Research paper

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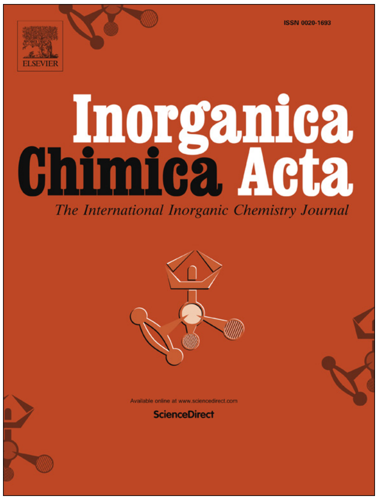

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Synthesis, structure and catalytic applications of octahedral nickel(II) benzoylhydrazone complex: Suzuki-Miyaura cross-coupling reaction of aryl bromides with arylboronic acid

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Abstract

A simple route for the synthesis of a new octahedral nickel(II) complex (**1**) containing 4-chloro-benzoic acid pyridin-2-ylmethylene-hydrazide ligand (HL, where H represents the dissociable proton) has been described. The characterisation of the complex having the formula [Ni(μ_3-O,N,N-L)$_2$] has been established by elemental analysis, ESI-MS, spectral methods and single crystal X–ray crystallography. Further, the new complex was found to act as an active homogeneous catalyst for the Suzuki-Miyaura reaction of substituted aryl bromides (mono and dibromides) with various arylboronic acids having different electronic effects under optimized conditions of solvent, base and catalyst loading. The biphenyl and triphenyl derivatives were obtained in moderate to excellent isolated yields.

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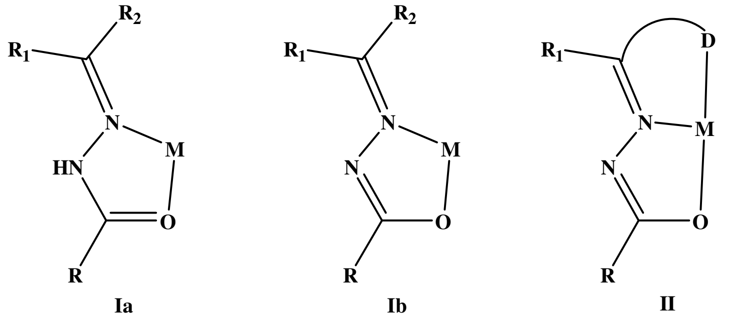
Keywords: Benzoylhydrazone ligand, Nickel(II) complex, Characterisation, Crystal structure, Suzuki-Miyaura reaction.

1. Introduction

Schiff bases are considered as ‘privileged ligands’ due to the fact that they are able to stabilize many different metals in distinct oxidation states, have chelating structure and are kinetically inert. Schiff bases can control the performance of metals in a diverse range of applications and can act as effective catalysts in organic synthesis [1-5], dyes and light emitting materials [6-8], biologically active substances [9,10], etc.. Acid hydrazones are unique and multifaceted N- and O- donor Schiff bases that possess synthetic flexibility and exhibit amide–imidol tautomerism. From a structural perspective, acid hydrazones are fascinating on account of their coordination versatility towards a diverse range of transition metals (Scheme 1). The coordination behaviour of acid hydrazones depend on metal ion, the pH of the medium, the nature of the substituent and position of hydrazone group relative to other nucleus. They can coordinate to a metal ion, *via* the azomethine–N either in the neutral amide form (**Ia**) or in the monoanionic imidolate form (**Ib**), as bidentate N,O donor ligands forming five–membered chelate rings with the metal [11-13]. When a third donor site (D) is incorporated into the acid hydrazone ligands, tricoordination (**II**) may take place resulting in the formation of 5,5- or 5,6-membered chelate rings [14,15].



Scheme 1. Coordination modes of acid hydrazone ligands

Biaryl and triaryl moieties are important structural framework found in fine chemicals, pharmaceuticals, agrochemicals, natural products and electronic materials [16-18]. Pd–catalyzed Suzuki–Miyaura reaction between an arylhalide and an arylboronic acid has become a mainstay of modern synthetic organic chemistry in the construction of carbon-carbon bonds for the preparation of bi- and triaryl compounds [19-21]. This C-C cross-coupling reaction offers many advantages such as mild reaction conditions, commercial availability of a large number of air and water stable boronic acid derivatives, easy handling, easy removal of boron residues as well as the low toxicity of reagents and by-products, thus explaining the increasing interest in academic and industrial research. However, the high cost of palladium has resulted in the exploration of less costly transition metals as alternatives to palladium systems for cross–coupling reactions while still retaining high levels of efficiency and functional group tolerance. Nickel appears to be the most promising replacement for palladium as catalysts for Suzuki–Miyaura reactions. The low cost, low toxicity and high reactivity of nickel is attractive, and a range of substrates have been shown to undergo nickel–catalyzed C–C coupling reactions. Nickel complexes containing various ligands have been developed as effective catalysts for the Suzuki–Miyaura reaction [22-25]. In addition, to the best of our knowledge the use of octahedral nickel(II) complex containing a benzoylhydrazone ligand as catalyst for the Suzuki–Miyaura cross–coupling reaction has not been explored so far.

As a part of our ongoing research on the synthesis, structural characterisation and catalytic applications of transition metal complexes [26-28], herein we report the synthesis and characterisation of a new octahedral Ni(II) complex (**1**) bearing a N,N,O– donor benzoylhydrazone ligand. The structure of the complex has been probed with the help of single crystal X-ray diffraction analysis. Further, the catalytic efficiency of the complex has been investigated for the homogeneous Suzuki–Miyaura cross–coupling reaction of aryl bromides (mono and dibromides) with substituted phenylboronic acids under optimized reaction conditions.

2. Experimental Section

2.1. Materials

$Ni(OAc)_2·4H_2O$ was purchased from Loba Chemie Pvt. Ltd, and used as received. Pyridine-2-carboxaldehyde, 4-chlorobenzoylhydrazide as well as the substrates for Suzuki-Miyaura reactions were purchased from Sigma-Aldrich and used without any further purification. All other reagents used were purchased from commercially available sources. The solvents were freshly distilled prior to use following the standard procedures [29].

2.2. Physical measurements and instrumentation

Microanalysis (C, H, N) was recorded by an Elementar Vario EL III analyzer. Magnetic susceptibility measurement was performed with the help of a Sherwood scientific balance. A Digisun DI-909 conductivity meter was used to measure the solution electrical conductivity. Mass spectrometric analysis was performed using the ESI technique on a Waters Q-TOF Micro mass spectrometer in solution of DMF. Infrared spectra were recorded in KBr pellets with a Perkin–Elmer 597 spectrophotometer in the range 4000–400 cm^{-1}. The NMR spectra were recorded with a Bruker 400 MHz spectrometer. The electronic spectra were recorded in DMSO solution with a Cary 300 Bio UV–Vis Varian spectrophotometer in the range 800–260 nm using cuvettes of 1 cm path length.

*2.3. Synthesis of the nickel(II) complex (**1**)*

An ethanolic solution (10 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.10 mmol) was added dropwise to a stirred ethanolic solution (10 mL) of HL (0.20 mmol). The reaction mixture was refluxed for 1 h and the progress of the reaction was monitored using TLC. The deep red solution formed was filtered and cooled to room temperature. Red single crystals of the complex (**1**) suitable for single crystal X-ray diffraction studies were obtained on slow evaporation of the reaction mixture over a period of 10-15 days. Colour: Red; Yield: 130 mg, 75%; Anal. Cald. for $C_{26}H_{18}Cl_2N_6NiO_2$: C, 54.02; H, 2.78; N, 14.54%. Found: C, 54.18; H, 2.81; N, 14.47%. ESI-MS Found m/z: 579.00 (11%), 577.00 (100%), 566.00 (10%), 434.61 (10%), 421.86 (80%), 423.00 (19%), 356.00 (10%), 300.83 (56%), 255.97 (10%). μ_{eff} (300 K) = 2.96 BM. Molar conductance, Λ_M (1×10^{-3} M, DMF): 8 S cm^2 mole^{-1}. Selected IR frequencies (KBr, cm^{-1}) (Symbols: s, strong; m, medium; w, weak): 2912(s), 1586(s), 1492(s), 1460(s), 1281(s), 1136(m), 1075(s), 915(w), 710(m), 693(m), 520(w). UV-Vis (DMSO, λ_{max}/nm; ε/dm^3 mol^{-1} cm^{-1}): 411 (sh, 10920), 393 (13320), 303 (5790), 287 (5730).

2.4. X-ray crystallography

Single crystals of complex **1** suitable for X–ray diffraction analysis were obtained by slow evaporation of the reaction mixture of the complex at room temperature. The data collection was carried out using Bruker AXS Kappa APEX II single crystal X–ray diffractometer using monochromated Mo K_α radiation (λ = 0.71073 Å). The absorption corrections were performed by multi-scan method using SADABS software [30]. Corrections were made for Lorentz and polarization effects. The structures were solved by SIR92 [31] and refined by full–matrix least squares on F^2 using SHELXL 97 [32]. All non–hydrogen atoms were refined anisotropically and the hydrogen atoms in these structures were located from the difference Fourier map and constrained to the ideal positions in the refinement procedure. The unit cell parameters were determined by the method of difference vectors using reflections scanned from three different zones of the reciprocal lattice. The intensity data were measured using ω and φ scan with a frame width of 0.5°. Frame integration and data reduction were performed using the Bruker SAINT–Plus (Version 7.06a) software [33]. The relevant data concerning data collection and details of structure refinement for the complex are summarized in Table 1.

Table 1. Crystal data and structure refinement for the complex **1**

Empirical formula	$C_{26}H_{18}Cl_2N_6NiO_2$
Formula weight	576.07
Colour	Red
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.126(2)
b (Å)	13.539(3)
c (Å)	17.517(4)
β (°)	93.428(3)
Volume (Å^3)	2397.2(9)
Z	4
Calculated density (g m^{-3})	1.596
Absorption coefficient (mm^{-1})	1.071
F(000)	1176
Crystal size (mm)	0.38 x 0.28 x 0.19
Theta range (°)	1.90 to 26.00
Limiting indices	$-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $-21 \leq l \leq 21$
Reflections collected/unique	4698/4286
Refinement method	Full–matrix least–squares on F^2
Data/restraints/parameters	4698/0/334
Goodness–of–fit on F^2	1.079
Final *R* indices [I>2σ(I)]	$R_1 = 0.0386$, $wR_2 = 0.0952$
R indices (all data)	$R_1 = 0.0425$, $wR_2 = 0.0976$
Largest diff. peak and hole	0.006 and 0.001 e. Å^{-3}

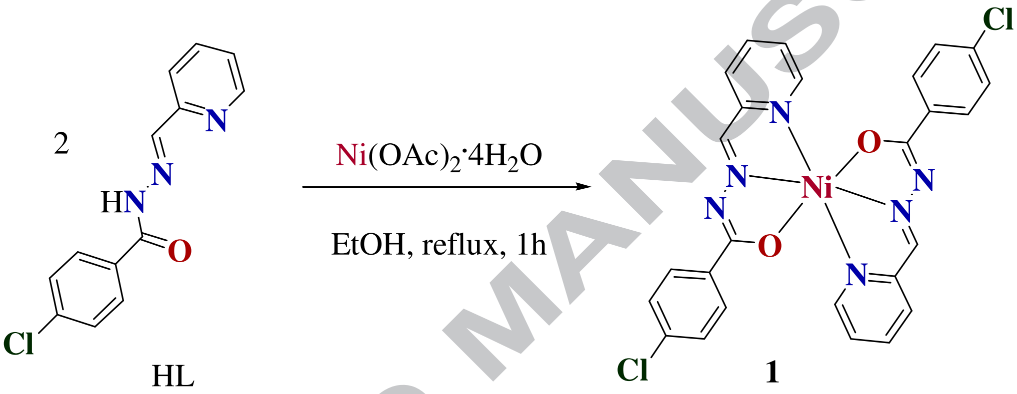
2.5. Typical procedure for the Suzuki-Miyaura reactions

To a mixture of a monobromide (1.0 mmol), arylboronic acid (1.0 mmol) and K_2CO_3 (2.0 mmol) in toluene (10 mL), **1** (0.5 mol%) were added. The resultant mixture was refluxed for 8 h, the reaction mixture was then cooled to room temperature, H_2O (10 mL) added and the organic layer was extracted with EtOAc (3 x 20 mL). The solvent was stripped off and the remaining residue was purified by column chromatography (*n*-hexane–EtOAc) to yield the pure product. The products were confirmed by ^{1}H NMR. For the double cross-coupling reaction the procedure was similar to that mentioned above where dibromide (1.0 mmol), arylboronic acid (2.0 mmol), **1** (1.0 mol%) and K_2CO_3 (4.0 mmol) in toluene (10 mL) were used.

3. Results and discussion

3.1. Synthesis and some properties

The Schiff base, 4–chloro–benzoic acid pyridin–2–ylmethylene–hydrazide, (HL, where H stands for the dissociable proton) was obtained in ~85% yield by the condensation of pyridine–2–carboxaldehyde and 4–chlorobenzhydrazide by following a procedure reported earlier [34]. The purity of HL was authenticated by IR, ESI-MS and ^{1}H NMR measurements. Treatment of $Ni(OAc)_2{\cdot}4H_2O$ with two equivalents of HL in ethanol under reflux resulted in the formation of the new red octahedral nickel(II) complex (**1**) of the formula, $[Ni(\mu_3\text{-O,N,N-L})_2]$ (Scheme 2). The complex is soluble in solvents such as dichloromethane, chloroform, methanol, toluene, dimethylformamide, dimethyl sulphoxide, acetonitrile, etc., producing intense red solution. It is non-hygroscopic and air stable in both solid and liquid states at room temperature. The complex has non-electrolytic nature in solution. The observed elemental analysis data of **1** was consistent with its composition and it appears from the formulation that the Schiff base coordinate to the nickel(II) centre as a monobasic tridentate ligand. The mass spectral study for the complex was investigated and selected mass fragmentations are listed in the Experimental Section. The obtained results definitely confirmed the molecular formula of the complex. The ESI spectrum of **1** show distinct m/z $\{M+H\}^+$ and $\{M+2+H\}^+$ peak patterns at 577 and 579 respectively, due to Ni-58 and Ni-60 isotopes. Magnetic susceptibility studies revealed that the complex is paramagnetic (μ_{eff} = 2.96 BM) at room temperature and is consistent with high spin configuration of a distorted octahedral environment around the nickel(II) centre [35].



Scheme 2. Synthesis of the nickel(II) complex

3.2. Spectral characterization

Infrared spectra of HL and **1** showed many vibrations of variable intensities in the region 4000-400 cm^{-1}. However, the assignment of the individual band to a specific vibration has not been attempted. The complex displays a $\nu_{C=N}$ stretch at 1586 cm^{-1} which is at a lower frequency than that of the free HL (1610 cm^{-1}) indicating coordination of azomethine nitrogen to Ni(II) ion. This is further supported by an increase in the ν_{C-H} stretching frequency of the azomethine moiety in **1** (2912 cm^{-1}) when compared to that of the free HL (2859 cm^{-1}). The free HL displayed ν_{N-H} and $\nu_{C=O}$ stretching frequencies at 3225 and 1670 cm^{-1} respectively. These bands were not observed in **1**, suggesting enolisation and subsequent coordination of the imidolate oxygen to Ni(II) ion. This is further supported by the appearance of new stretching frequency due to $\nu_{C–O}$ (1281 cm^{-1}) in **1** [36]. The electronic spectra of the free HL and **1** were recorded in DMSO solution at room temperature. The free HL showed strong absorption at 298 nm (ε = 22400 M^{-1} cm^{-1}) which was ascribed to the ligand centered n → π^* transition. The band showed a hypochromic shift in **1**; the decrease in intensity may be attributed to the coordination of the hetero-atoms in HL to the metal centre. In addition, **1** displayed absorptions at 393 nm and shoulder at 411 nm which were assigned to ligand-to-metal-charge-transfer (LMCT) transitions. The electronic absorption data of **1** in solution suggests an octahedral structure [37], which was further confirmed with X-ray crystal structure analysis.

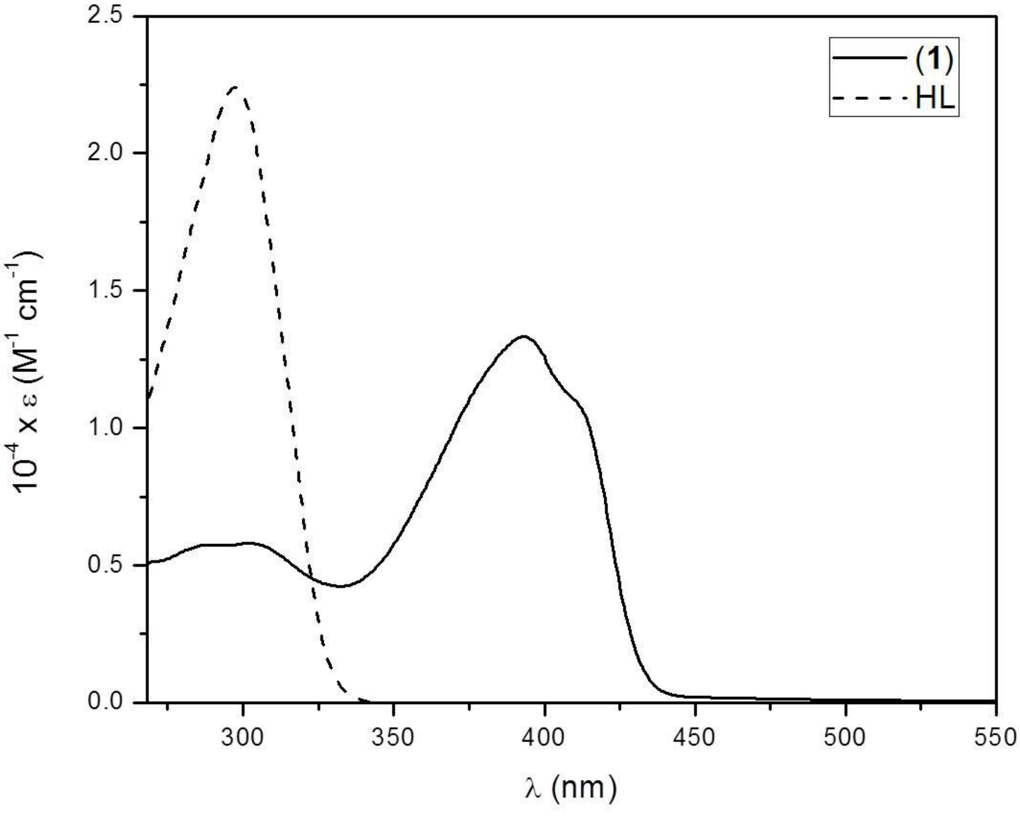


Figure 1. Electronic spectra of HL (dashed line) and **1** (solid line) in DMSO.

*3.3. Single crystal X-ray structure of **1***

The molecular structure of the complex **1** has been probed by single crystal X–ray diffraction to confirm the coordination mode of the ligand and geometry of the complex. The ORTEP view of complex **1** with ellipsoids of 30% probability along with the atom numbering scheme is shown in Figure 2 whereas selected bond parameters are listed in Table 2. The complex crystallizes in a monoclinic system with $P2_1$/n space group. The complex consists of two aroylhydrazone ligands coordinating to the nickel(II) ion in a tridentate fashion to afford a six–coordinate geometry by employing the following donor atoms of each L^- ion: a pyridyl–N, an imine–N and an enolate–O. The chelate donor atoms adopt a meridional coordination mode; thus the two imine-N atoms occupy *trans* positions whereas each of the two pairs of pyridyl–N atoms and enolate–O atoms takes adjacent positions to give a *trans*,*cis*,*cis*–coordination arrangement consistent with the rigidity and planarity of the Schiff-base ligand. Nickel is therefore sitting in a N_4O_2 coordination environment from the two ligand units and the complex has a distorted octahedral geometry as is reflected in the bond parameters around metal centre. Two five membered chelate rings are formed by each ligand. Around the nickel(II) ion, the chelate bite angles in the five membered rings formed by the pyridine-N and imine-N (78.44° and 78.37°) are slightly larger than that formed by the amide-O and imine-N (76.10° and 75.86°), indicating a better chelation in the latter ring. The N–N, N–C and C–O bond distances in the =N–N=C(O^-)– moiety of the coordinated benzoylhydrazone are consistent with the enolate form of the amide function. The Ni–N(pyridine), Ni–N(imine) and Ni–O bond distances observed are also in good agreement with reported data on related nickel(II) acid hydrazone complexes [35-41]. The *trans* angles, O(1)–Ni–N(1) = 154.37°, N(2A)–Ni–N(2) = 171.08° and O(1A)–Ni–

N(1A) = 154.21°, show significant deviation from the expected 180° which could be due to the rigidity of the coordinated planar ligand.

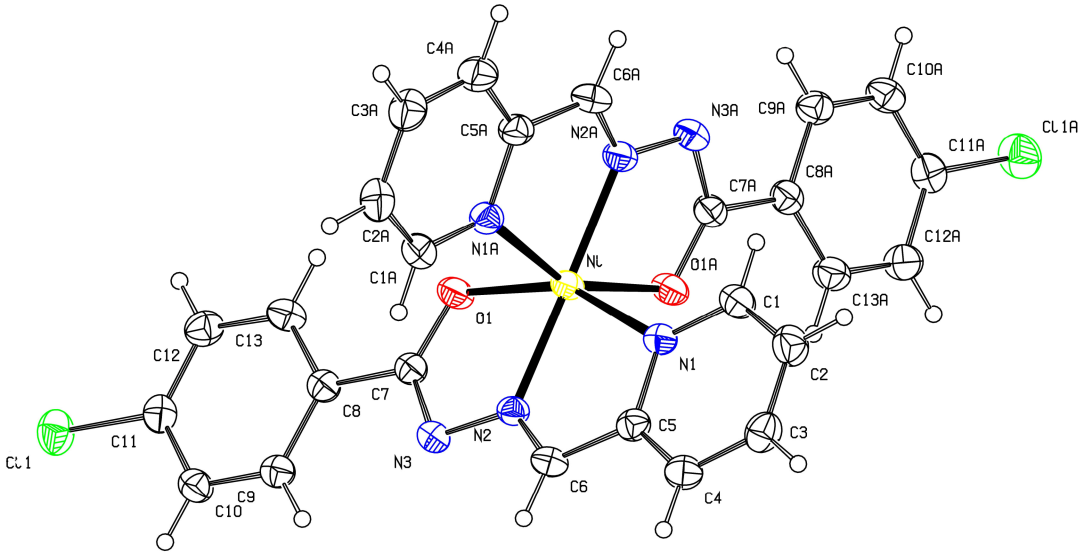


Figure 2. ORTEP view of **1** at 30% probability.

Table 2. Selected bond parameters for the complex **1**

Bond lengths (Å)		Bond angles (°)	
Ni-N1	2.1127(19)	N2-Ni-N1	78.44(7)
Ni-N2	1.9821(19)	N2-Ni-O1	76.10(7)
Ni-O1	2.0936(17)	O1-Ni-N1	154.37(7)
N3-N2	1.359(2)	C7-N3-N2	108.04(17)
N3-C7	1.340(3)	O1-C7-N3	125.8(2)
O1-C7	1.264(3)	N2A-Ni-N1A	78.37(8)
Cl1-C11	1.742(2)	N2A-Ni-O1A	75.86(7)
Ni-N1A	2.136(2)	O1A-Ni-N1A	154.21(7)
Ni-N2A	1.9804(19)	C7A-N3A-N2A	108.41(18)
Ni-O1A	2.1128(17)	O1A-C7A-N3A	125.5(2)
N3A-N2A	1.358(3)	N1-Ni-N1A	90.65(8)
N3A-C7A	1.343(3)	N2A-Ni-N2	171.08(8)
O1A-C7A	1.262(3)	O1-Ni-O1A	93.39(7)
Cl1A-C11A	1.748(3)		

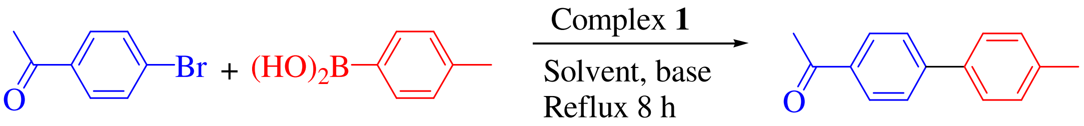
ESD in parenthesis

*3.4. Catalytic activity of **1***

3.4.1 Optimization of solvent and base

The coupling reaction between 4'–bromoacetophenone with 4–methylphenylboronic acid to yield 1-(4'-methyl-biphenyl-4-yl)-ethanone using **1** as catalyst was selected as a model reaction (Table 3). Various solvents were screened in the beginning (entries 1–5). As can be inferred from the scrutiny of the obtained results, the reaction proceeded relatively well in toluene under reflux. Among the different bases screened (entries 5–10) in toluene, K_2CO_3 gave excellent results. Other bases were less active or inactive under the studied conditions. Controlled experiments also indicated that no cross–coupling product was observed in the absence of the catalyst or base. For further optimization reaction, K_2CO_3 in toluene was used.

Table 3. Optimization of reaction conditions[a]



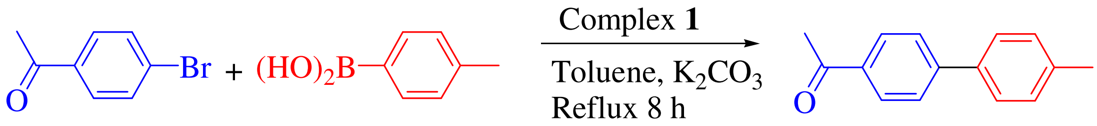
Entry	Solvent	Base	Yield[b] (%)
1	DMF	Na_2CO_3	48
2	EtOH	Na_2CO_3	52
3	1,4-Dioxane	Na_2CO_3	67
4	MeCN	Na_2CO_3	60
5	Toluene	Na_2CO_3	94
6	Toluene	K_2CO_3	98
7	Toluene	KOH	42
8	Toluene	CH_3COOK	27
9	Toluene	Et_3N	<10
10	Toluene	Pyridine	<10

[a] Reaction conditions: 4'-bromoacetophenone (1 mmol), 4-methyl-phenylboronic acid (1 mmol), base (2 mmol), complex **1** (1 mol%), solvent (10 mL), reflux for 8 h.
[b] Isolated yield after column chromatography based on arylbromide (average of two runs).

3.4.2 Optimization of catalyst loading

In order to achieve maximum conversion, the above coupling reaction was carried out under different catalyst loadings (Table 4). Good isolated yields of the coupled product were obtained when 1.0 or 0.5 mol % of the catalyst (entries 1 and 2) was used. Attempts to further decrease the catalyst loading to 0.25 or 0.125 mol % (entries 3 and 4) failed, leading to poor isolated yield. Hence, for further reactions with various substrates, catalyst loading of 0.5 mol % was used.

Table 4. Effect of catalyst loading[a]



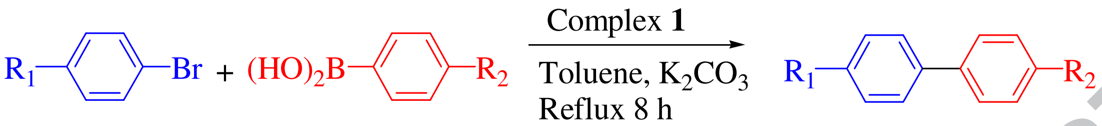
Entry	Catalyst (mol%)	Yield[b] (%)
1	1.0	98
2	0.5	95
3	0.25	70
4	0.125	36

[a] Reaction conditions: 4'–bromoacetophenone (1 mmol), 4–methylphenyl–boronic acid (1 mmol), K_2CO_3 (2 mmol), toluene (10 mL), reflux for 8 h.
[b] Isolated yield after column chromatography based on arylbromide (average of two runs).

3.4.3. Suzuki–Miyaura cross-coupling reaction of monobromides

Using the above mentioned optimized reaction conditions, the scope of the catalytic system was explored with various substituted phenylboronic acids and phenylbromides (Table 5). It was observed that all the arylbromides reacted smoothly with the various arylboronic acid derivatives and the desired biaryl compounds (entries 1–20) were formed in moderate to excellent isolated yields. It is also inferred that for a given boronic acid derivative, aryl bromides with electron-withdrawing groups (such as 4–$COCH_3$ or 4–CHO) coupled effectively and gave better isolated yields of the desired product than that of (unsubstituted) bromobenzene, which in turn gave better yields than the aryl bromides containing electron–donating groups (such as 4–CH_3 or 4–OCH_3) [42]. On the other hand, electron–donating groups (such as 4–CH_3 or 4–OCH_3) on arylboronic acid gave the best isolated yields of the desired product, whereas electron–withdrawing group (such as 4–Cl) on the arylboronic acid reduced the yields of the desired product. The yield with phenyl boronic acid (unsubstituted) is somewhere between the higher and lower ranges [43].

Table 5. Suzuki–Miyaura reaction of aryl bromides with arylboronic acids[a]



Entry	R_1	R_2	Yield[b] (%)
1	4-$COCH_3$	4-Cl	88
2	4-$COCH_3$	4-H	92
3	4-$COCH_3$	4-CH_3	95
4	4-$COCH_3$	4-OCH_3	97
5	4-CHO	4-Cl	84
6	4-CHO	4-H	89
7	4-CHO	4-CH_3	93
8	4-CHO	4-OCH_3	95
9	4-H	4-Cl	76
10	4-H	4-H	83
11	4-H	4-CH_3	89
12	4-H	4-OCH_3	92
13	4-CH_3	4-Cl	69
14	4-CH_3	4-H	77
15	4-CH_3	4-CH_3	84
16	4-CH_3	4-OCH_3	88
17	4-OCH_3	4-Cl	64
18	4-OCH_3	4-H	71
19	4-OCH_3	4-CH_3	78
20	4-OCH_3	4-OCH_3	83

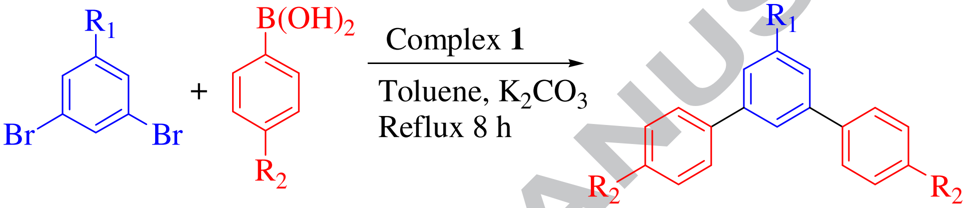
[a] Reaction conditions: Aryl bromide (1.0 mmol), arylboronic acid (1.0 mmol), complex **1** (0.5 mol%), K_2CO_3 (2.0 mmol), toluene (10 mL), reflux for 8 h.

[b] Isolated yield after column chromatography based on arylbromide (average of two runs).

3.4.4. Suzuki–Miyaura cross-coupling reaction of dibromides

Encouraged by these promising results, the protocol was also applied to the double Suzuki–Miyaura coupling reaction of dibromides with arylboronic acid derivatives to yield triaryl compounds (Table 6). The trend in the reactivity was similar to that observed as in the case of monobromo derivatives.

Table 6. Suzuki-Miyaura reaction of dibromobenzenes with arylboronic acids[a]



Entry	R_1	R_2	Yield[b] (%)
1	H	4-Cl	67
2	H	4-H	74
3	H	4-CH_3	81
4	H	4-OCH_3	89
5	CH_3	4-Cl	60
6	CH_3	4-H	68
7	CH_3	4-CH_3	77
8	CH_3	4-OCH_3	82

[a] Reaction conditions: Dibromide (1.0 mmol), arylboronic acid (2.0 mmol), complex **1** (1.0 mol%), K_2CO_3 (2.0 mmol), toluene (10 mL), reflux for 8 h.
[b] Isolated yield after column chromatography based on dibromide (average of two runs).

The ultimate objective in designing the Suzuki–Miyaura coupling catalyst is to form active species that can catalyze the coupling of the less expensive and much less reactive aryl chloride substrates. However, no catalytic activity was observed in the coupling of 4'–

chloroacetophenone with 4–methoxyphenylboronic acid using complex **1** in toluene/K_2CO_3 under reflux even after 24 h. This trend is consistent with the increasing strength of carbon–halide bonds from aryl bromide to aryl chloride. Furthermore, the catalytic efficiency of complex **1** is found to be comparable or even superior to some of the previously reported nickel(II) catalysts for the Suzuki–Miyaura reaction of arylbromides with arylboronic acids [44-49]. When compared to nickel, palladium complexes are much more efficient catalysts for this coupling reaction and excellent conversions have been reported even for the less reactive aryl chlorides at low catalyst loading [50,51]. Much recent attention in Suzuki–Miyaura cross-coupling has been focused on the nickel catalysts because nickel is much cheaper and more abundant in earth than the palladium metal. Therefore, the use of nickel catalysts would be far more cost-effective, unless a coupling reaction is workable with a very low level of palladium loading, or only with a very high nickel catalyst loading. On the other hand, the redox state of palladium is typically Pd(0)/Pd(II), albeit the catalysis chemistry of high valent palladium such as Pd(III) and Pd(IV) has been increasingly investigated in recent direct C–H functionalization. In contrast, the early transition metal nickel usually displays Ni(0)/Ni(II) as well as Ni(I)/Ni(III) oxidation states and is more nucleophilic due to its smaller size. As such, nickel cannot be simply considered to be a substitute for palladium, it possesses distinctive catalytic properties that palladium does not have. Indeed, extensive studies have clearly demonstrated that the nickel-based catalysts were more versatile and powerful catalysts for the C–C, C–N, and C–P bond forming reactions of a diverse class of electrophiles, which are conventionally challenging in the presence of palladium catalysts [23,25,52].

4. Conclusions

In conclusion, a new octahedral nickel(II) complex bearing monoanionic tridentate N,N,O- donor benzoylhydrazone ligand was synthesized and characterized by ESI-MS, analytical, spectral and X–ray diffraction studies. The utility of the complex as an effective catalyst for the Suzuki–Miyaura cross–coupling reaction has been highlighted by the coupling reaction of a variety of aryl bromides with various arylboronic acids under optimized reaction conditions. The biphenyl and triphenyl derivatives were obtained in moderate to excellent isolated yields.

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with Cambridge crystallographic center, CCDC No. 916211. Copies of this may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, 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. Supplementary data (ESI-MS of HL and **1**) associated with this article can be found in the online version.

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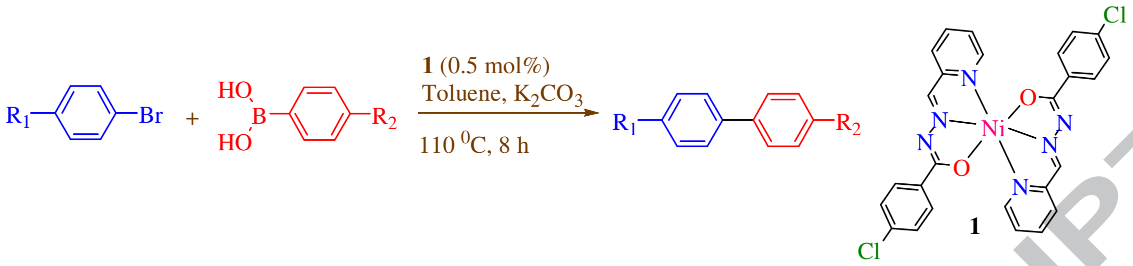
Graphical Abstract - Pictogram



Graphical Abstract - Synopsis

The synthesis and characterization of octahedral nickel(II) benzoylhydrazone complex is described. The complex was used as a potential catalyst for the Suzuki-Miyaura cross-coupling reaction of different aryl bromides with various arylboronic acids. Under optimized reaction conditions bi- and triaryls were obtained in moderate to excellent isolated yield.

Highlights

1. New Ni(II) benzoylhydrazone complex is synthesised and characterized.

2. The catalytic activity of the complex is explored for the Suzuki-Miyaura reaction.

3. Aryl bromides coupled effectively with boronic acids to form bi- and triaryls.