



Cobalt pincer complex catalyzed Suzuki-Miyaura cross coupling – A green approach



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ABSTRACT

A series of cobalt complexes with tridentate pincer ligands were synthesized to study their catalytic activity in Suzuki-Miyaura coupling reactions. Cobalt complexes, C-1, C-2, C-3 bearing asymmetrical PNCOP pincer ligand [$C_6H_4-1-(NHPPH_2)-3-(OPPh_2)$] (**L-1**) and symmetrical PNCNP, PNNNP pincer ligands [$C_6H_4-2,6-(NHPPH_2)_2$] (**L-2**) and [$C_5H_3N-2,6-(NHPPH_2)_2$] (**L-3**) were synthesized by the reaction of diphenylchlorophosphine with *m*-aminophenol, *m*-phenylenediamine and 2,6-diaminopyridine respectively in a 1:2 ratio in the presence of triethylamine as a base and tetrahydrofuran as solvent media. The synthesized complexes were examined for their C-C coupling efficiency in cross-coupling between phenyl boronic acid and para substituted bromobenzenes. Effect of variation of the ligand on the catalytic activity of cobalt pincer complex was explored based on the coupling yields. It is observed that as the number of 'N' atoms increases in the side arm of the ligand, the donating ability of the ligand increases which leads to the increased catalytic activity of the complex. The symmetrical PNNNP pincer complex (C-3) was found to be more effective as a catalyst among the complexes synthesized and reported in the present study.

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1. Introduction

Pincer complexes have emerged over the last two decades as a potential class of organometallic compounds capable of having extended utility in the field of homogeneous catalysis [1,2]. Ever since their introduction to the inorganic field in the late 1970s, the pincer skeletons with their tridentate arrangement of donor sites have been productively used in ligand-metal mediated catalysis, inorganic chemistry and materials science [3]. Their exceptional thermal stability often accompanied with the unique chemical stability of the σ -M-central atom and the rigid tridentate pincer motif, avoids the dissociation of the metal from the ligand. This in turn, makes the pincer metal interaction retain throughout the catalytic reactions and can attribute to the enhanced catalytic activity of the pincer complexes [4–7]. Suzuki-Miyaura cross-coupling reaction shows functional group tolerance for a wide variety of substrates which makes it an indispensable tool in organic synthesis [8,9]. Research studies reported hitherto emphasize the use of pincer complexes with mostly palladium [10–14] and some

instances, with nickel [15–17], ruthenium [18,19] for Suzuki-Miyaura cross-coupling reactions. Use of palladium metal in the complexes, even though affords high yield due to its massive catalytic activity, is an expensive affair due to the less abundance and consequently heavy cost of the metal. Metals like Ni, Ru remain close to Pd in its activity but are not appreciably environmentally benign. Therefore, if quite an analogous outcome in terms of yield and efficiency can be obtained using less expensive and substantially benevolent metal complexes, the effort positively renders an economical and a green approach towards the research study. In their review article on non precious metal complexes with anionic PCP pincer architecture, Murugesan and Kirchner [20] have provided an overview of the advancements in the pincer catalysis employing cheap and abundant metals such as nickel, cobalt, and iron with PCP pincer ligands which could result in the development of novel, versatile, and efficient catalysts for atom-efficient catalytic reactions. Their study also emphasized that the cobalt PCP pincer complexes were not applied to any catalytic reactions. Cobalt complex with NNN type pincer ligand has been reported to efficiently catalyze polymerization of 1,3-butadiene [21]. The catalytic involvement of cobalt pincer complexes in the cross coupling of aryl halides and organoboron compounds is however unreported and this fact made us opt for cobalt metal in the synthesis of pincer

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complexes for carrying out Suzuki coupling reactions. Pursuing our research interest in the synthesis of pincer complexes and their potential application on beneficial organic transformations, we report in this paper, the synthesis of PNCOP pincer complex (**C-1**), PNCNP pincer complex (**C-2**), PNNNP pincer complex (**C-3**) followed by their novel application in cross coupling of aryl halides and organoboron compounds with good yields of biaryls. Effect of variation of the ligand on the catalytic activity of cobalt pincer complex is being observed in this study report.

2. Experimental

2.1. Materials

Cobalt (II) acetate was purchased from Merck, India and used as received. Other chemicals like *m*-aminophenol, *m*-phenylenediamine, 2,6-diaminopyridine, chlorodiphenylphosphine, tetrahydrofuran (THF), triethylamine (Et₃N), acetonitrile (ACN), phenylboronic acid and aryl halides were purchased from Sigma-Aldrich and used without further purification.

2.2. Synthesis of ligands (L-1, L-2 and L-3)

2.2.1. Synthesis of [C₆H₄-1-(NHPPH₂)-3-(OPPh₂)](**L-1**)

In a round bottomed flask, *m*-aminophenol (1 g, 9.2 mmol,) was stirred in THF (20 mL). Triethylamine (1.85 g, 18.3 mmol) was added to the RB flask and stirred well. The mixture was then cooled to 0 °C and chlorodiphenylphosphine (4.04 g, 18.3 mmol) was added drop wise with stirring. The solution was warmed to room temperature and set to reflux overnight. The solution was then filtered, washed with anhydrous hexane (2 × 10 mL) and the solvent was removed under vacuum to afford ligand (**L-1**) as yellow solid.

Yield: 83.0%.

¹H NMR (400 MHz, CDCl₃) δ 7.89–7.75 (m, 9H), 7.65–7.43 (m, 15H), 4.02 (br s, 1H, NH). (Supplementary Information Fig. S1).

³¹P{¹H} NMR (161.8 MHz, DMSO): δ (ppm) 25.5 (s, PN), 31.3 (s, PO) (Supplementary Information Fig. S2).

IR (KBr): ν 3350, 3177, 3055, 1607, 1489, 1437, 1177, 1126, 982, 752, 725, 694, 557, 527 cm⁻¹.

MS-ESI: (*m/z*): 477.0 (Supplementary Information Fig. S3).

Elemental analysis calculated for C₃₀H₂₅NOP₂ (M_r = 477.1): C, 75.46; H, 5.28; N, 2.93. Found: C, 74.90; H, 5.30; N, 2.59%.

2.2.2. Synthesis of [C₆H₄-1,3-(NHPPH₂)₂](**L-2**)

m-phenylenediamine (1 g, 9.3 mmol), THF (20 mL) was taken in a RB flask, to which triethylamine (1.87 g, 18.5 mmol) was added and stirred well. The mixture was then cooled to 0 °C and chlorodiphenylphosphine (4.08 g, 18.5 mmol) was added drop wise with stirring. The solution was warmed to room temperature and set to reflux overnight. The solution was then filtered through a short plug of celite, washed with anhydrous hexane (2 × 10 mL) and the solvent was removed under vacuum to afford ligand (**L-2**) as brownish black solid.

Yield: 78.9%.

¹H NMR (400 MHz, CDCl₃) δ 7.82–7.62 (m, 8H), 7.61–7.54 (m, 4H), 7.53–7.40 (m, 12H), 4.02 (br s, 2H, NH) (Supplementary Information Fig. S5).

³¹P{¹H} NMR (161.8 MHz, DMSO): δ (ppm) 25.47 (s, PN). (Supplementary Information Fig. S6).

IR (KBr): ν 3360, 3055, 2922, 2365, 1607, 1437, 1184, 1121, 1022, 995, 750, 725, 694, 559, 529 cm⁻¹.

MS-ESI: (*m/z*): 477.1 (Supplementary Information Fig. S7).

Elemental analysis calculated for C₃₀H₂₆N₂P₂ (M_r = 476.1): C, 75.62; H, 5.50; N, 5.88. Found: C, 75.01; H, 5.41; N, 5.69%.

2.2.3. Synthesis of [C₅H₃N-2,6-(NHPPH₂)₂](**L-3**)

To a suspension of 2,6-diaminopyridine (1 g, 9.2 mmol) in THF (20 mL) was added triethylamine (1.85 g, 18.3 mmol). The mixture was then cooled to 0 °C and chlorodiphenylphosphine (4.04 g, 18.3 mmol) was added drop wise with stirring. The solution was warmed to room temperature and set to reflux overnight. The solution was then filtered, washed with anhydrous hexane (2 × 10 mL) and the solvent was removed under vacuum to afford ligand (**L-3**) as orange solid.

Yield: 87.2%.

¹H NMR (400 MHz, CDCl₃) δ 7.82–7.62 (m, 9H), 7.61–7.54 (m, 3H), 7.53–7.40 (m, 8H), 7.40–7.27 (m, 3H), 3.78–3.49 (br s, 2H, NH) (Supplementary Information Fig. S9).

³¹P{¹H} NMR (161.8 MHz, DMSO): δ (ppm) 25.46 (s, PN) (Supplementary Information Fig. S10).

IR (KBr): ν 3441, 3076, 1589, 1483, 1180, 1069, 959, 754, 727, 694, 552 cm⁻¹.

MS-ESI: (*m/z*): 478.4 (Supplementary Information Fig. S11).

Elemental analysis calculated for C₂₉H₂₅N₃P₂ (M_r = 477.1): C, 72.95; H, 5.28; N, 8.80. Found: C, 72.15; H, 5.03; N, 8.56%.

2.3. Synthesis of complexes

2.3.1. Synthesis of [Co(COOCH₃){C₆H₄-1-(NHPPH₂)-3-(OPPh₂)](**C-1**)

Cobalt acetate (0.13 g, 0.5 mmol) in THF (3 mL) was refluxed for 4 h with L-1 (0.25 g, 0.5 mmol) in THF (5 mL). Complex obtained was filtered and washed with ether. Yield: 79.6%.

IR (KBr): ν 3052, 1435, 1132, 1052, 997, 754, 727, 692 cm⁻¹.

MS-ESI: (*m/z*): 595.4 [M]⁺ (Supplementary Information Fig. S4), Elemental analysis calculated for C₃₂H₂₇CoNO₃P₂ (M_r = 594.1): C, 64.66; H, 4.58; N, 2.36. Found: C, 63.95; H, 4.41; N, 2.18%.

2.3.2. Synthesis of [Co(COOCH₃){C₆H₅-1,3-(NHPPH₂)₂]}(**C-2**)

Cobalt acetate (0.13 g, 0.5 mmol) in THF (3 mL) was refluxed for 4 h with L-2 (0.25 g, 0.5 mmol) in THF (5 mL). Complex obtained was filtered and washed with ether. Yield: 77.4%.

IR (KBr): ν 3055, 2361, 1589, 1435, 1142, 1057, 1026, 993, 756, 694, 563 cm⁻¹.

MS-ESI: (*m/z*): 594.2 [M]⁺ (Supplementary Information Fig. S8), Elemental analysis calculated for C₃₂H₂₈CoN₂O₂P₂ (M_r = 593.1): C, 64.76; H, 4.76; N, 4.72. Found: C, 63.89; H, 4.52; N, 4.43%.

2.3.3. Synthesis of [Co(COOCH₃)₂{C₅H₃N-2,6-(NHPPH₂)₂]}(**C-3**)

Cobalt acetate (0.13 g, 0.5 mmol) in THF (3 mL) was refluxed for 4 h with L-3 (0.25 g, 0.5 mmol) in THF (5 mL). Complex obtained was filtered and washed with ether. Yield: 82.3%.

IR (KBr): ν 3446, 3051, 1562, 1435, 1138, 1057, 995, 756, 729, 694, 567 cm⁻¹.

MS-ESI: (*m/z*): 655.1 [M]⁺ (Supplementary Information Fig. S12), Elemental analysis calculated for C₃₃H₃₁CoN₃O₄P₂ (M_r = 654.1): C, 60.56; H, 4.77; N, 6.42. Found: C, 59.85; H, 4.43; N, 6.28%.

2.4. General procedure for the Suzuki reaction

Aryl halide (1.0 mmol) was added to a mixture of phenylboronic acid (1.3 mmol), cobalt pincer complex (0.005 mmol) and base (2.0 mmol) in 5 mL of solvent and heated to 80 °C. The mixture was then cooled to room temperature and the organic phase analyzed by gas chromatography.

2.5. Characterization methods

The C, H and N contents of the compounds were determined by

ThermoFlash EA1112 series elemental analyzer. Magnetic susceptibility measurement was recorded on a Sherwood Scientific magnetic susceptibility balance (UK). Thermal analysis was carried out (EXSTAR-6000) from room temperature to 700 °C at a heating rate of 10 °C/min. The electronic spectrum of the complex was recorded in analytikjena SPECORD S600. FT-IR spectra were recorded on a Bruker-Alpha ECO-ATR FTIR spectrometer. ^1H NMR (400 MHz) spectrum was recorded in Bruker AV 400 instrument using TMS as internal standard. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.8 MHz) spectrum was recorded in Varian instrument using H_3PO_4 as internal standard. Molecular mass of the compounds was determined using a Waters Q-ToF micro mass spectrometer with an ESI source. The coupling reaction product analysis was carried out using Gas Chromatography (GC) (Shimadzu 2014, Japan), siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector. The column temperature was increased at the rate of 10 °C/min. Nitrogen gas was used as the carrier gas.

3. Results and discussion

3.1. Characterization studies

The procedures for the synthesis of the ligands and the complexes are shown in Schemes 1 and 2 respectively. The ligands and the complexes were characterized by FTIR, mass spectra and elemental analysis. All the results were in full agreement with the proposed structure. ^1H NMR spectral analysis of the ligands also substantiates the structures proposed for the ligands.

FTIR analysis of the ligands L-1, L-2 and L-3 showed medium intensity N-H stretching indicating the bond formation between N and P. Formation of bond between O and P in L-1 is indicated by the absence of broad peak for O-H stretching. A sharp peak at 694 cm^{-1} is assigned to the P-N stretching in both the ligands and the complexes [22]. Formation of the complex was further confirmed through magnetic susceptibility study, UV–Visible spectroscopy and Thermal analysis.

The magnetic susceptibility measurements in the solid state show that the complexes are paramagnetic at room temperature with magnetic moment values 2.34, 2.41 and 1.96 BM respectively

corresponding to the presence of one unpaired electron. The ligands which give low-spin complexes usually have donor atoms of low electronegativity such as P, As or C capable of forming π bonds [23]. Complexes, C-1 and C-2 are low spin four coordinate complexes whose magnetic moments very well matches to the calculated range of 2.1–2.9 B.M for square planar Co(II) species and magnetic moment of C-3 very much lies in the specified range for five co-ordinate cobalt(II) complexes [24,25].

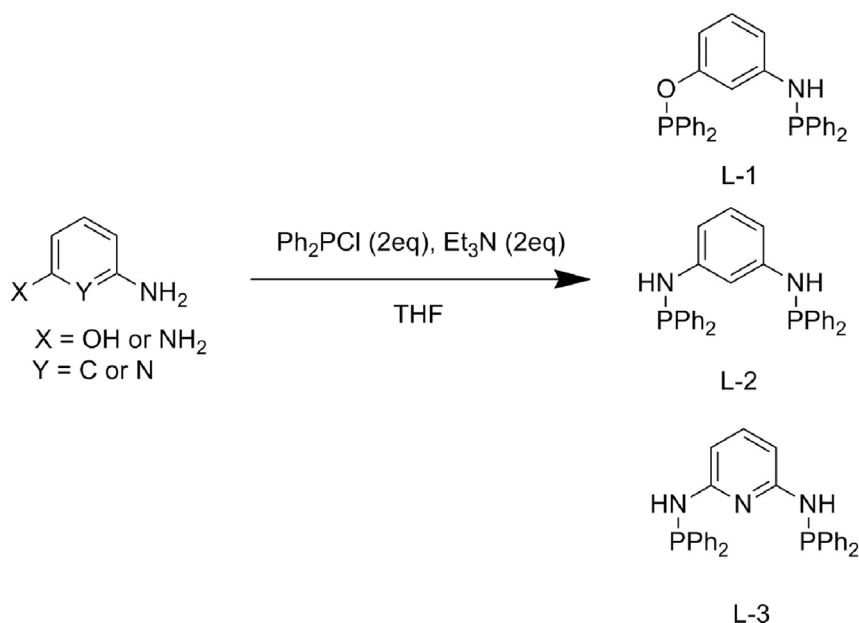
In the UV–Visible spectra (Fig. 1), there is a shift in the absorption band from the ligand to the complex perceptibly indicating the complex formation. The absorption bands observed in the spectra of the free ligand have shifted to lower energy region in the spectra of complexes due to the coordination of the ligand with metal ion. All the transitions are majorly due to intra ligand charge transfer transitions (ILCT) and ligand to metal charge transfer transitions (LMCT).

The thermal analysis (TGA) result of the complexes is represented in the Fig. 2. The TG curves obtained are typical curves representing single step dissociation of the complexes. The dissociation of the ligands is observed well after the temperature of 500 °C indicating the exceptional stability of the pincer complex formed. The TGA curves also support the proposed structures of the complexes with respect to the weight loss of the ligands and residual mass as cobalt oxide.

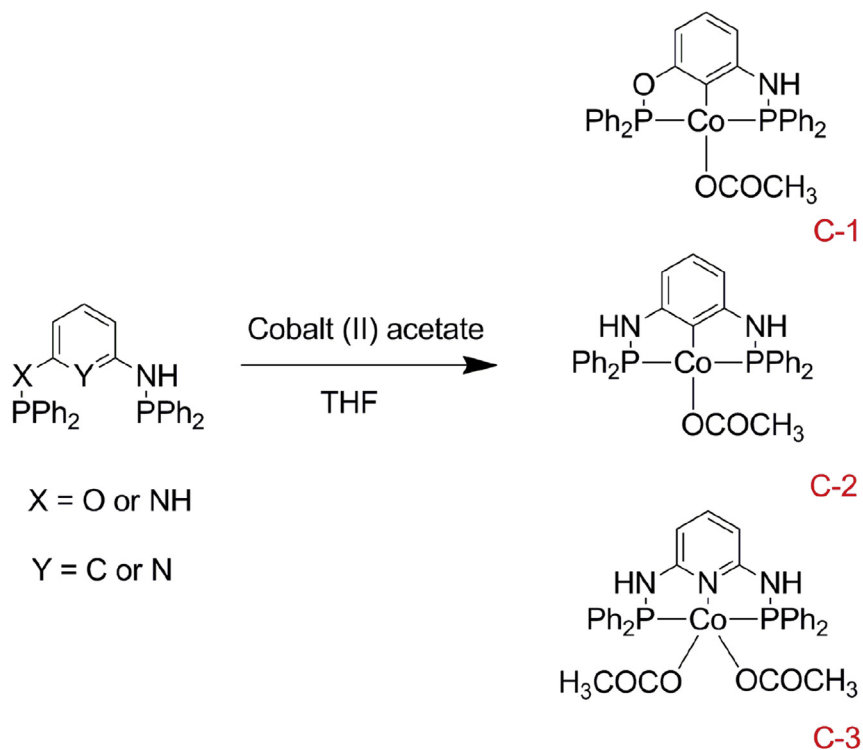
3.2. Catalytic activity studies

Pincer complexes have been considerably employed to catalyze cross coupling of aryl halides with organoborons since their advent to the field of catalysis. Researchers have explored different ways to enhance the catalytic activity for C–C cross coupling using pincer complexes, however with palladium as the chief catalyzing metal. An optional and alternative method to complement the existing approach of catalysis is emphatically the use of 3d transition metal complexes. The synthesized complexes using cobalt as the catalyzing metal explicitly corroborates the green approach and provides an alternative inexpensive catalyst for Suzuki cross coupling.

The reaction between 4-bromobenzonitrile and phenyl boronic acid was chosen as a model reaction to evaluate the catalytic



Scheme 1. Synthesis of ligands: a) PNCOP pincer ligand (L-1); b) PNCNP pincer ligand (L-2); c) PNNNP pincer ligand (L-3).



Scheme 2. Synthesis of complexes C-1, C-2 and C-3.

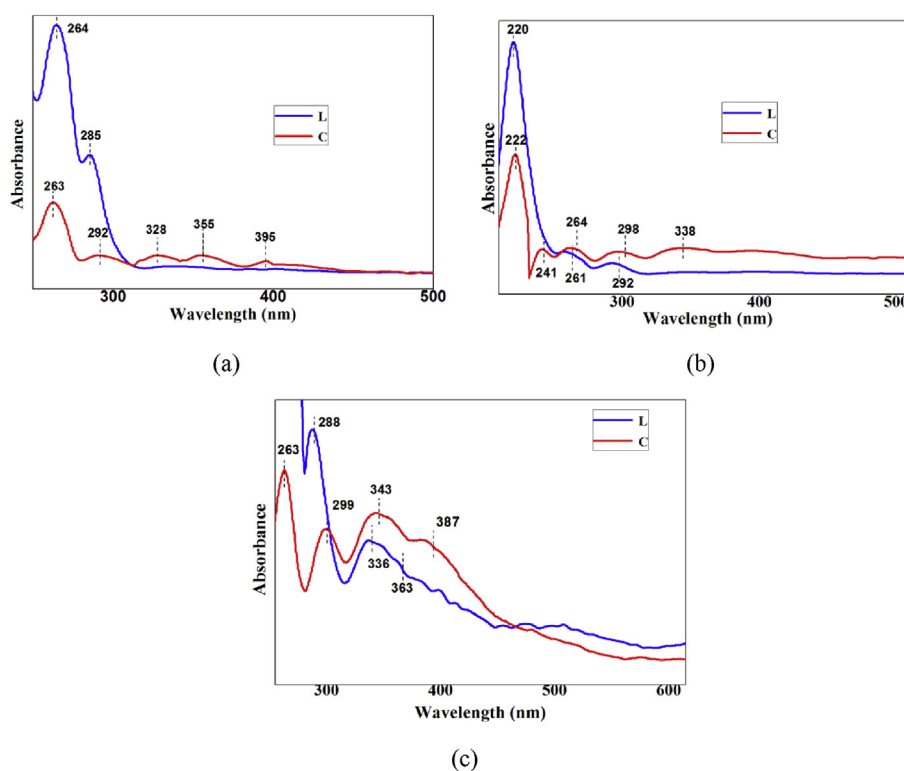


Fig. 1. UV–Vis spectrum of: a) Ligand L-1 and complex C-1 (b) Ligand L-2 and complex C-2 (c) Ligand L-3 and complex C-3.

activity of the Co-pincer catalyst (C-3) in the Suzuki coupling of aryl halides with phenyl boronic acid. Various factors including solvent, catalyst loading, base, temperature and time were screened to

optimize the reaction conditions. The results are summarized in Tables 1–3. Amongst the solvents tested (Fig. 3), highest catalytic activity was observed with dioxane as the solvent media (Table 1,

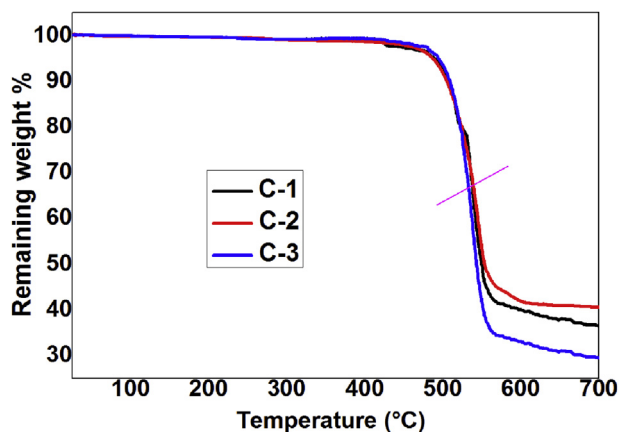


Fig. 2. TGA curves of the complexes C-1, C-2 and C-3.

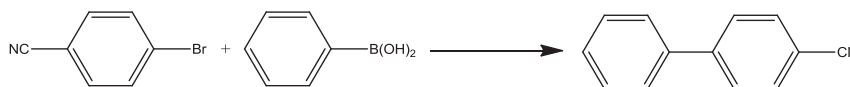
acetonitrile as a solvent may be attributed to the property of acetonitrile to act in itself as a ligand with its exceptional coordinating property. The other parameter considered for optimization is the reaction temperature. As illustrated in Table 1 (entries 6 & 7), 80 °C is the best temperature for the chosen reaction in acetonitrile media.

Catalyst loading for the reaction was also considered for optimization. 0.5 mol% of the catalyst proved to be well efficient in catalyzing the reaction in acetonitrile media (Table 1, entry 7). Increase in catalyst loading to 0.75 mol% and 1.0 mol% was found not to increase the yield appreciably (Table 1, entries 9 & 10); the fact which substantiates that the product yield is not very sensitive to catalyst loading at higher concentration. Since no remarkable difference in the yield was observed when reactions were performed under argon or open air (Table 1, Entries 7 & 11), it was decided to carry out all further reactions under air.

The effect of bases on the product yield was examined for the

Table 1

Solvent and temperature study for the Suzuki coupling of 4-bromobenzonitrile and phenyl boronic acid using catalyst C-3.



Entry	Solvent	Base	Temperature (°C)	Yield (%) ^a
1	MeOH	K ₂ CO ₃	50	54
2	EtOH	K ₂ CO ₃	60	72
3	EtOH:H ₂ O (1:1)	K ₂ CO ₃	90	49
4	1,4-dioxane	K ₂ CO ₃	100	84
5	Toluene	K ₂ CO ₃	100	75
6	ACN	K ₂ CO ₃	70	73
7	ACN	K ₂ CO ₃	80	80
8 ^b	ACN	K ₂ CO ₃	80	71
9 ^c	ACN	K ₂ CO ₃	80	82
10 ^d	ACN	K ₂ CO ₃	80	83
11 ^e	ACN	K ₂ CO ₃	80	78

Reaction conditions: 4-bromobenzonitrile (1.0 mmol), Phenylboronic acid (1.3 mmol), K₂CO₃ (2.0 mmol), catalyst (0.5 mol%), solvent (5.0 mL), 16 h under inert atmosphere.

^a GC yields.

^b Catalyst (0.25 mol%).

^c Catalyst (0.75 mol%).

^d Catalyst (1.0 mol%).

^e Atmospheric condition.

entry 4). Acetonitrile was the second most productive solvent in terms of conversion (Table 1, entry 7). Moderate catalyst activities were found in other solvents such as methanol, ethanol, ethanol/aqueous mixture and toluene (Table 1, entries 1–3 and 5). Acetonitrile was chosen as the optimum solvent for carrying out the reactions considering the lower reaction temperature of acetonitrile (at 80 °C) and since the difference in yield between dioxane and acetonitrile is quite marginal. The enhanced activity of

coupling reaction. Cs₂CO₃ was found to be the most effective base (Table 2, entry 3) followed by the organic base Et₃N (Table 2, entry 5). Slightly lower yields were obtained when K₂CO₃, Na₂CO₃, KO^tBu were used as base (Table 2, entries 1, 2 and 4).

The proceedings of the reactions were traced by GC. Most of the 4-bromobenzonitrile was converted by the completion of 14 h. Nevertheless, dependence of product yield on the reaction time was scrutinized for a period of 20 h (Fig. 4). Yield variance is apparent to a notable extent up to 16 h of the reaction time, further advance in reaction time showed no much effect on the percentage conversion of the product, owing to which the reaction time for the catalytic conversion was optimized for 16 h.

Further, the cross coupling reaction was extended to the coupling between phenyl boronic acid and different aryl halides using the optimized reaction conditions. The results of these reactions are summarized in Table 3.

As can be seen from the results, various substituted aromatic halides underwent Suzuki coupling effectively. Electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas presence of electron donating groups brought about lesser conversion. Lowest conversion was observed

Table 2

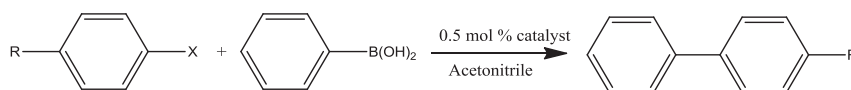
Study of effect of base on Suzuki coupling of 4-bromobenzonitrile and phenyl boronic acid using catalyst C-3.

Entry	Solvent	Base	Yield (%) ^a
1	ACN	K ₂ CO ₃	80
2	ACN	Na ₂ CO ₃	76
3	ACN	Cs ₂ CO ₃	87
4	ACN	KO ^t Bu	65
5	ACN	Et ₃ N	83

Reaction conditions: 4-bromobenzonitrile (1.0 mmol), Phenylboronic acid (1.3 mmol), base (2.0 mmol), catalyst (0.5 mol%), solvent (5.0 mL), 16 h.

^a GC yields.

Table 3
Catalytic activity study for complexes.



Entry	X	R	Yield (%) ^a		
			C-1	C-2	C-3
1	Br	H	50	54	56 (51.6)
2		CN	81	83	89 (86.4)
3		OCH ₃	68	70	76 (72.6)
4		COCH ₃	77	80	84 (81.3)
5		NHCOCH ₃	75	81	87 (85.2)
6		F	36	40	41 (36.0)
7	I	CH ₃	53	54	59 (54.7)
8		OH	69	71	76 (73.0)
9		CN	87	90	92 (90.2)
10	Cl	CHO	64	68	71 (66.8)

Reaction conditions: Aryl halide (1.0 mmol), Phenylboronic acid (1.3 mmol), Cs₂CO₃ (2.0 mmol), catalyst (0.5 mol%), solvent (5.0 mL), 16 h.

^a GC yields, average of 3 trials (Isolated yield).

when aryl halide with fluorine atom in the para position was being employed which perhaps occurs due to the destabilization of the

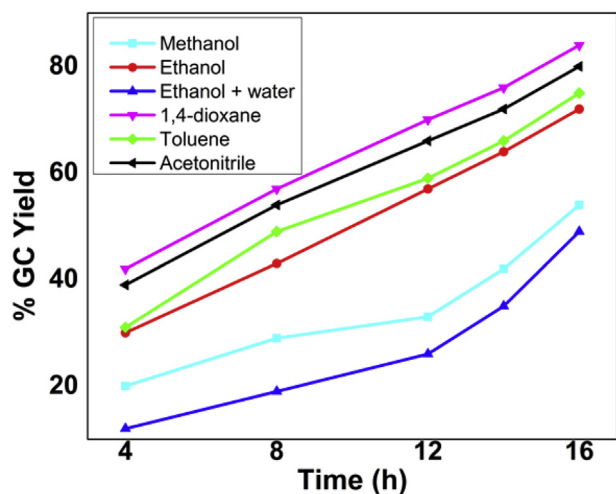


Fig. 3. Effect of solvent on C-3.

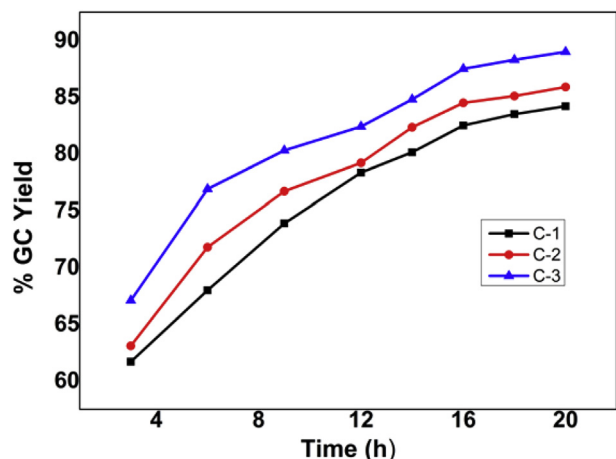


Fig. 4. Effect of reaction time on the product yield.

aromatic ring due to the competing inductive and resonance effects generally shown by halides attached directly on the aromatic ring. Presence of iodide is preferred as a better leaving group among the halides which is reflected in the results. (Entry 2 and 9, Table 3).

Among the three catalysts reported in this paper, highest catalytic activity is shown by complex C-3 which possesses tridentate PNNNP pincer ligand. When one of the side arm substituent is oxygen, it results in PNCOP pincer complex C-1 which shows comparatively lesser activity. The results of this study imply the effect of the donating capability of the atoms linked to the main donor atom 'P'. As the number of 'N' atoms increases in the side arm of the ligand, the donating ability of the ligand increases which consequently results in the increased catalytic activity of the complex (Fig. 5).

3.3. Mechanism consideration

Mechanism of the cobalt(II) catalyzed C–C coupling reaction is quite a complex supposition and requires comprehensive study in understanding the process. The catalytic metal component Co(II) getting reduced to either Co(0) or Co(I) is both a possibility, and speculating on the existent active species formed in the catalytic process is quite difficult. We tentatively assume that the catalyst

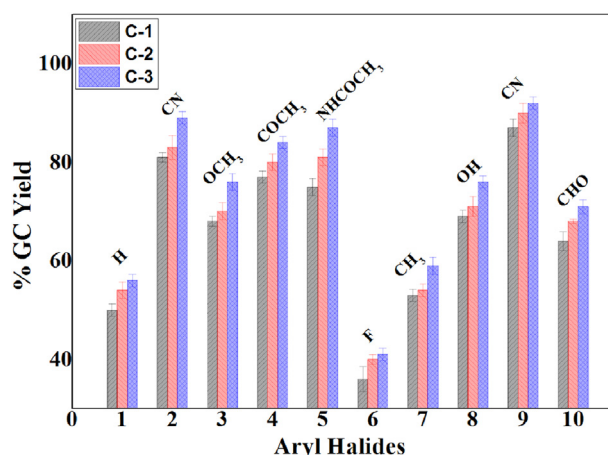


Fig. 5. Graphical representation of % GC conversion of various substituted aryl halides.

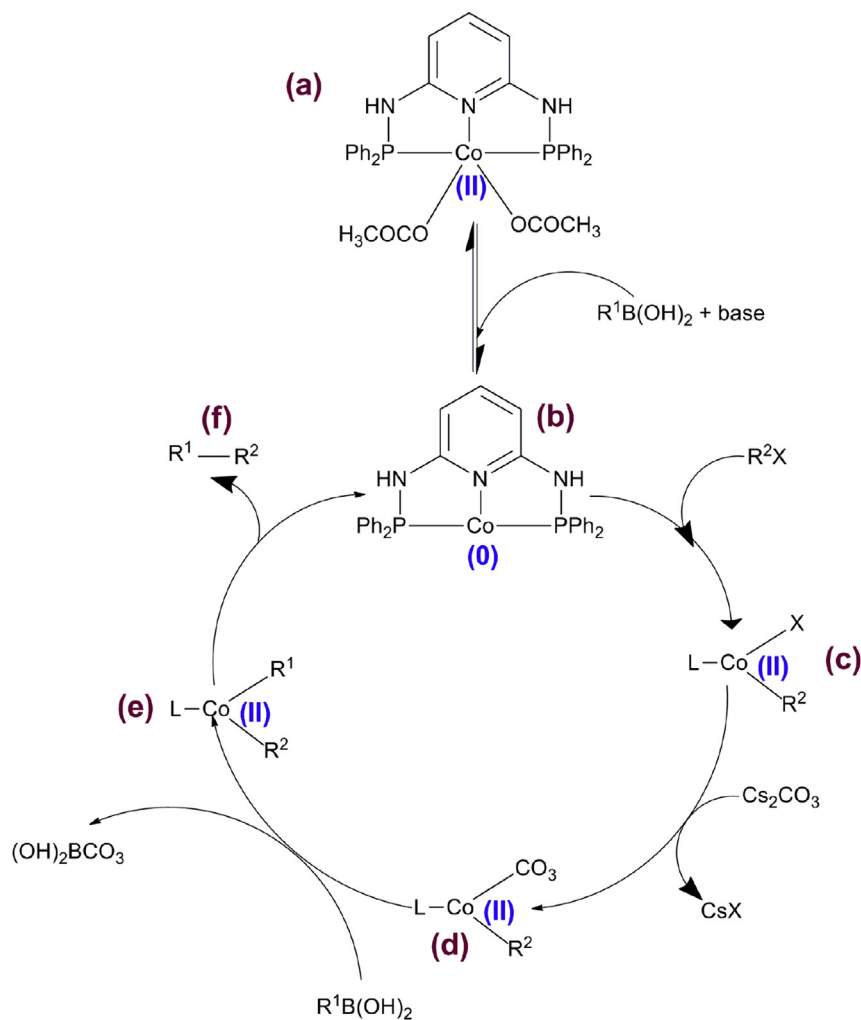


Fig. 6. Possible mechanism for C-C coupling by C-3.

precursor (a) gets reduced to active Co(0) species (b) in the presence of phenylboronic acid and base (Fig. 6). The coupling process may then start with the oxidative addition of aryl halide to the Co(0) center to form an R^2 -Co(II) intermediate (c). Subsequent nucleophilic substitution of the halide group and transmetalation between phenylboronic acid and R^2 -Co(L)-CO₃ (d) would result in biaryl R^1 -Co(L)- R^2 species (e). In the last step, reductive elimination supposedly takes place yielding the target biaryl (f) and also regenerating Co(0) species [26].

4. Conclusions

In conclusion, the method proposes the use of low cost, abundant and environmentally benign cobalt metal in the synthesis of complex which can be efficiently used as a catalyst in cross coupling reaction. Synthesis of the complexes is simple and can be achieved in a facile manner from the commercially available starting materials. The present study has led to the consideration of the role of ligands and their electron donating ability in enhancing the catalytic activity of a complex. It is observed that as the number of 'N' atoms increases in the side arm of the ligand, the donating ability of the ligand increases which consequently results in the increased catalytic activity of the complex.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2016.11.005>.

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