# Synthesis, characterization and catalytic activities of homoleptic Nickel(II) N-heterocyclic carbene complex bearing square planar geometry§

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**Abstract**

A rare homolepticorganonickel(II) biscarbene complex with square-planar geometry has been synthesized and structurally characterized which reveals the presence of interesting zigzag water- bromide hydrogen bonded chain decorated by molecular nickel(II) biscarbene. The complex depicted an efﬁcient catalytic activity towards the Suzuki–Miyaura and Heck cross-coupling reactions. Besidesa high catalytic activity toward Suzuki–Miyaura cross-coupling reaction in DMF and water medium. These catalytic reactionsdepict a wide array of substrate scopeto afford the desired product in moderate to high yield.

Keywords:*Nickel, N-heterocyclic carbene, Square-planarnickel,Suzuki-Miyaura cross-coupling, Heck coupling*

**1. Introduction**

Cross-coupling chemistry is one of the mostimportant methods for producingC-C bonds [1].Transition-metal-catalyzed cross-coupling reactions such as Suzuki–Miyaura [2], Heck [3],Stille [4],Kumada [5],Negishi [6],Hiyama [7], and Sonogashira [8] are the reliable methods for the formation of C–C bonds, which widely used to synthesize natural products, pharmaceuticals, and organic materials [9].The palladium catalyzed Suzuki–Miyaura reaction has been jointly (Heck and Negishi coupling reactions) honored with the 2010 Nobel Prize in chemistry [2a,10,11].Nowadays, manycatalytic systems developed to construct C-C bond are based on expensive precious metal catalysts *i.e*., palladium-based catalysts. It is obvious that the palladium catalysts dominate the cross-coupling ﬁeld. On the contrary, it is the urgent need to develop and encourage economical and reasonably available materials to conquer against the dwindling of precious metal-reserve of nature and their consequential dramatic price raise. The European commission emphasizes to increasingly employ profuse, low-cost 3d series transition metals for homogeneous catalysis [12].Thus, the scientists striving to increase the exploitation of earth-abundant metals like Fe, Cu, and Ni on the compulsion driven by economical and ecological concerns. Nevertheless, nickel has been provedas cost-effective and feasible alternative for many of the palladium-assisted transformations [13].Since, nickel, palladium and platinum are residing to the same group in the periodic table, nickel can be used as a catalyst in the place of palladium and platinum. On the other hand, the cost of nickel (on molar basis) is only 0.05 % and 0.01 % of the cost of palladium and platinum respectively [14].These facts make the nickel as a low-cost substitute catalyst for cross-coupling reactions [15].Nickel facilitates the oxidative addition of phenol derivatives and aryl fluorides which is somewhat difficult in palladium system due to the poor nucleophilicity of Pd compared with Ni [16,17,18].

There is no reason to wonder about the boost in catalytic activity of Ni(II)-based systems when the phosphine and amine ligands are substituted with NHC ligands as this is already experienced with other metallic systems. Consequently, the Ni(II)-based NHC complexes are considerably diversified [19].In the latest scenario, some Ni(II)-based NHC systems display superior catalytic activity over their Pd(II) analogues with an added advantage of benign reaction conditions [20].Despite the before mentioned advancements, many of the previously reported catalytic methods adopt catalyst-rich loading (typically ≥ 5 mol%) and lavish addition of phosphine-supporting ligands [21]. The Ni(II)-based NHC systems are dominates the Pd(II)-based NHC systems in many ways such as higher catalytic activity, etc., [21a,22].These results underscore the significance of carrying out control experiments when probing the catalytic C-C bond generation activity of powerful Ni(II)-based catalytic systems. Alas, such a potentially active Ni(II)-based NHC catalytic systems towards C-C bond formation reactions is rare[23-25].Based on the above fact, a great success of NHC ligands in cross-coupling chemistry has been accomplished mostly through ligand manipulation. When walk through the Ni(II)bis-carbene systems, it seems that both mono and bis NHC ligands furnishes a diverse square-planar complexes of the type NiII(NHC2)X2 (X = halide or pseudohalide) which exhibits good stability. They were synthesized directly by reacting the NHC ligands or their precursors with the halides of divalent nickel [26,27]. Alternatively, it can be achieved through the oxidative addition of aryl/alkyl halides and organic cyanides to zero-valent nickel bis-carbene systems [28,29,30]. It is noteworthy that, in all the above mentioned instances, the NHC ligands have been arranged in *trans* orientation with each other. Surprisingly, *cis* oriented complexes also known [31]. In addition, there are few instances in the literature for homoleptic[NiII(NHC2)2].2Br- systems [26,32].We start our quest to exploit bidentate chelates of NHC-ligated bivalent nickel systems to perform C-C coupling reactions which is supplemented with the previous critiques on literature and our earlier triumphs on employing the bis-NHC as a supporting ligand in Ni-based catalytic reactions [33].

**2. Results and discussion**

*2.1. Synthesis and characterization of* ***2***

The bivinyl imidazolium dibromide salt **1**was obtained by reacting vinylimidazole with 1,2-dibromoethane [35]. The neat reaction of **1** with anhydrous nickel(II) acetate and tetrabutyl ammonium bromide (TBAB) at 128oC yielded [Ni(1,2-di(*N*-vinyl-*N*′-imidazol-2-ylidene)ethane)2](Br-)2 (**2**) as a light yellow solid in very good yield (Scheme 1**)**. **2** is soluble in CH2Cl2, CHCl3, CH3CN, DMSO and insoluble in diethyl ether. The formation of **2** was confirmed by FT-IR, multinuclearNMR and elemental analysis, and the structure was confirmed by single crystal X-ray crystallography. Remarkably, **2** is stable at ambient conditions and its stability looks akin to that of Ni-NHC complexes of similar type reported earlier [40,33b].

Complex **2** is lacking the 1H NMRlines of imidazolium (NC*H*N) protons when compared with that of **1** which confirms the formation of **2**.The signature for the backbone of imidazolium ring is observed at about 7.61-7.72 ppm. In addition, a series of signals appeared for -NCH2 protons in the region 4.79-4.84 and 5.57-5.62 ppm. In addition, the vinyl proton showed doublet of doublet in the region 7.16-7.22 ppm.

The absence of the 1H NMR signals of -NCHC- whiles the presence of downfield 13C NMR signal of N*C*N carbene carbon at 169.71 ppm in **2** confirms the Ni-Ccarbene bond formation [39].The peak appeared between 124.22 and 120.52 ppm was attributed to imidazolium carbon.In 13C NMR, the vinyl carbon appears at 106.94 ppm and -NC*H*2- carbon appears at 47.34 ppm.

The structure of **2** was confirmed through single-crystal XRD techniques. The structural parameters are listed in table 1. The crystal apposite for the single crystal XRD analysis was developed from its dichloromethane solution at room temperature.**2** was crystallized-out in the anorthic pinacoidal space group (*Pī*) with [Ni(1,2-di(*N*-vinyl-*N*′-imidazol-2-ylidene)ethane)2], one bromide ion along with a couple of water molecules in the asymmetric unit. Figure 1 depicts the structure of **2**.The selected bond lengths and angles are tabulated in table 2. As shown in figure 1, the nickel atom in **2** displays a square-planar geometry with four C-donor atoms lying on the same plan. The distances of the Ni-Ccarbene bonds (1.892(4) and 1.916(4) Å) in **2** are comparable to those of the square-planar [Ni(NHC2)2].2Br- complexes (1.896-1.906(2) Å) [33b,40].The C(8)–Ni–C(8)’ and C(3)–Ni–C(3)’ angles are 180oand it is comparable with previously reported [Ni(NHC2)2].2Br- type complexes (180.00(11)o)[33b,40].While the C(8)–Ni–C(3) and C(8)–Ni–C(3)’ bond angles (90.30o and 89.70o) shows negligible deviation from 90o. It The coordination environment around nickel is satisfied by four carbene carbons, C(3), C(8), C(3)’ and C(8)’ forming the basal plane, while one of -CH2-CH2-, proton shows a weak C–H···Ni hydrogen bonding interaction at the apical position of NiC4 plan. The C–H···Ni angle is 100.9o with H···Ni distance of 2.866 Å which is much stronger than C–H···Ni hydrogen bonding interaction fond in the earlier reports[40-42].

*2.2 Catalysis*

*2.2.1.Suzuki-Miyaura cross coupling*

With the intension of optimizing the efficiency of the present catalytic system, the coupling of iodobenzene and phenylboronicacid in the presence of **2** was fixed as the prototype reaction. Thin layer chromatography technique is used to follow the course of reaction and the correspondingyields are tabulated as table 3. In order to assess the crucial role of base in promoting the generation of nickel intermediates all along the catalytic cycle, various bases such as K2CO3, NaHCO3, KHCO3, NaOH, KOH, KO*t*Bu and NaO*t*Bu were screened. Among the bases employed, a mild, inexpensive yet effective base K2CO3 was found to be the best and led to higher yield for this reaction (Table 3, entry 6). To make sure the catalytic role, a control experiment was executed without the base or the catalyst. As expected, there was no reaction even after an extended reaction time (12 h) (Table 3, entry 18). In order to examine the influence of solvents on our catalytic system, we have carried out the reaction in the presence of K2CO3 by using the common solvents such as toluene, acetonitrile, 1,4-dioxane, DMSO, ethanol, DMF-H2O, DMF and H2O (Table 3, entries 1-6 and 9-11). Among the various solvents, the DMF-water system was found to be most suitable (Table 3, entry 6). The solvent such as acetonitrile, ethanol and xylene were quite unsuccessful (Table 3, entry 2, 4, 9). The etheral solvent dioxane and midpolar solvent toluene were not effective (entries 3, 1). The reaction was performed in water, but the desired biphenyl was not observed (Table 3, entry 11). The same reaction when carrying out in a 50% (v/v) aqueous DMF, afforded a highly polar co-solvent environment capable of homogenize the substrates with ease.We further optimized the reaction for the influence of catalyst loading on the catalytic activity (Figure 2). The reactions were performed by changing the quantity of the catalysts ranging from 0.5 to 4 mol%.The results revealed that the rate of the catalytic reactions is influenced by the catalyst loading which is in connection with the reaction time and the production yield.The catalytic loading of 3 mol % is found to be the optimized amount of catalyst to perform the catalytic reaction. No significant increase in the rate and thereby the efficiency of the reaction is observed on further raise of catalyst loading to 4 mol % (Figure 2). To our delight, the catalyst **2**was active enough to promote the Suzuki reactions under milder conditions in air and in DMF-water system.

With the aim of determining the usefulness and drawbacks of our present method, reactions of a variety of aryl boronic acid derivatives with substituted/unsubstituted aryl halides were studied under the optimized conditions. The results are collated in table 4 from which we can find that all the reactions take place gently and furnished the corresponding biphenyls in good to high yield (Table 4, entries 1-26). The characteristics of substituents on both the aryl halides and aryl boronic acids will play with Suzuki-Miyaura cross-coupling reaction (Table 4, entries 1-26). The reaction of 4-formylphenylboronic acid with iodobenzene and 4-bromo-nitrobenzene, eventuated gently to offer the preferred biphenyl compounds in 99 % yield (Table 4, entries 4, 17). Both the electron rich and electron poor aryl bromides were fruitfully transformed to the corresponding products in excellent yields (Table 4, entries 6,7,9,16,17,18,19,21,22,24,25). The electron poor phenyl boronicacids afford the desired biphenyls in good yields (Table 4, entries 4,23,24,21,17). The coupling of 1-bromonaphthalene with phenylboronic acid and 4-methoxy phenylboronic acids gives the coupled products in excellent yield (Table 4, entries 8, 20). Furthermore, aryl iodides were excellent substrates for the coupling reaction could be converted effectively (Table 4, entries 1,2,3,4,5,10,11,12,13,14,15). Subsequently, the reaction scope of **2**was examined with few aryl chlorides comprising electron withdrawing and donating substituents underwent coupling reactions with arylboronic acids to provide the expected biaryls in moderate to good yields (Table 4, entries 21, 26). The turn over number was obtained in the range 13.3 to 33.2 s-1(Figure4). While the turn over frequency was noticed in the range of 1.7 to 4.1 s-1. However, our present catalytic system 2, shows greater activity towards Suzuki-Miyaura cross-coupling reaction, on comparing with previously demonstrated Ni-NHC complexes of the similar type [Ni(NHC2)2].2Br- [40].

We trust that the C ̶ C bond formation reaction in presence of nickel-NHC system follows the mechanism, which was comprehensively investigated by Liu, Xu, Xie and others [44].Both the steric and electronic factors amalgamate to arbitrate the C-C bond formation process. In C-C cross-coupled bond formation reaction, the bis-carbene Ni(II)-NHC systems are supposed to be reduced *in-situ* to active zero-valent nickel, which catalyzes the coupling reaction via a Ni(0)↔Ni(II) cycle.Initially, the strong σ-donating ability of NHC ligand favors the reduction of Ni(II)↔Ni(0) along with the activation of aryl halides by the oxidative addition reaction [20,43].Generally, the voluminous NHC ligands might hamper the coordination of confronting catalytic species and it could further decrease the activity of central nickel metal [23j,45].Our current homoleptic Ni(NHC2)2X2 catalytic system gives a different tactic to revamp the coordination sphere of the metal by contemplating both the electronic and steric atmosphere of the nickel center for incoming catalytic substrates.

The catalytic activities of complex **2** were better when compared with that of previously reported Ni(II)-NHC systems ([Ni(NHC)2Br].Br-) [13e,13f].It is worth mentioning that all the reactions are performed under phosphine free condition [43].

*3.2.Heck reaction*

It is a straight forward and excellent method to synthesis Csp2-Csp2 single bonds through base-promoted cross-coupling strategy within aryl halides and olefins [46].For the better optimizing condition, a screening was done for a prototype reaction of iodobenzene with butyl acrylate. Figure 3 and 4 summarize the influence of solvent, base and catalyst loading on heck reaction.Among the bases employed, an excellent yield of desired product was achieved in presence of K2CO3. It was found that K3PO4 and Cs2CO3 also afforded good conversion, but Cs2CO3 is costlier than other bases.Out of different solvents tested, DMF was identified as the best solvent towards the cross-coupling reaction (96 % yield, Figure 4). Water was found to be ineffective for this system.

With the purpose of inspecting the purview of the present catalytic system, the reactions of different arylchlorides with olefins were carried out under the optimized condition (3 mol % catalyst, 2 eq. K2CO3, DMF, 100˚C, 4 h).Table 5, summarizes the obtained product yield, turnover number (TON) and turnover frequency (TOF). Thin layer chromatography is used to screen the course of the reactions.The observation revealed that the coupling between aryl iodides and ethyl/butyl acrylates proceeded in excellent yield (Table 5, entries 1,2,3,4,5,6,7). Similarly, the styrene was successfully coupled with various aryl halides produced the appropriate products with the yield ranging from 83 to 99 % (Table 5, entries 11,12,13,14,15,16,17, 18). The electron-rich as well as the electron-deficient aryl bromides were showed a high activity when electron-deficient olefins are used (Table 5, entries 7,8,9,10). By adopting the identical reaction condition, the aryl chloride was successfully converted to the desired product in 83-98 % yield (Table 5, entries 17). Even, bromonaphthalene reacted nicely with electron poor butyl acrylate (Table 5, entries 10).

On the basis of earlier literature report [47], we believe that the biscarbene Ni(II)-NHC complexes arereduced *in-situ* to active zero-valent nickel, and the activation of aryl halides was further achieved by the oxidative addition. In the second step, an olefin substrate coordinates to the nickel metal with the subsequent insertion of the alkene at the C-Ni. Final step is an intramolecular *β*-hydride elimination which led to the formation of desired product by removal of HX.

**4. Conclusions**

In conclusion, we have described a rare homolepticorganonickel(II) biscarbene complex **2**. The Ni-NHC complex was characterized by elemental analysis, FT-IR and NMR (1H and 13C) spectrometry. The structure of the complex **2** was confirmed using single-crystal XRD technique, which unveiled that the complexes adopt a square planar structure with chelating bis(diimidazolylidene) NHC ligands along with two non-coordinating bromide counter ions in tetradentate C4 fashion. Surprisingly, the presence of interesting zigzag water bromide hydrogen bonded chain decorated by molecular nickel(II) biscarbene through hydrogen bonding was found in the Ni-NHC complex **2**. The complex **2** was found to be active catalyst in Suzuki–Miyaura with 18 examples and Heck cross-coupling reaction with 24 examples. The Suzuki–Miyaura cross-coupling reaction could be tolerated several electronically distinct aryl halides and arylboronic acids offered the biphenyl derivatives in good to excellent yields without any additive. In Heck reaction, the complex **2** shows excellent activity towards the aryl halides and electron poor olefins as well as styrene. At present, we are experimenting to explicate the application of **2** in coupling of cyclohexene oxide with CO2 reaction.

**5. Experimental**

*5.1. General procedures and methods*

All manipulations were carried out under argon using Schlenk-vaccum line techniques and argon filled glove box. The solvents were puchased from commercial sources and purified according to standard procedures [34]. Unless otherwise stated, the chemicals were purchased from commercial sources. **1** was synthesiszed as reported [35].FT-IR measurement (neat) was carried out on a Bruker Alpha-P Fourier transform spectrometer. NMR spectra were recorded on Bruker Ultrashield-400 spectrometers at 25 oC unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. The crystal structure of **2**was measured on an Oxford Xcalibur 2 diffractometer. Data were collected at 150 K. The structure of **2** was solved by direct methods using the Olexprogram [36] and refined with a full matrix least-squares method on F2 using the SHELXL-97 program [37,38].**2** depicts three “B level” alerts. The U(eq) value of an C(7) atom is compared with the average U(eq) for to non-hydrogen atoms bonded to it. Large differences may indicate that the high thermal parameter of terminal carbon atom. The short non-bonding inter H(2B)..H((12A) contact could be due to the strong bite angle of NHC ligand. Potential hydrogen bond donors are checked for the presence of suitable acceptors using commonly used (Jeffrey) H-bond criteria. As a general rule there should be an acceptor for each donor. In **2**, this could be due to the absence of acceptor for O(2)-H(2B)as the hydrogen atoms have been fixed by calculated position. CCDC 1832286 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

*5.2.Synthesis of* ***2***

A mixture of bisvinyl imidazolium dibromide salt **1** (0.100 g, 0.26 mmol), anhydrous nickel(II) acetate (0.047 g, 0.26 mmol) and tetra butyl ammonium bromide (0.400 g, 1.24 mmol) were mixed and heated under vacuum in Schlenk tube at 60 oC for 1 h, followed by at 128 oC for 5 h. The molten reaction mixture was allowed to attain at room temperature, water (10 mL) was added to the reaction mixture.The resulting mixture was extracted with dichloromethane (40 mL).The organic layer was collected, dried on sodium sulphate and concentrated then stored at room temperature to get the desired product as light yellow crystals.Yield: 65% (Based on nickel(II) acetate) Mp: 260-262 °C (decomp.). Anal. Calcd (%) for C24H32Br2N8Ni (648.0481): C, 44.27; H, 4.95; N, 17.21; found: C, 44.2; H, 5.0; N, 17.21. 1H NMR (CDCl3, 400 MHz): *δ*4.79-4.84 (4H, m, NC*H*2), 3.66-3.70, 4.99-5.01 (4H, d, 3*J*HH=7.6 Hz, NCH=CH*H*cis ), 5.28-5.31 (4H, d, 3*J*HH=15.3 Hz,NCH=CH*H*trans), 5.57-5.62 (4H, m, NC*H*2), 7.16-7.22 (4H, dd, vinylC*H*), 7.61(4H, s, Im*H*), 7.72 (4H, s, Im*H*). 13C NMR (100 MHz, CDCl3): *δ*169.71 (*Ni-C*), 131.61(N*C*N), 124.22 (Im*C*), 120.52 (Im*C*), 106.94 (vinyl-*C*), 47.34 (N*C*H2). FT‒IR (neat, *ῡ*, cm‒1): 3419 (w), 3371 (w), 3082 (w), 3055 (w), 2970 (w), 1632 (s), 1444 (m), 1398 (s), 1329 (m), 1246 (s), 1188 (m), 1080 (w) 1040 (m), 960 (m), 913 (s), 730 (m) 680 (s).

*5.3. General procedure for the Suzuki-Miyaura reaction*

The typical procedure is as follows. Oven dried Schlenk tube was equipped with stirrer bar, was charged with aryl halides (1 mmol), aryl phenylboronic acid (1.2 mmol), K2CO3 (2 mmol) and catalyst **2** (3 mol %) in1:1 mixture of DMF/H2O medium. The reaction mixture was stirred in an oil bath at 100oC in the presence of air. After completion of the reaction, the reaction mixture was then cooled to room temperature and diluted with Et2O/H2O (1:1, 20 mL). The organic layer was alienated and dried with anhydrous MgSO4. The product was filtered and dried under vacuum. The resulting crude compound waspurified by column chromatography on silica gel to afford the corresponding products.

*5.4. General procedure for the Heck reaction*

The typical procedure is as follows. Oven dried Schlenk tube was equipped with stirrer bar, was charged with aryl halides (1 mmol), acrylates (1.2 mmol), K2CO3 (2 mmol) and catalyst**2** (3 mol %) in DMF medium. The reaction mixture was stirred in an oil bath at 100⁰C under argon atmosphere for an appropriate period of time. After completion of the reaction, the reaction mixture was then cooled to room temperature and diluted with Et2O/H2O(1:1, 20 mL). The organic layer was alienated and dried with anhydrous MgSO4. The product was filtered and dried under vacuum. The resulting crude compound waspurified by column chromatography on silica gel to afford the corresponding products.

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**Appendix A. Supplementary data**

Supplementary data (1H and 13C NMR spectra of the synthesized complex. Catalysis protocols and characterization data of coupling products) related to this article can be found at. CCDC 1832286. Single crystal X-ray data can be obtained free of charge from the Cambridge Crystallographic Data center via [www.ccdc.cam.ac.uk/data\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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**Scheme 1.** Synthesis of **2**.

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**Figure 1.** Top: The solid state structure of **2**. Two water molecules and two bromide ions have been omitted for clarity. Bottom: The geometrical representation of nickel centre in **2**. Two water molecules, two bromide ions and hydrogen atoms on carbons have been omitted for clarity.

**Figure 2.** Effect of catalyst (mol%) with respect to time on amination of aryl chlorides

**Figure 3.** Effect of catalyst (mol%) and base on Heck coupling of iodobenzene with butyl acrylate.

**Figure 4.** Effect of solvent on Heck coupling of iodobenzene with butyl acrylate.

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**Table 1.** Crystal data and structure refinement parameters of **2**.

**Table 2**. Selected structural parameters of **2**.

**Table 3.** Evaluation of conditions for the Suzuki-Miyaura cross-coupling reaction using **2**.

**Table 4.** Complex **2** catalyzed Suzuki-Miyaura coupling of aryl halides and arylboronic acids

**Table 5.** Complex **2** catalyzed Heck coupling of aryl halides and acrylates