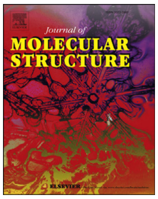
Journal of Molecular Structure 1134 (2017) 85–90

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Synthesis, characterization and crystal structure of Cu(II) complex of *trans*-cyclohexane-1,2-diamine: Application in synthesis of symmetrical biaryls

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ARTICLE INFO

Article history:
Received 29 October 2016
Received in revised form
20 December 2016
Accepted 20 December 2016
Available online 24 December 2016

Keywords:
Copper complex
Crystal structure
Biaryls
C–C coupling
Homogenous catalyst

ABSTRACT

A new Cu(II) complex $[Cu(cyhxn)_2(H_2O)_2][OTf]_2$ was synthesised by the reaction of ligand cyhxn (cyhxn = *trans*-cyclohexane-1,2-diamine) with $Cu(OTf)_2$ in methanol at room temperature. The complex was fully characterized by elemental analysis (CHN), FT-IR, UV–Vis and EPR spectroscopic techniques. The structure of the complex was confirmed by single crystal X-ray diffraction study. The EPR spectrum is isotropic type having $g_{iso} = 2.078$, which indicates a distorted octahedral geometry of the complex. The complex was found to be an active homogeneous catalyst for the homocoupling reactions of arylboronic acid to obtain symmetrical biaryls at room temperature in methanol without the use of any additives such as a base and or an oxidant.

1. Introduction

The coupling reactions are one of the most important tool in organic synthesis for formation of C–C and C–X bonds (X = N, O, S etc) [1,2]. During the last two decades, the C–C bond formations have allured much interest and revolutionized the organic synthesis [3]. The C–C bond formation has emerged as an important synthetic methodology for generating more complicated organic compounds from simpler ones [4]. Specifically, the C–C coupling products, symmetrical and unsymmetrical biaryls, are in huge demand in synthesis of natural products, fine chemicals [5–11], agrochemicals and optically active ligands [12]. They are synthesised by various methods reported in literature such as, Suzuki reaction [13], Ullmann reaction [14], and Kumada-Corriu-Tamao reaction [15] etc. Suzuki coupling reaction is one of the most important methodology for synthesis of symmetrical biaryls from a single aryl precursor [16]. Arylboronic acids are most extensively used as a precursor for coupling reactions owing to their ease of availability, stability and non-toxic nature [17].

In 1996, the homocoupling of arylboronic acids was first reported by Moreno-Manas et al. using palladium complexes of monodentate phosphines [18]. Consequently, homocoupling of aryl boronic acid using palladium-based catalysts are frequently used [19]. However, reported methods have some limitations. Palladium is expensive and requires additional ligands [20] and stoichiometric amount of oxidants to stabilize and, to restore the catalytically active palladium(II) species, respectively [21]. The reaction often requires a base [22] and generally needs high temperature [23]. Other catalysts based on Au [24], Rh [25], Ni [26], Cr [27] and Cu [28–35] also have been reported to facilitate the homocoupling of arylboronic acids. Recently, Singh et al. reported Ru-catalyzed oxidative homocoupling of arylboronic acid [36]. However, Cu-based catalysts such as $Cu(OAc)_2$ [28], $[\{(1,10\text{-phenanthroline})Cu(\mu\text{-}OH)\}_2Cl_2]\cdot 3H_2O$ [29], $CuSO_4$ [30], CuCl [31], Fe_3O_4 nanoparticles-supported Cu(II)- β-cyclodextrin complex [32], Cu terephthalate metal organic frameworks [33], nano rod CuO [34] and CuFAP [35] have emerged as cheap catalysts for obtaining symmetrical biaryls by the homocoupling reaction of arylboronic acids.

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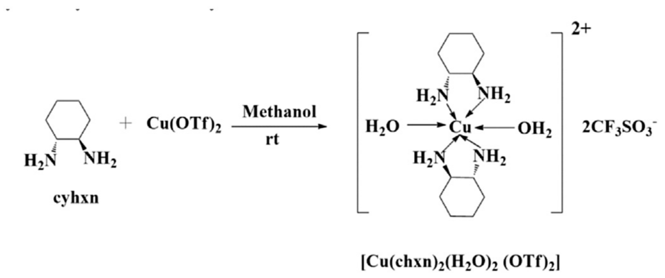
http://dx.doi.org/10.1016/j.molstruc.2016.12.053

Table 1
Crystal data and refinement parameters of $[Cu(cyhxn)_2(H_2O)_2][OTf]_2$ complex.

CCDC deposition number	1473725
Chemical formula	$C_{14}H_{32}CuF_6N_4O_8S_2$
Formula weight	626.09 g/mol
Temperature	103(2) K
Wavelength	1.54178 Å
Crystal size	0.080 × 0.120 × 0.180 mm
Crystal system	Monoclinic
Space group	*P2(1)/c*
Unit cell dimensions	
a (Å)	10.0558(2)
b (Å)	10.2611(2)
c (Å)	25.0451(4)
α (°)	90
β (°)	99.2522(9)°
γ (°)	90
V(Å^3)	2550.62(8)
Z	4
Density (calculated)	1.630 g/cm^3
Absorption coefficient	3.576 mm^{-1}
F(000)	1292
R_{int}	0.0398
$R_1[I > 2\delta(I)]$	0.0445
wR_2 (all data)	0.1092
Largest diff. peak and hole	0.654 and −0.492 eÅ^{-3}
R.M.S. deviation from mean	0.071 eÅ^{-3}



Scheme 1. Synthesis of $[Cu(cyhxn)_2(H_2O)_2][OTf]_2$ complex.

Majority of reported approaches involves the use of stoichiometric amount of catalyst, oxidant, co-catalyst, malodorous solvent, a base and require high temperature and prolong reaction time for completion of the reaction. In order to circumvent these inherited drawbacks, a quest for the rational design of new catalyst capable of catalyzing the reaction at room temperature without the use of a base or oxidant, was realized. Herein, we describe the synthesis and characterization of a new Cu(II) complex, $[Cu(cyhxn)_2(H_2O)_2][OTf]_2$, and its application in the synthesis of symmetrical biaryls by homocoupling reaction of arylboronic acids without the use of a base and oxidant at room temperature.

2. Experimental

2.1. Materials and instrumentations

All reagents and solvents for the synthesis and analysis were purchased from commercially sources. Trans-cyclohexane-1,2-diamine (cyhxn), phenylboronic acids and other required chemicals were purchased from Merck and Sigma Aldrich and used as received without further purifications.

FT-IR spectra were recorded on a Perkin Elmer Spectrometer (Model: Cary 660) in the range of 4000–400 cm^{-1} using KBr pellets in which MCT used as a detector with scan number 20, and resolution 8 cm^{-1}. Electronic absorption spectral analysis was recorded on a Shimadzu UV-1800 Spectrophotometer in the wave length range of 200–1100 nm using methanol as solvent. Elemental analyses were carried out using a Heraeus CHN-Rapid elemental analyzer. The NMR spectra of the isolated products were recorded on a Bruker AvIII HD-300 MHz and 400 MHz spectrometer in $CDCl_3$ using TMS as the internal Standard. Melting points were recorded on a Yazawa micro melting point apparatus.

2.2. Synthesis of $[Cu(cyhxn)_2(H_2O)_2][OTf]_2$ complex

A methanolic solution of ligand *trans*-cyclohexane-1,2-diamine (0.1142 g, 1 mmol) was added dropwise to a clear solution of Copper(II) trifluoromethanesulfonate (0.1808 g, 0.5 mmol) in methanol (10 mL). The resultant solution was stirred at room temperature for 6 h to produce a dark blue coloured solution. The diffraction quality crystals of the titled complex were obtained directly by slow evaporation of the deep bluish methanolic solution at room temperature. Yield: 0.272 g, 75%, m.p: 258 °C, Anal. Calc. for $C_{14}H_{32}CuF_6N_4O_8S_2$: C, 26.86; H, 5.15; N, 8.95. Found: C, 26.54; H, 5.32, N, 8.78. Selected FT-IR (KBr), cm^{-1}: $\nu(NH_2)$ 3332–3279, $\nu(CH_2)$ 2967–2861, ν(OH) 3463, ν(Cu–N) 628, ν(Cu–O) 514. UV–Vis [λ_{max}(nm), ε (L mol^{-1} cm^{-1})]: 243 (8940), 548 (89).

2.3. General procedure for synthesis of biaryls

In a 25-mL round-bottomed flask, a solution of copper(II) complex (2 mol %) and substituted phenylboronic acid (1.5 mmol) in methanol (5 mL) was stirred at room temperature for 3–4 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed and the product was washed with water and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure to give crude product which was purified by column chromatography by using petroleum ether/ethyl acetate (4:1) as an eluent.

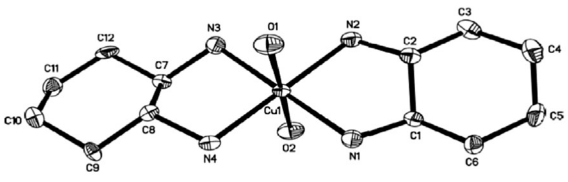


Fig. 1a

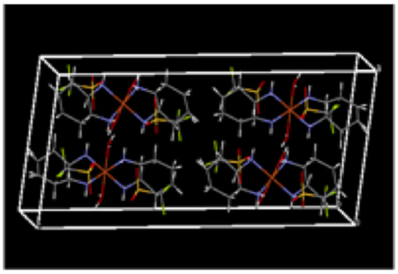


Fig. 1b

Fig. 1. **(a)** ORTEP diagram of complex $[Cu(cyhxn)_2(H_2O)_2][OTf]_2$ (Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and triflate anions are removed for clarity.) **(b)** Packing structure of complex.

Table 2
Selected bond distances (Å) and bond angles (°) of $[Cu(cyhxn)_2(H_2O)_2]$ $[OTF]_2$.

Bond distances	
Cu1–N1	2.036(2)
Cu1–N2	2.013(2)
Cu1–N3	2.036(2)
Cu1–N4	2.009(2)
Cu1–O1	2.442(19)
Cu1–O2	2.455(19)
C1–N1	1.487(5)
C2–N2	1.546(5)
C7–N3	1.536(5)
C8–N4	1.484(5)
Bond angles	
N1–Cu1–N2	84.28(9)
N1–Cu1–N3	179.71(9)
N2–Cu1–N3	95.47(9)
N1–Cu1–N4	95.89(9)
N2–Cu1–N4	179.80(9)
N3–Cu1–N4	84.36(9)
N1–Cu1–O1	86.90(9)
N2–Cu1–O1	88.27(9)
N3–Cu1–O1	93.23(9)
N4–Cu1–O1	91.63(9)

2.4. Single crystal X-ray structure determination of copper(II) complex

The X-ray diffraction intensity data were measured at 103 K with a Bruker Kappa diffractometer equipped with a CCD detector, employing Cu radiation (λ = 1.54178 Å), with the SMART suite of programs [37]. All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS [38]. All the calculation were carried out using the SHELXTL suite of programs [39]. The integration of the data using a monoclinic unit cell yielded a total of 9213 reflections to a maximum θ angle of 26.47° (0.80 Å resolution), of which 2345 were independent (average redundancy 3.929, completeness = 99.6%, R_{int} = 5.67%, R_{sig} = 5.24%) and 1875 (79.96%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.0558(2) Å, b = 10.2611(2) Å, c = 25.0451(4) Å, α = 90°, β = 99.2522(9)°, γ = 90°, volume = 2550.62(8) $Å^3$, are based upon the refinement of the XYZ-centroids of 8003 reflections above 20 σ(I) with $8.909° < 2\theta < 133.2°$. All non hydrogen atoms were refined with anisotropic thermal parameters. The cyclohexane rings are disordered, these are modelled in two alternative sites with equivalent occupancy of 0.5. Appropriate restraints (SIMU and ISOR) were applied for C3, C6, C3A and C6A atoms. A summary of the crystallographic and refinement data are given in Table 1.

3. Results and discussion

The reaction of ligand *trans*-cyclohexane-1,2-diamine and Copper(II) trifluoromethanesulfonate in 2:1 ratio in methanol at room temperature (Scheme 1) afford the complex $[Cu(cyhxn)_2(H_2O)_2]$ $[OTf]_2$ as a deep blue crystalline solid. Block shaped crystals, suitable for X-ray crystallography were obtained by slow evaporation of the blue solution at room temperature. The complex was fully characterized by elemental analysis (CHN), FT-IR, UV–Vis and EPR analysis and the structure was confirmed by single crystal X-ray diffraction study.

Table 3
Study of reaction optimization conditions.

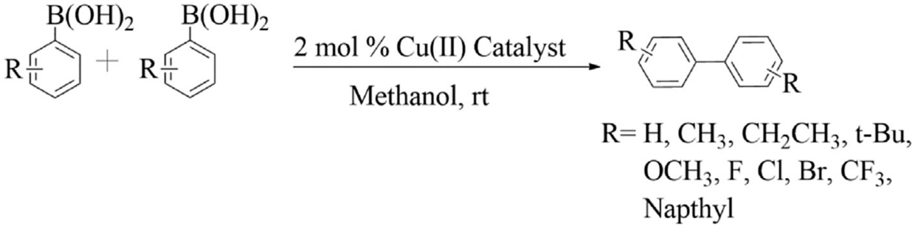
Entry	Solvent	Catalyst loading (mol %)	Time (h)	Yield, %[a]
1	CH_3OH	–	24	00
2	CH_3OH	1	05	70
3	CH_3OH	2	03	85
4	CH_3OH	5	03	75
5	H_2O	2	08	40
6	$C_6H_5CH_3$	2	08	70
7	C_6H_5CN	2	12	53
8	DCM	2	12	25
9	DMF	2	12	25

[a] Isolated yield.

3.1. X-ray crystal study

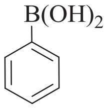
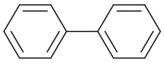
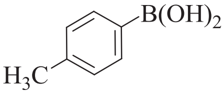
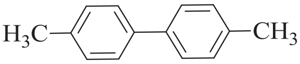
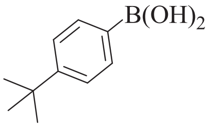
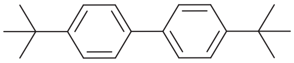
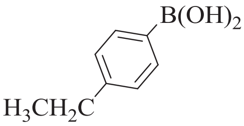
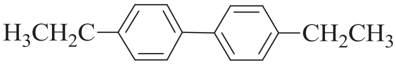
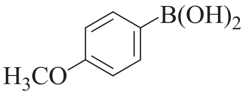
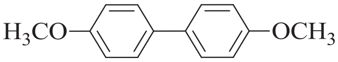
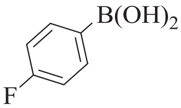
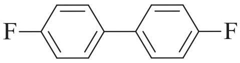
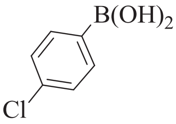
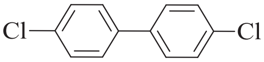
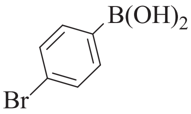
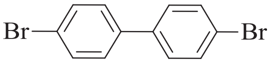
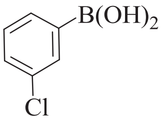
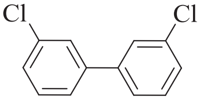
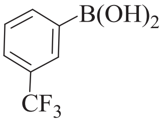
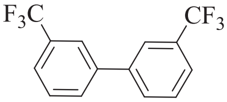
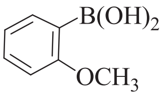
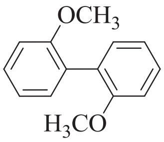
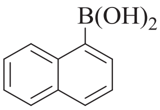
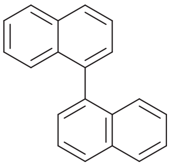
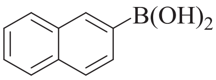
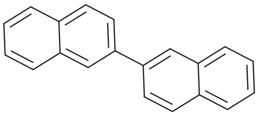
The diffraction quality crystals were obtained by the slow evaporation of methanolic solution of complex at room temperature. The structure of the complex was elucidated by single crystal X-ray diffraction. Fig. 1 represent an ORTEP view and atom-labelling scheme of the dicationic $[Cu(cyhxn)_2(H_2O)_2]^{2+}$ complex. The structure reveals a six-coordinated species with a distorted octahedral geometry. Selected bond distances and bond angles are listed in Table 2. The four nitrogen atoms of two cyclohexyldiamine molecules bind in an equatorial fashion to the copper ion which forms two five-membered rings, while the two oxygen atoms of weakly coordinated water molecules bind to copper ion in an axial fashion. The Cu–O and Cu–N bond lengths of this complex are lies in the range of 2.4425 (19) Å to 2.4555 (19) Å and 2.009 (2) Å to 2.036 (2) Å respectively, which are in close agreement with the values of previously reported other copper(II) diamine complexes [40,41]. The complex shows two types of N–Cu–N bond angles, in the range of 84.28(9)-95.89(9) and 179.71(9)-179.80(9) which are similar with previously reported Cu(II) complexes [42].

The FT-IR spectra of free ligand and complex are shown in Fig. S1 (See Supporting information). The FT-IR spectrum of free ligand shows characteristics band at 3355-3279 cm^{-1} and 2924-2851 cm^{-1} assignable to $\nu(NH_2)$ and $\nu(CH_2)$ respectively [43]. A band at 3463 cm^{-1} in the spectrum of the complex was assigned to the presence of coordinated H_2O [44]. The intense band in the IR spectrum around 1320-1170 cm^{-1} confirms the presence of triflate anion [45]. A comparison of the IR spectrum of the complex with the ligand indicated two new bands at 628 cm^{-1} and 514 cm^{-1}. These bands were assigned to ν(Cu–N) and ν(Cu–O) vibrations, respectively [46]. Presence of these bands confirms the



Scheme 2. Synthesis of biaryl derivatives.

Table 4
Synthesis of biaryls from various arylboronic acid in presence of Cu(II) catalyst under the optimized reaction conditions.

Entry	Boronic acid	Product	Time	Yield[a]
1			3	85
2			2	80
3			3	75
4			3	80
5			2.5	85
6			3	65
7			3	80
8			3	75
9			2.5	70
10			2.5	75
11			3	60
12			3	40[b]
13			3	50[b]

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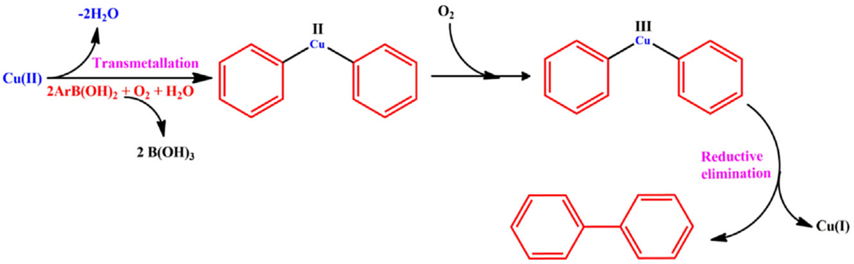
[a] Isolated yield after work up.

[b] By-product naphthalene.

Table 5
A comparison study of catalyst [Cu(cyhxn)$_2$(H$_2$O)$_2$][OTf]$_2$ with the previous reported catalysts in synthesis of biaryls.

Entry	Catalyst	Additive	Base	Temp (°C)	Catalyst loading (mol %)	Time (h)	Yield (%)	Ref.
1	Au/CeO$_2$	–	K$_2$CO$_3$	60	5	15	100	[24]
2	Fe$_3$O$_4$–Cu$_2$–β–CD	–	–	70	10	24	90	[31]
3	Pd(OAc)$_2$	[Bmim]PF$_6$	K$_2$CO$_3$	60	3.6	3	92	[20]
4	Cu(OAc)$_2$	–	–	RT	50	24	78	[27]
5	Ru catalyst	Cu(OAc)$_2$	Na$_2$CO$_3$	70	2.5	4	67	[35]
6	[Cu(cyhxn)$_2$(H$_2$O)$_2$] [OTf]$_2$	–	–	RT	2	3	85	Present work



Scheme 3. Tentative mechanism for synthesis of biaryl derivatives.

coordination of copper with N and O atoms of the ligand and H$_2$O molecule, respectively.

The UV–Vis spectra of ligand and complex are shown in Fig. S2 (See Supporting information). The UV–Vis spectra of ligand depicted a strong peak at 219 nm due to n–σ* transition of N–C bond. However, UV spectra of the complex showed a slight shift in the position and intensity of this band at around 243 nm. The spectrum of the complex also shows an additional broad band at 548 nm, assignable to $^2B_{1g} \rightarrow {}^2E_g$ transition of a tetragonally distorted Cu(II) in Octahedral geometry [47].

3.2. EPR study

The EPR spectrum of the complex recorded at room temperature is shown in the Fig.S3 (See Supporting information). The EPR spectrum of the powdered complex [Cu(cyhxn)$_2$(H$_2$O)$_2$][OTf]$_2$ at 300 K, revealed an isotropic behaviour with broad signal having $g_{iso} = 2.078$ with no hyperfine structure and confirmed a six-coordinated distorted octahedral geometry of the complex [48].

3.3. Catalytic studies

The catalytic activity of the complex was screened for the synthesis of biaryls (Scheme 2). Various phenylboronic acids were chosen as substrates. Several parameters such as catalyst loading, solvent and time were studied and optimized. The results are summarised in Table 3. Initially phenylboronic acid was chosen as an ideal substrate. On stirring a methanolic solution (without catalyst) of phenylboronic acid for 24 h at room temperature did not yield any product (Table 3, entry 1). However, when the reaction was carried out in presence of 1 mol % of the catalyst, 70% yield of the desired product was obtained in 5 h (Table 3, entry 2). Increasing the catalyst loading to 2 mol % resulted in 85% yield of the desired product in 3 h (Table 3, entry 3). However, no significant improvement in yield was observed by further increasing the amount of catalyst to 5 mol % (Table 3, entry 4). It indicated that 2 mol % of the catalyst is optimum. In order to found the best solvent, the reaction was carried out in different solvents such as, CH$_3$OH, H$_2$O, C$_6$H$_5$CH$_3$, CH$_3$CN, DCM and DMF (Table 3) at room temperature. Among all the solvents used, CH$_3$OH (Table 3, entries 2–4) was found to be the best solvent.

It can be concluded that the nature of the substituent, either electron donating or withdrawing groups, did not show a significant change in the overall yields (Table 4, entries 2–11). However, *para*- and *meta*-substituted arylboronic acids afforded biaryls in good yield (Table 4, entries 2–10). On the contrary, *ortho*-substituted arylboronic acids resulted in relatively lower yield of the product (Table 4, entries 11–12). Bulky acids afforded low yields which may be ascribed to steric effects. The reaction of 1-napthyl- and 2-napthylboronic acids yielded the expected homocoupled products in 40–50% yield only, along with protodeboronation by-products (Table 4, entries 12–13). These observations are in consonance with the previous observations [28]. The organic products were soluble in common organic solvents and fully characterized by melting point, ^{1}H and ^{13}C NMR and FT-IR spectra. The spectra are given in the supporting information (Fig. S4–Fig. S25). In order to establish the efficacy of the new catalyst [Cu(cyhxn)$_2$(H$_2$O)$_2$][OTf]$_2$, a comparison was made with the previously reported catalysts for the synthesis of biaryls in terms of temperature, time, catalyst loading etc (Table 5). The results indicate that our catalytic system exhibits better catalytic activity as compared to other reported catalysts.

A tentative mechanism for synthesis of biaryls is proposed in Scheme 3. We speculate that the reaction proceeds by coordination of aryl groups to Cu(II) centre by displacement of labile water molecules from octahedral Cu(II) complex [49], generating aryl-copper intermediate which undergoes oxidation by air to give a putative Cu(III) intermediate. This intermediate undergoes reductive elimination to give Cu(I) and the desired homocoupled product (biaryl), as reported earlier [30,34].

4. Conclusion

In conclusion, a new complex [Cu(cyhxn)$_2$(H$_2$O)$_2$][OTf]$_2$ has been synthesized and fully characterised by various spectroscopic techniques (Elemental analysis (CHN), FT-IR, UV–Vis, EPR) and by single crystal X-ray structure determination. The catalytic application of the complex has been demonstrated in the synthesis of symmetrical biaryls from arylboronic acids. The homocoupling reaction proceeds smoothly in methanol at room temperature at a low catalyst loading (2 mol %) and without the use of any additives and bases.

Acknowledgment

We are thankful to the SAIF Panjab University, Chandigarh and IISER, Bhopal for providing help in the analysis of the samples and we also grateful to NTU, Singapore for the single crystal X-ray analysis. Bhumika Agrahari, Samaresh Layek and Anuradha acknowledge the receipt of IIT (ISM), Dhanbad fellowship.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.12.053.

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