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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.

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 indispensible 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 (Et_3N), 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 [C_6H_4-1-($NHPPh_2$)-3-($OPPh_2$)]**(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%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.75 (m, 9H), 7.65–7.43 (m, 15H), 4.02 (br s, 1H, NH). (Supplementary Information Fig. S1).

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

IR (KBr); ν3350, 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 $C_{30}H_{25}NOP_2$ (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 [C_6H_4-1,3-($NHPPh_2$)$_2$] **(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%.

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{31}P{^{1}H} 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 $C_{30}H_{26}N_2P_2$ (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 [C_5H_3N-2,6-($NHPPh_2$)$_2$] **(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%.

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{31}P{^{1}H} 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 $C_{29}H_{25}N_3P_2$ (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($COOCH_3$){C_6H_4-1-($NHPPh_2$)-3-($OPPh_2$)}]**(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 $C_{32}H_{27}CoNO_3P_2$(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($COOCH_3$){C_6H_5-1,3-($NHPPh_2$)$_2$}]**(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 $C_{32}H_{28}CoN_2O_2P_2$ (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($COOCH_3$)$_2${C_5H_3N-2,6-($NHPPh_2$)$_2$}]**(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 $C_{33}H_{31}CoN_3O_4P_2$ (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