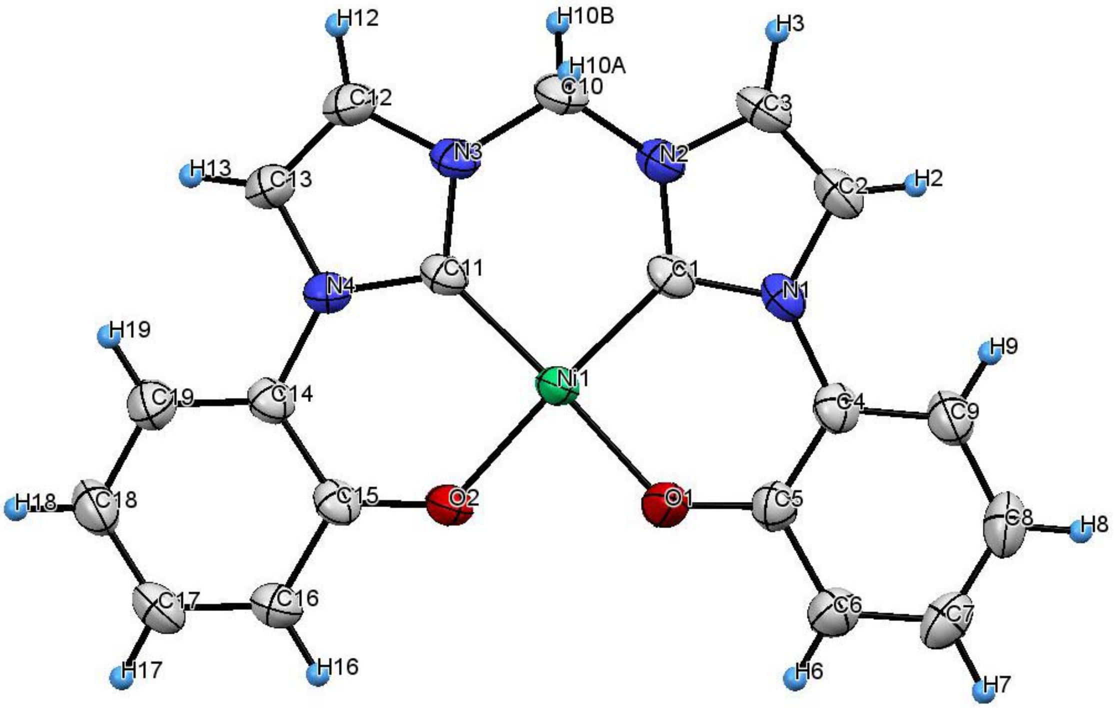


Fig. 1. ORTEP plot of complex **1**. Thermal ellipsoids are drawn at the 50% probability level

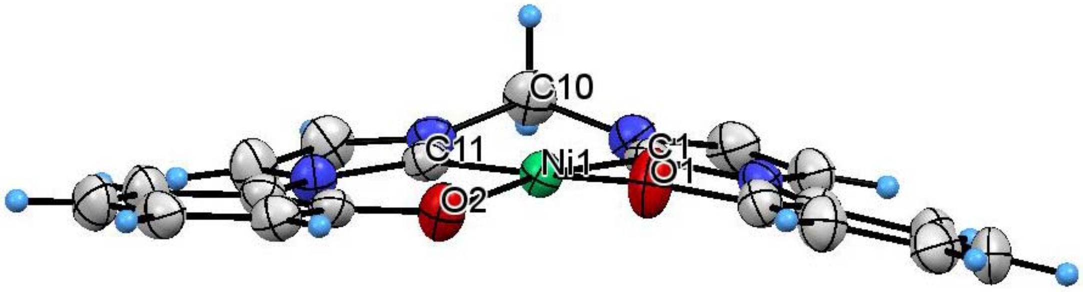


Fig. 2. ORTEP drawing of complex **1** side view (50 % probability)

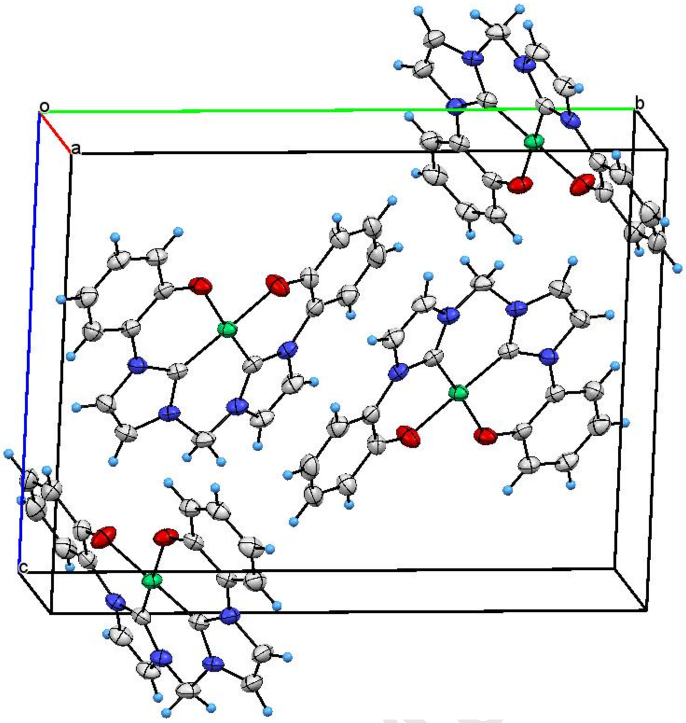


Fig. 3. Packing diagram of complex **1**

Therefore, the present structural variations among the complex reflect the attachment of two carbenic carbons and two aryloxy groups onto one nickel atom. The use of two carbenic carbon donor atoms represents an alternative strategy to efficiently modulate the coordination environment around the center metal, mostly due to the different electric and/or steric influences of the two carbenic groups.

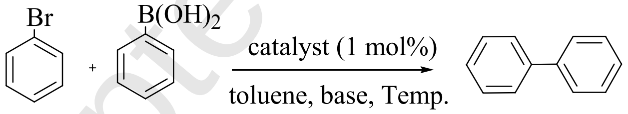
3. Catalysis

3.1 Suzuki-Miyaura cross coupling

Evaluation of conditions for Suzuki-Miyaura cross coupling

Although using aryl halides as cross-coupling partners is the de facto standard, accessing the desired halide coupling partner is not always trivial and can sometimes be extremely challenging. To investigate a promising catalytic system, the screen was performed for a model reaction between bromobenzene and phenylboronic acid. The results are depicted in **Table 2**. All the reactions were run *without* any additive such as PPh_3 as is often the case [37]. The progress of the reaction was monitored by GC. It is a well-known fact that the choice of solvent significantly influences the Suzuki-Miyaura reactions. Thus, to study the effect of solvents in our system, we performed a series of reactions between bromobenzene and phenylboronic acid in the presence of different solvents such as toluene, THF, dioxane, EtOH, acetonitrile and *i*PrOH. Among them **toluene** was the solvent of choice, which resulted in a high yield after 4 h (Table **2**, entry **6**). To study the effect of amount of catalyst, the reactions were carried out at different amount of catalysts ranging from 0.25 – 1 mol %. The yield increased as **42, 79** and **99 %** respectively. An increase in the catalyst mol % did not improve the yield further. Conversely, a decrease in catalyst mol % diminished the yield of the product significantly (**Fig. 4**). Considering the pivotal role of base in promoting the formation of nickel intermediates during the catalytic cycle, different bases including K_2CO_3, NaOAc, Cs_2CO_3 and K_3PO_4 were screened. It was found that K_3PO_4 and Cs_2CO_3 were useful bases in these reactions at 110 °C. Cs_2CO_3 is also an effective base in this reaction as shown in fig. 4, but it is expensive when compared to other bases. Furthermore, the results showed that **1.0 mol %** catalyst in toluene was sufficient to push this reaction and the most suitable reaction temperature was 110 °C.

Table 2. Evaluation of conditions for Suzuki- Miyaura coupling of bromobenzene with phenylboronic acid[a]



Entry	Solvent	$PhB(OH)_2$ (.equiv)	K_3PO_4 (.equiv)	Temp (°C)	Time (h)	Yield (%)[b]
1	Dioxane	1.1	2.2	90°C	2	45
2	Dioxane	1.1	2.2	90°C	4	52
3	*i*PrOH	1.1	2.4	85°C	2	15
4	*i*PrOH	1.3	2.6	85°C	4	29
5	Toluene	1.3	2.6	110°C	2	91
6	**Toluene**	**1.3**	**2.6**	**110°C**	**4**	**>99**
7	Acetonitrile	1.3	2.6	85°C	4	26
8	Acetonitrile	1.3	2.6	85°C	6	42
9	THF	1.3	2.6	70°C	12	46
10	EtOH	1.3	2.6	85°C	12	30

[a] Reaction conditions: bromobenzene (1 mmol), phenylboronic acid (1.1-1.3 mmol), K_3PO_4 (2.2-2.6 mmol), catalyst (1 mol %) and solvent (3 ml).

[b] Conversion determined by GC.

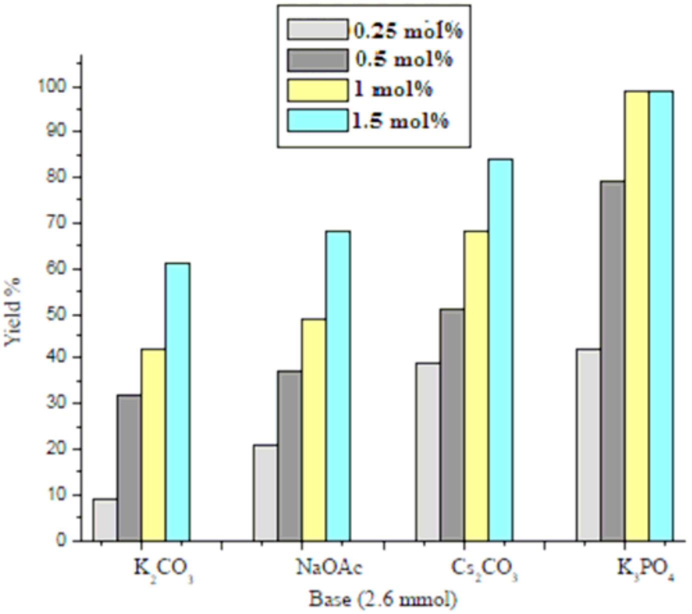
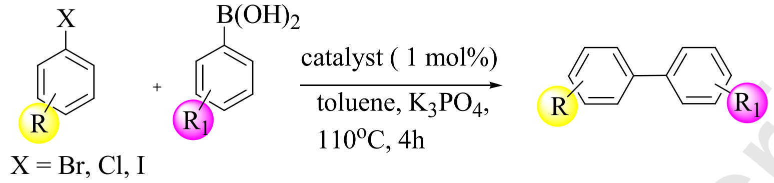


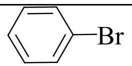
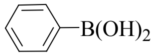
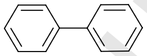
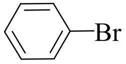
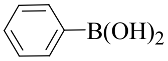
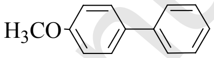
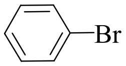
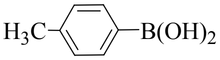
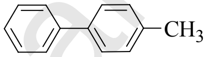
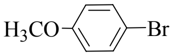
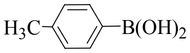
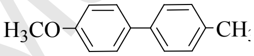
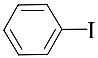
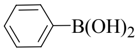
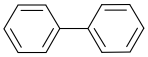
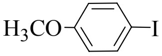
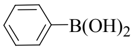
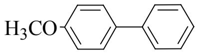
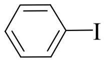
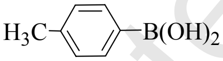
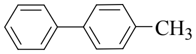
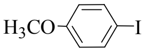
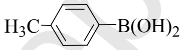
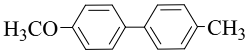
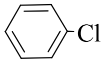
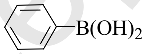
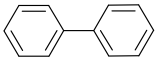
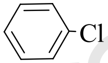
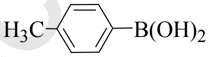
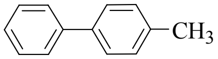
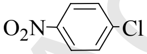
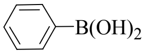
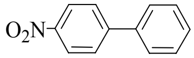
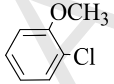
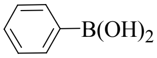
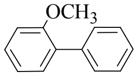
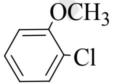
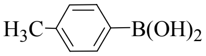
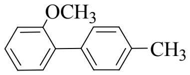
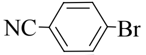
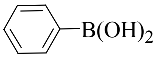
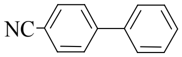
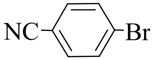
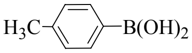
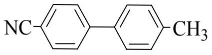
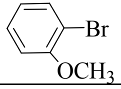
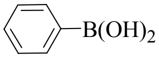
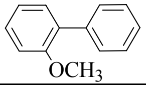
Fig. 4. Effect of catalyst (mol %) and base on Suzuki–Miyaura cross-coupling of bromobenzene with phenylboronic acid

With an optimized catalytic system in hand, a number of structurally diverse aryl halides and arylboronic acids were screened to demonstrate the general applicability and efficacy of this protocol and the results are summarized in **Table 3**. To our delight all reactions took place smoothly to give the corresponding biphenyls in good to high yields (Table **3**, entry **1-16**). The reaction scope of this complex has been examined with a short series of aryl bromides bearing electron-withdrawing and donating substituent undergo coupling reactions with arylboronic acids, effectively affording the desired biaryls in excellent yields **84 - >99%** (Table **3**, entry **1-4, 14-16**). The reaction of aryl iodides proceeded smoothly to produce the desired biphenyl compounds in high yields **90-93 %** (Table **3**, entry **5-8**). While the reaction of 4-nitrobenzene with aryl boronic acid, the complex showed lower activity even when the reaction was performed for 24 h (Table **3**, entry **11**). We have also examined the effectiveness of the current catalytic system in the cross-coupling chemistry of aryl chlorides using 4-chlorobenzene, and 2’-

chloroacetophenone with arylboronic acids. The desired biphenyls were isolated in **81**, **83 and 84, 86 %** yields respectively after 4 h.

Table 3. Complex **1** catalyzed Suzuki-Miyaura coupling of aryl halides and arylboronic acids[a]



Entry	Aryl halide	Aryl boronic acid	Time (h)	product	Yield (%)[b]	TON[c]	TOF[d]
1			4		>99	99	25
2			4		88	88	22
3			4		84	84	21
4			4		95	95	24
5			4		92	92	23
6			4		90	90	23
7			4		93	93	23
8			4		90	90	23
9			4		81	81	20
10			4		83	83	21
11			24		58	58	15
12			4		84	84	21
13			4		86	86	22
14			4		92	92	23
15			4		90	90	23
16			4		92	92	23

[a] Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol)

and catalyst (1 mol %) in toluene (3 ml).
[b] Conversion determined by GC.
[c] Molar ratios of product formed with the catalyst used.
[d] TOF = TON/time

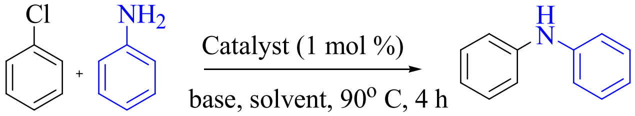
Numerous monodentate free carbenes [38-40], bidentate bridged carbenes [41], functionalized carbenes [16b, 42] and pincer-type ligands based on NHCs have been reported and successfully applied in catalysis. The precise reaction mechanism remains to be elucidated. Nevertheless, a few comments can be made. We believe that the catalytic C □ C coupling reaction with nickel complex follows the “reductive elimination” pathway, extensively studied by Liu, Xu, Xie and others [43]. The Ni(II) complexes are believed to be *in situ* reduced to active Ni(0) species by the homocoupling of phenylboronic acid via a mechanism previously postulated for related Pd(II) species and for other nickel based systems, which catalyze these reactions *via* a Ni(0) ↔ Ni(II) cycle [43c, 44]. Accordingly, it is commonly accepted that, in a typical C □ C coupling catalytic cycle, the strong σ-electron donating ability of a NHC ligand aids the initial reduction and the oxidative addition [16b]. Moreover, the steric bulkiness of a NHC ligand can increase the rate of the reductive elimination [44]. However, it is reasonable to consider that a bulky NHC ligand may also hinder the coordination of incoming substrates to the center metal and hence decrease the activity of center metal. In order to overcome the aforementioned problem, the incorporation of additional donor functionalities in the side chains has been particularly fruitful for catalytic applications as well. Especially, the hemilabile donor functionalities based on nitrogen, oxygen or sulfur allow for efficient stabilization of the catalytic species, while rapidly opening up free coordination sites for incoming substrates. Therefore, the use of a flexible NHC ancillary ligand could constitute a solution. This trend agrees with our working hypothesis that an increase in the stability of ligand could lead to improve catalytic properties, possibly through the stabilization of the putative Ni(0) species. This prompted us to develop a dazzling variety of these dianionic bis(aryloxy-NHC) nickel(II) complex **1** of type $[Ni(NHC)_2O_2]$, because such structural variation may serve as an alternative strategy to modulate the coordination sphere of the central metal by considering both the electronic and steric environment of the nickel centre.

The activities of $[Ni(NHC)_2O_2]$ complex **1** were superior to those of other reported nickel NHC complexes [15e,15d]. In addition, complex **1** effectively catalyzed the cross-coupling between arylboronic acids and a range of aryl halides without the need of additives such as PPh_3. The overall activity of our system, representing the first catalytic study on oxygen-functionalized NHC nickel complexes, is nevertheless encouraging.

3.2 Buchwald-Hartwig reactions

Evaluation of conditions for the complex 1 catalyzed amination reaction: Initial studies focused on the coupling of chlorobenzene with aniline in dioxane at 90 °C for 4 h in the presence of 1.3 mmol of KO^tBu as a base and 1 mol % of complex **1** as a possible catalyst precursor. It was found that the bases used, drastically affect the reaction. For example, high yield of diphenylamine was obtained when KO^tBu was used as the base and in the presence of all other bases such as NaO^tBu, KOH, NaOH, K_2CO_3, Na_2CO_3 and $KHCO_3$, no reaction or only trace amount of product was observed (Table **4,** entry **1-7**). To this end, we noticed that a strong base was required to promote the reaction. We examined the effect of solvents with the aid of catalyst on model reaction, and the results are described in **Table 4**. Out of different solvents tested during the course of optimization, the solvent such as CH_3CN, DMSO and *i*PrOH were found to be completely ineffective. Solvents such as THF, toluene and Et_2O could bring about only a little conversion. However, when the reaction was carried out in dioxane, we were amazed and delighted to observe a single-handedly magic effect of dioxane resulting in 96 % isolated yield at the temperature of 90 °C (Table **4,** entry **7**). To study the effect of amount of the catalyst, the reactions were carried out at different amount of catalyst ranging from 0.15-1.0 mol %. When the catalyst loading was lowered to 0.5 mol % a longer reaction time (12 h) was necessary to achieve high yield. When the catalyst loading was further lowered to 0.25 mol %, the complex showed much lower activity even when the reactions were performed for 12 h. In the presence of 0.15 mol %, inferior results were observed (**Fig. 5**). Complex **1**, in which the carbene carbon chemical shift was observed around 152.23 ppm, implying stronger σ-donation effect, which may be the reason for more efficient amination reactions consistent with previous literature reports. Under these conditions, complex **1** which has shown to be a convenient and highly active catalyst precursor for the amination of aryl chlorides gave an encouraging yield after 4 h of reaction.

Table 4. Evaluation of conditions for C □ N coupling reaction[a]



Entry	Base	Solvent	Temp (^{o}C)	Yield (%)[b]
1	NaO^{t}Bu	Dioxane	90 ^{o}C	17
2	KOH	Dioxane	90 ^{o}C	10
3	NaOH	Dioxane	90 ^{o}C	31
4	K_2CO_3	Dioxane	90 ^{o}C	n. r
5	Na_2CO_3	Dioxane	90 ^{o}C	46
6	$KHCO_3$	Dioxane	90 ^{o}C	n. r
7	**KO^{t}Bu**	**Dioxane**	**90^{o}C**	**96**
8	KO^{t}Bu	THF	65 ^{o}C	39
9	**KO^{t}Bu**	**DMF**	**153 ^{o}C**	**82**
10	KO^{t}Bu	CH_3CN	85 ^{o}C	n. r
11	KO^{t}Bu	DMSO	190 ^{o}C	n. r
12	KO^{t}Bu	Toluene	110 ^{o}C	74
13	KO^{t}Bu	*i*PrOH	83 ^{o}C	n. r
14	KO^{t}Bu	Et_2O	35 ^{o}C	41
15	KO^{t}Bu[c]	Dioxane	90 ^{o}C	n. r
16	KO^{t}Bu[c]	DMF	90 ^{o}C	n. r

[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 ^{o}C for 4 h.

[b] Isolated yield after column chromatography

[c] No catalyst was used; n.r: no reaction

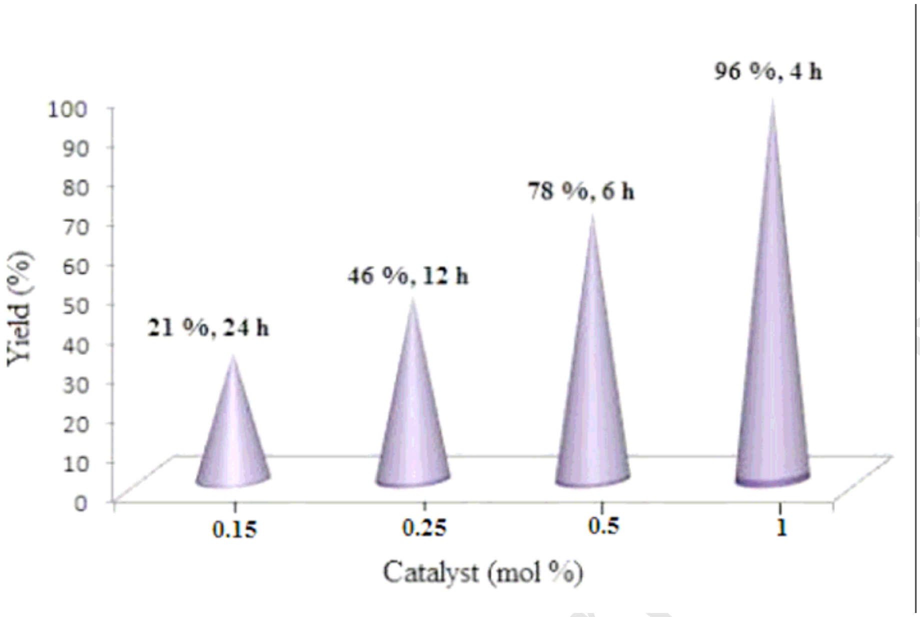
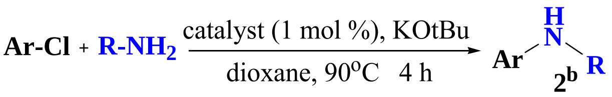


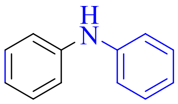
Fig. 5. Effect of catalyst (mol %) with respect to time on amination of aryl chlorides

Amination of aryl chlorides with primary amines: With an active catalyst in hand and reliable conditions are identified for this Ni-catalyzed amination, we studied the scope of arylchlorides with primary amines that undergo these amination reactions, and the results are summarized in **Table 5**. All reactions proceeded smoothly and afforded the desired coupling products in reasonable to excellent yields upon isolation. The results in Table **5** demonstrate that the catalytic process is able to tolerate variety of functional groups and substitutions like CH_3, OCH_3, Cl, CN and F. Various primary amines having both electron donating and electron withdrawing groups underwent the reaction smoothly and gave rise to good to excellent product yields (Table **5,** entry **2a-2p**). The relative substituents in the aryl chloride have hardly any influence on the coupling reactions. For example, almost identical results were observed for an electron rich and electron deficient aryl chlorides (Table **5,** entry **2a-2b**). The reactions of an amine containing a secondary alkyl group still coupled with aryl chlorides afforded the products in higher yield 78-84 % (Table **5**, entry **2h, 2i, 2l**). With regards to the reactivities of amines, the primary amines containing aryl (**3k**), and heteroaryl (**2m**) groups reacted well to furnish excellent yields (**88-92 %**). Sterically hindered primary amines which are less reactive substrates were also tested under the optimal reaction condition. To our delight, all reactions took place smoothly to give the aminated products in good to high yields (Table **5**, entry **2n**). A sterically hindered chloroarene such as (3-

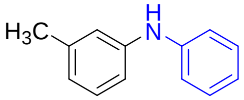
chloro-phenyldimethylamine) gave the corresponding aminated products in excellent yields (Table **5**, entry **2o, 2p**).

Table 5. Complex **1** catalyzed coupling of arylchlorides with primary amines[a]

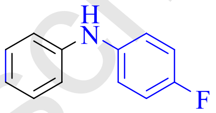




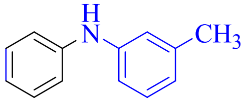
2a; 96 %



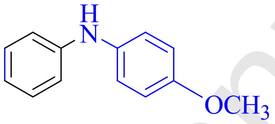
2b; 94 %



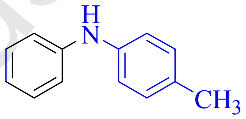
2c; 90 %



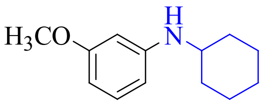
2d; 94 %



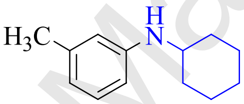
2e; 98 %



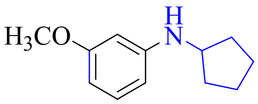
2f; 89 %



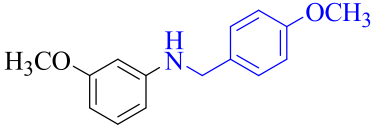
2g; 81 %



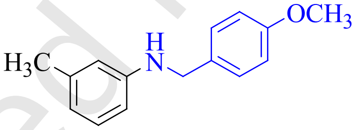
2h; 84 %



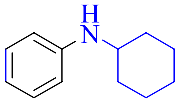
2i; 78 %



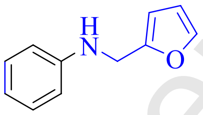
2j; 97 %



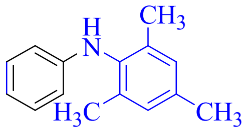
2k; 92 %



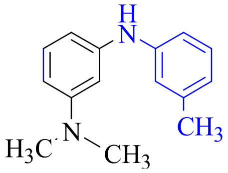
2l; 84 %



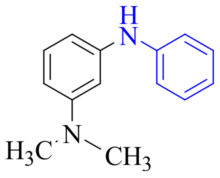
2m; 88 %



2n; 94 %



2o; 98 %



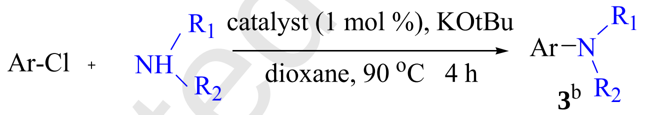
2p; 91 %

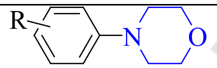
[a] All reactions carried out using aryl chlorides (1 mmol), primary amines (1.3 mmol), KO^{t}Bu (1.3 mmol), catalyst (1 mol %), and dioxane (2 ml) at 90 °C for 4 h.

[b] Isolated yield after column chromatography.

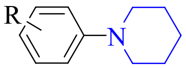
Amination of aryl chlorides with secondary amines: In order to check the versatility of our catalyst, we decided to study the expanded substrate scope of the catalyst **1** with a variety of aryl chlorides with secondary amines. As can be seen from **Table 6**, all reactions proceed smoothly to give the corresponding aminated products in good to high yield (entry **3a-3o**). The relative positions of the substituents in the aryl chloride have hardly any influence on the coupling reactions. *O/m/p*-chlorotoluene underwent the reaction smoothly and produces almost identical results (Table **6**, entry **3a-3c**). Higher yields of products **3d (97 %)** and **3e (88 %)** could be obtained for the reaction involving *m* and *p*-chloro anisoles. In addition, dimethylamino *p*-substituted aryl chlorides were also tolerated to give the corresponding coupling product in high yields (Table 6, entry **3g**). Considering the wide synthetic utility of substituted amines, we also examined the amination of aryl chlorides with other amines such as piperidine, pyrrolidine, *N*-methyl benzylamine and *N*-methylaniline. For the reactions of piperidine with aryl chlorides to give good yields (Table **6**, entry **3h-3k**, **3m**). On extending the scope to pyrrolidine, aminated products were obtained in moderate yields (Table **6**, entry **3n, 3o**).

Table 6. Complex **1** catalyzed coupling of arylchlorides with secondary amines[a]

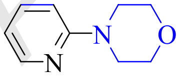




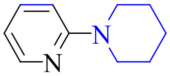
3a (R = H) 92 %
3b (R = *m*-CH_3) 93 %
3c (R = *p*-CH_3) 98 %
3d (R = *m*-OCH_3) 97 %
3e (R = *p*-OCH_3) 88 %
3f (R = *p*- F) 96 %
3g (R = *p*- NMe_2) 90 %



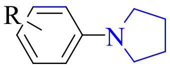
3h (R = H) 79 %
3i (R = *p*-CH_3) 91 %
3j (R = *m*-OCH_3) 85 %
3k (R = *p*-OCH_3) 80 %



3l; 94 %



3m; 90 %



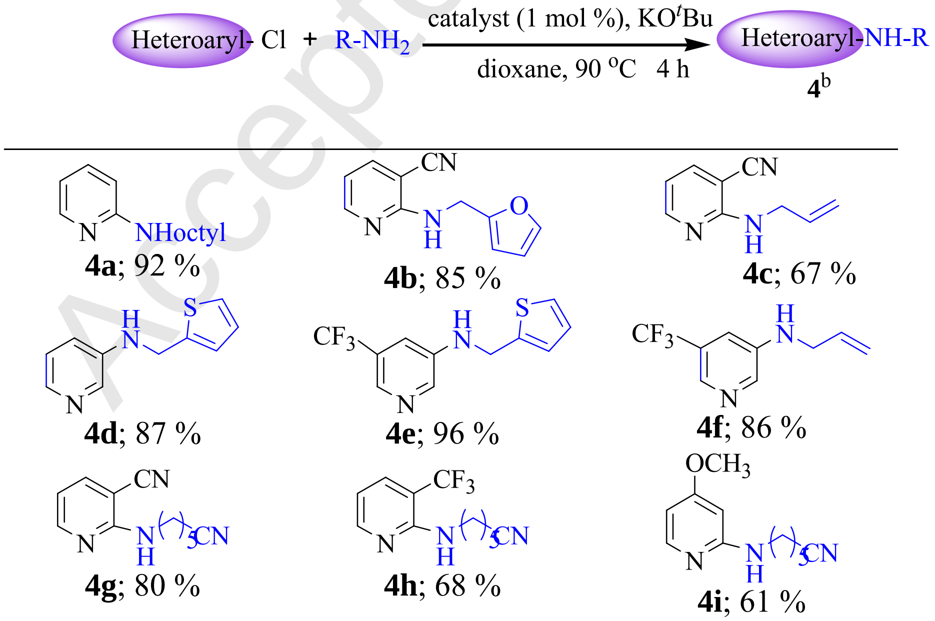
3n (R = H) 74 %
3o (R = *p*-CH_3) 72 %

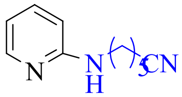
[a] Reaction conditions: All reactions were carried out using aryl chlorides (1 mmol), secondary amines (1.3 mmol), KO^{t}Bu (1.3 mmol), catalyst (1 mol %), and dioxane (2 ml) at 90 °C for 4 h.

[b] Isolated yield after column chromatography.

Amination of hetero aryl chlorides with primary amines: Encouraged by these promising results, we turned our attention to cross-coupling reactions between nitrogen containing heteroaryl chlorides and primary amines catalyzed by 1 mol % of catalyst are summarized in **Table 7.** Nitrogen containing heterocycles containing amino substituents are of particular importance for pharmaceutical applications. However, the C □ N coupling reactions between nitrogen containing heteroaryl electrophiles and primary amines are challenging, 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 under optimized condition. The reaction of 2-chloropyridine was carried out with octylamine to obtain *N*-octyl-3-aminopyridine (Table **7**, entry **4a**) in **92%** yield. Next, several substituted heteroaryl chlorides, underwent this amination reaction encompassed with 2-pyridyl and 3-pyridyl chlorides containing both electron-donating and electron- withdrawing substituents in the *ortho* and *para* position are well-tolerated, these reactions affording the corresponding aminated products in good to excellent yields ranging from **61 to 96%** (Table **7**, entry **4b–4j**). It is worth mentioning that complex **1** can also catalyze the amination of heteroaryl chlorides with primary amines, which is more sustainable for the synthesis of heterocyclic amines.

Table 7. Complex **1** catalyzed coupling of hetero arylchlorides with primary amines[a]





4j; 72 %

[a] Unless otherwise specified, all reactions were carried out using hetero 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.

Based on previous literature reports [45], it appears to us that both steric and electronic effects combine to mediate the coupling process. Initially, the electron donor properties of the carbene facilitate the activation of aryl chlorides. A secondary effect may be provided by the hemilabile donor functionality based on oxygen in the side chains for efficient stabilization of the catalytic species. Accordingly, the Ni(II)-NHC complex **1** may formally be regarded as an intermediate (oxidative adduct) in the catalytic cycle and hence it has the possibility for generating Ni(0) species *in situ* by attack of nucleophiles and subsequent reductive elimination prior to the normal catalytic cycle [46]. This new protocol provides an extremely convenient, highly efficient and less expensive alternative for the synthesis of aryl amines. Studies are currently underway in our laboratory to further expand the scope of this methodology as well as to ascertain mechanistic details of this process.

4. Conclusions

The present work reveals that the “one metal ion + one ligand” approach, i.e., using a tetradentate NHC ligand to form robust Ni(II) complex, is an appealing strategy to develop highly efficient organonickel(II) complex of the type [Ni(C_2O_2)] which was synthesized from bis (aryloxy-NHC ligand) and Ni(OAc)$_2$.4H$_2$O or [NiCl$_2$(PPh$_3$)$_2$] in presence of ethanol and Et$_3$N at 80 °C afforded the corresponding complex **1**. Crystal structure of the complex has been described. For enhancing the rigidity of the stable Ni(II) complex supported by tetradentate NHC ligand, our studies demonstrate that the simultaneous coordination of two carbenic carbons and two aryloxy groups to one nickel centre can be used as an alternative strategy to significantly improve the catalytic activity of Ni(II) complex. This is because this structural variation can modulate both the electric and steric environment of the nickel centre in a straight forward manner. The complex was found to be an active catalyst in Suzuki-Miyaura cross-coupling reaction. The reaction progresses efficiently at low catalyst loading (1 mol %, complex **1**). This new protocol is effective for many electronically diverse aryl halides and arylboronic acids, providing biphenyl derivatives in good to excellent yields. Furthermore, this catalyst system has been demonstrated to C □ N cross coupling reactions. The reaction can tolerate a wide array of substrates. Under mild conditions, all reactions performed very well to give corresponding aminated products in moderate to almost quantitative yield, enriching a convenient and alternative method for the amination of aryl chlorides in extremely short reaction times. We hope that nickel will continue to gain recognition, not only as an inexpensive substitute for palladium, but also possessing a number of inherent properties that provide a complement to catalysis by other metals.

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 were performed by Merck silica gel 60 (0.063–0.200 mm). Microanalysis of carbon, hydrogen and nitrogen were carried out using a Vario EL III elemental analyzer at SAIF, Cochin, India. Infrared spectra of the ligands and the metal complex were recorded as KBr discs in the range of 4000−400 cm^{-1} using a Nicolet Avatar model FT-IR spectrophotometer. Electronic spectra of the ligand and its complex have been obtained in dichloromethane using a Shimadzu UV - 1650 PC spectrophotometer in 800-200 nm range. ^1H (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. Electrospray ionization mass spectra were recorded by liquid chromatography–mass spectrometry quadrupole time-of-flight Micro Analyzer (Shimadzu) at SAIF, Panjab University, Chandigarh. Melting points were determined in open capillary tubes on a Technico micro heating table and are uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with DP-5 column of 30 m length, 0.53 mm diameter and 5.00 µm film thickness. 1-(2'-methoxy phenyl)imidazole and the nickel metallic precursor [$NiCl_2(PPh_3)_2$] were prepared according to literature methods [47,48].

5.1.1 Synthesis of 1-(2'-methoxy phenyl) imidazole

CuI (0.0952 g, 0.5 mmol) and K_3PO_4 (4.245 g, 20.0 mmol) were added to a 100 ml flask equipped with stirrer and reflux condenser. 2-Propanol (10 ml), ethylene glycol (11 ml, 20.0 mmol), 2-iodoanisole (1.3 ml, 10.0 mmol), and imidazole (0.82 g, 12.0 mmol) were added at room temperature. The reaction mixture was heated at 80°C for 72 h to furnish a pale yellow suspension, and then allowed to cool to room temperature. Water (ca. 5 ml) was added, and the mixture was extracted with diethyl ether (3 ×10 ml). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was removed by rotary evaporation to yield the crude product as a deep yellow residue that was purified by column chromatography on silica gel using a solvent mixture (hexane/ ethyl acetate = 20/ 1) afforded 1-(2'-methoxy phenyl)imidazole (62 % yield) as yellow solid. ^1H NMR (300.13 MHz, $CDCl_3$): 3.64 (s, 3H, OCH_3), 6.92 (s, 1H, imi-H), 7.04 (s, 1H, imi-H), 7.21-7.28 (m, 1H, Ar-H), 6.84 (d, 1H, J = 7.5 Hz, Ar-H), 7.48 (s, 1H, NCHN), 7.61 (t, 1H, Ar-H), 8.24 (d, 1H, J = 7.5 Hz, Ar-H).

5.1.2 Synthesis of 1,1'-di(2-methoxy-phenyl)-3,3'-methylene diimidazolium dibromide

To a suspension of 1-(2'-methoxy phenyl)imidazole (3.48 g, 20.0 mmol) in dibromomethane (5.0 ml, 71 mmol) was stirred at 100°C for 48 h, and then stored at room temperature. The resultant white precipitate was filtered and washed with acetone and then dried under air. Yield: 82 %. Anal. Calcd for $C_{21}H_{22}O_2N_4Br_2$: C, 48.30; H, 4.25; N, 10.73 %. Found: C, 48.42; H, 4.40; N, 10.81 %. Mp: 42-46 ºC. ^1H NMR (300.13 MHz, DMSO-*d*$_6$) : δ 3.90 (s, 6H, OMe), 5.67 (s, 4H, CCH_2N), 6.82 (s, 2H, NCH_2), 7.43 (dd, J = 7.5 Hz; J = 4.4 Hz, 2H, Ar-H), 7.59 (d, J = 7.5 Hz, 2H, Ar-H), 7.66 (d, J = 7.5 Hz, 2H, Ar-H), 7.85 (t, 2H, Ar-H), 7.94 (s, 2H, imi-H), 8.04 (s, 2H, imi-H), 9.82 (s, 2H, NCHN). ^{13}C NMR (75.47 MHz, DMSO-*d*$_6$): δ 29.24

(OCH_3), 58.21 (CCH_2N), 116.1 (Ar-C), 119.4 (Ar-C), 121.1 (Ar-C), 122.6 (Ar-C), 122.7 (imi-C), 123.4 (imi-C), 123.8 (Ar-C), 124.5 (Ar-C), 142.4 (NCHN), 155.6 (C-O).

5.1.3 Synthesis of 1,1'-di(2-hydroxy-phenyl)-3,3'-methylene diimidazolium dibromide (H_4LBr_2)

A solution of 1,1'-di(2-methoxy-phenyl)-3,3'-methylene diimidazolium dibromide (3.91 g, 7.91 mmol) in 47 % HBr (30 ml) and CH_3COOH (30 ml) was refluxed at 110°C for 48 h. The mixture was stored at room temperature, and the resultant white precipitate was collected and washed with acetone. Yield 87 %. Mp: 54-61°C. White solid. Anal. Calcd for $C_{19}H_{18}O_2N_4Br_2$: C, 46.18; H, 3.67; N, 11.34 %. Found: C, 46.27; H, 3.71; N, 11.42 %. IR (KBr, cm^{-1}): 3383 (O-H), 1333 (C-O), 1562 (N-C-N), 3046 ($CH_{C=C}$), 1418 (C-O). UV λmax(□$_{max}$) : 344 (12489), 318 (16791), 275 (4542). ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 5.42 (s, 4H, CCH_2N), 6.71 (s, 2H, NCH_2), 7.38 (dd, J = 7.5 Hz; J = 4.4 Hz, 2H, Ar-H), 7.42 (d, J = 7.5 Hz, 2H, Ar-H), 7.51 (t, 2H, Ar-H), 8.07 (s, 2H, imi-H), 8.24 (s, 2H, imi-H), 8.56 (d, J = 7.5 Hz, 2H, Ar-H), 10.01 (s, 2H, NCHN), 11.08 (s, 2H, OH). ^{13}C NMR (75.47 MHz, DMSO-*d*$_6$): δ 149.83 (C-O), 138.02 (NCHN), 130.9 (Ar-C), 124.99 (imi-C), 123.28 (imi-C), 121.52 (Ar-C), 121.47 (Ar-C), 119.35 (Ar-C), 116.82 (Ar-C), 118.4 (Ar-C), 118.2 (Ar-C), 57.64 (CCH_2N). ESI-MS (*m/z*): calcd. 167.18 $[M-2Br]^{2+}$ ($z = 2$). Found, 167.15 $[M-2Br]^{2+}$

5.1.4 Synthesis of {1,1'-di(2-hydroxy-phenyl)-3,3'-methylene diimidazolin-2,2'-diylidene} nickel(II) complex.Ni (L) 1

A suspension of $Ni(OAc)_2{\cdot}4H_2O$ (0.0455 g, 0.183 mmol) or $[NiCl_2(PPh_3)_2]$ (0.1197 g, 0.183 mmol) in ethanol (15 ml) was treated with H_4LBr_2 (0.082 g, 0.165 mmol) and Et_4NBr (0.165 g, 0.785 mmol), Et_3N (74.0 μl, 0.531 mmo1) was added, and the mixture was gently stirred at 80°C for 6 h. The precipitated greenish yellow powder of complex **1** was filtered and the solid was thoroughly washed with small amount of ethanol and diethyl ether. Single crystals suitable for X-ray determination was grown in DMSO solution of **1** for one month at room temperature. Yield: 82 %. Mp: >300°C. Greenish yellow solid. Anal. Calcd for $C_{19}H_{14}O_2N_4Ni$: C, 58.66; H, 3.63; N, 14.40 %. Found: C, 58.74; H, 3.70; N, 14.51 %. IR (KBr, cm^{-1}): 1393 (C-O), 1573 (N-C-N), 3114 ($CH_{C=C}$), 1417 (C-O). UV λmax(□$_{max}$) : 430 (<1000), 399 (3500), 369 (14421), 330 (15291). ^{1}H NMR (300.13 MHz, DMSO-*d*$_6$): δ 5.89 (s, 4H, CCH_2N), 7.64 (t, 2H, Ar-H), 7.89

(s, 2H, imi-H), 7.94 (s, 2H, imi-H), 8.14 (t, 2H, Ar-H), 8.24 (d, J = 7.5 Hz, Ar-H) 8.41 (d, J = 7.5 Hz, 2H, Ar-H). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ 60.58 (CCH_2N), 120.66 (imi-C), 121.32 (imi-C), 124.6 (Ar-C), 126.17 (Ar-C), 128.56 (Ar-C), 131.19 (Ar-C), 132.76 (Ar-C), 133.28 (Ar-C), 148.76 (C-O), 152.23 (Ni-C). ESI-MS (*m/z*): calcd. 389.03 $[M]^+$. Found: 389.09 $[M]^+$.

5.2 Catalysis

5.2.1 General procedure for the Suzuki-Miyaura reaction: The typical procedure is as follows. A two necked 25 ml flask fitted with a reflux condenser and septum was charged with aryl halides (1 mmol), aryl phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol) and catalyst (1 mol %) in 3 ml toluene. The reaction mixture was immediately heated with vigorous stirring in an oil bath at 110°C under argon atmosphere for an appropriate period of time. The reaction mixture was cooled to room temperature. A 1:1 mixture of diethyl ether/ water (20 ml) was added. The organic layer was separated and the aqueous layer extracted with another 10 ml portion of diethyl ether, and dried with anhydrous $MgSO_4$. The solution was then filtered. Conversions and yields of the reactions were determined by GC using dodecane as internal standard.

5.2.2 General procedure for the Buchwald-Hartwig reaction: Under an N_2 atmosphere, KO^tBu (1.3 mmol), complex **1** (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 4-7. The resulting amines were identified by comparison of the ^{1}H & ^{13}C NMR data with those previously reported (ESI†).

5.3 X-ray crystallography

Crystal of complex **1** was mounted on glass fibers used for data collection. Crystal data were collected at 295 K using a Gemini A 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 [49]. Refinement and all further calculations were carried out using SHELXL [49]. 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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Electronic supplementary information (ESI) available:

NMR (^{1}H and ^{13}C) and mass spectra of ligand and the complex. Catalysis protocols, characterization data for aminated products and selected ^{1}H and ^{13}C NMR spectra of coupling products. CCDC 985756. These data can be obtained free of charge from the Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif.

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Graphical abstract

Nickel(II) complex incorporating methylene bridged tetradentate dicarbene ligand as an efficient catalyst towards C-C and C-N bond formation reactions

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A new air-stable nickel(II) complex containing dianionic bis(aryloxy-NHC) ligand was synthesized and structurally characterized. The Ni complex possesses a square planar geometry with the ligand coordinating through bi-negative tetradentate C_2O_2 fashion. The new complex was found to be an efficient catalyst towards C-C and C-N bond formation reactions.

Research Highlights

- A new Nickel(II) dicarbene complex has been synthesized and characterized.
- X-ray studies revealed a square planar geometry of the new complex.
- The new complex catalyzes the Suzuki-Miyaura cross-coupling reaction effectively.
- The Ni(II) complex also efficiently catalyzes the amination of aryl chlorides.