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Synthesis, characterization and catalytic activity of a new series of Ni(II), Cu(II) and Zn(II) complexes of N,N-O,O mixed-bidentate ligands for C-C cross-coupling reactions

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A new series of air stable transition metal(II) complexes [M(II)(L)(Phen)], [M(II)(L)(Pip)] (M = Ni, Cu and Zn) (H₂L = 2,2'-methylenebis(4-nitrophenol)) (Phen = 1,10-phenanthroline) (Pip = Piperazine) has been synthesized by incorporating the metal ion with bisphenol and 1,10-phenanthroline / piperazine ligands. The prepared metal complexes were characterized by FT-IR, UV-Visible, ¹H NMR, EPR and mass spectrometry. The metal(II) complexes were potent catalysts for Suzuki-Miyaura and Kumada-Corriu coupling of various aryl halides under optimized conditions.

Keywords: Transition metal complexes; Mixed bidentate ligands; Spectroscopic studies; Catalytic activity; C-C Cross-coupling

1. Introduction

Ligands containing oxygen and nitrogen donors with transition metals are important in physical, chemical, biological [1, 2] and catalysis research areas [3-5]. Mixed-monodentate and mixedbidentate ligand systems have been used for enantioselective [6], chemoselective [7] and stereoselective [8] cross coupling reactions. However, reports on mixed-bidentate ligand systems are less frequent than mixed-monodentate ligand systems [9]. Cross coupling reactions such as C-C, C-N, C-O and C-S catalyzed by transition metals open a variety of synthetic organic compounds for pharmaceutical and material chemistry [10, 11]. Procedures for C-C coupling reactions *viz.*, Suzuki [12], Heck [13], Negishi [14], Meyers [15], Lipshutz [16], Kharasch [17], Semmelhack [18], Ullmann [19], Hiyama [20], Stille [21] and Kumada-Corriu [22] have been reported. Among these protocols, Suzuki-Miyaura and Kumada-Corriu are powerful strategies

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that emerged for generation of C-C skeleton due to the utilization of inexpensive starting reagents, mild reaction conditions, thermal stability, functional group tolerance, low toxicity, eco-friendly and with high turnover numbers [23, 24]. There are several synthetic methods available for the Suzuki-Miyaura and Kumada-Corriu (Grignard reagent) cross-coupling reactions using aryl halides catalyzed by various transition metal complexes derived from N-heterocyclic carbene [25], thiosemicarbazide [26-28], amine bis(phenol) [29-31], Schiff bases [32], pincer type [33] as well as cyclometallated ligands containing nitrogen, oxygen, phosphorus and sulphur donor [34] ligands. Transition metal(II) complexes containing bidentate ligands are customarily used as catalysts in C-C [35, 36] cross-coupling reaction and nitrogen containing ligands might enhance the catalytic activity [37]. Complexes derived from cobalt, nickel, copper and zinc have been used as catalysts in many organic transformations [38].

Herein, we describe the synthesis and characterization of Ni(II), Cu(II) and Zn(II) complexes of mixed-bidentate ligand systems (N,N-O,O) incorporated with 2,2'-methylenebis(4-nitrophenol) and 1,10-phenanthroline / piperazine. Complexes **1** and **2** have been employed as catalysts in carbon-carbon bond formation with and without use of K_2CO_3 as base in Suzuki-Miyaura and Kumuda-Corriu reactions, respectively. The catalytic efficiency of our catalysts is comparable or better than that of the others in literature.

2. Experimental

2.1. Chemicals and reagents

Commercial nickel acetate tetrahydrate $[Ni(OAc)_2 \cdot 4H_2O]$, copper acetate monohydrate $[Cu(OAc)_2 \cdot H_2O]$ and zinc acetate dihydrate $[Zn(OAc)_2 \cdot 2H_2O]$ have been purchased from Merck. Formaldehyde, 4-nitrophenol, 1,10-phenanthroline and piperazine are from SRL Pvt. Ltd., India. The phenyl boronic acid, phenyl magnesium chloride and their corresponding aryl halides, utilized in the catalytic research, were received from Aldrich and Merck. Solvents of AR quality were purified and dried according to standard techniques [39].

2.2. Physical measurements

Carbon, hydrogen and nitrogen analyses were performed on a VarioEL III CHNS analyzer. IR spectra were carried out on a Bruker 783 spectrometer. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. ¹H NMR spectra of the complexes were recorded on a Bruker

400 MHz spectrometer using TMS as an internal standard. EPR spectra in liquid state were recorded inside the X-band frequency on an EPR-JEOL / 82 spectrometer with a microwave energy of 1 mW and a modulation amplitude of 20 G at liquid nitrogen temperature. Electrospray ionization mass spectra (ESI) have been recorded on an ES-MS Q-TOF mass spectrometer.

2.3. Synthesis of 2,2'-methylenebis(4-nitrophenol) (H_2L)

2,2'-Methylenebis(4-nitrophenol) (H_2L) was synthesized according to a published procedure [40].

2.4. Synthesis of metal complexes

2.4.1. Synthesis of [Ni(L)(Phen)] (1). To a stirred methanolic solution of 2,2'-methylenebis(4nitrophenol) (0.2902 g, 1 mmol), 1,10-phenanthroline (0.180 g, 1 mmol) in methanol was added. Then a concentrated methanolic solution of Ni(OAc)₂·4H₂O (0.248 g, 1 mmol) and a few drops of triethylamine were added. The solution was refluxed for 8 h in inert (N₂) atmosphere. The nickel complex was obtained as yellow solid. Anal. Yield 77%; m.p. 211 °C; C₂₅H₁₆N₄O₆Ni; Calcd: C, 56.96; H, 3.06; N, 10.63. Found: C, 56.90; H, 3.02; N, 10.58 %. ESI-MS: m/z 527; ¹H NMR (300 MHz, 295K, DMSO): δ 8.49-7.54 (m, ArH, 12H); 6.87 (s, ArH, 2H); 3.82 (s, ArCH₂, 2H). FT-IR: ArCH₂ 1487 cm⁻¹; Ar(C-O) 1282 cm⁻¹. The Ni(II) (0.248 g, 1 mmol), Cu(II) (0.210 g, 1 mmol) and Zn(II) (0.219 g, 1 mmol) complexes were prepared by following the above procedure using 2,2'-methylenebis(4-nitrophenol) (0.2902 g, 1 mmol) (H₂L) and 1,10phenanthroline (0.180 g, 1 mmol) / piperazine (0.086 g, 1 mmol).

2.4.2. Synthesis of [Cu(L)(Phen)] (2). Yield 69%; color: green solid; m.p. 270 °C; $C_{25}H_{16}N_4O_6Cu$; Calcd: C, 56.45; H, 3.03; N, 10.53. Found: C, 56.39; H, 3.00; N, 10.48 %. ESI-MS: m/z 531; FT-IR: ArCH₂ 1477 cm⁻¹; Ar(C-O) 1289 cm⁻¹.

2.4.3. Synthesis of [Zn(L)(Phen)] (3). Yield 67%; color: green solid; m.p. 288 °C; $C_{25}H_{16}N_4O_6Zn$; Calcd: C, 56.25; H, 3.02; N, 10.50. Found: C, 56.21; H, 3.00; N, 10.46 %. ESI-MS: m/z 533; ¹H NMR (300 MHz, 295K, DMSO): δ 8.36-7.72 (m, ArH, 12H); 6.90 (s, ArH, 2H); 3.86 (s, ArCH₂, 2H). FT-IR: ArCH₂ 1486 cm⁻¹; Ar(C-O) 1287 cm⁻¹.

2.4.4. Synthesis of [Ni(L)(Pip)] (4). Yield 71%; color: yellow solid; m.p. 220 °C; $C_{17}H_{18}N_4O_6Ni$; Calcd: C, 47.15; H, 4.19; N, 12.94. Found: C, 47.11; H, 4.16; N, 12.91 %. ESI-MS: m/z 432; ¹H NMR (300 MHz, 295K, DMSO): δ 8.31-7.64 (m, ArH, 4H); 6.76 (s, ArH, 2H); 3.85 (s, ArCH₂, 2H); 2.51 (br s, (CH₂)₄ 8H). FT-IR: (CH₂)₂ N-H 3217 cm⁻¹; ArCH₂ 1486 cm⁻¹; Ar(C-O) 1285 cm⁻¹.

2.4.5. Synthesis of [Cu(L)(Pip)] (5). Yield 81%; color: green solid; m.p. 278 °C; $C_{17}H_{18}N_4O_6Cu$; Calcd: C, 46.63; H, 4.14; N, 12.79. Found: C, 46.60; H, 4.12; N, 12.75 %. ESI-MS: m/z 438; FT-IR: $(CH_2)_2$ N-H 3223 cm⁻¹; ArCH₂ 1486 cm⁻¹; Ar(C-O) 1282 cm⁻¹.

2.4.6. Synthesis of [Zn(L)(Pip)] (6). Yield 48%; color: green solid; m.p. 277 °C; $C_{17}H_{18}N_4O_6Zn$; Calcd: C, 46.43; H, 4.13; N, 12.74. Found: C, 46.39; H, 4.12; N, 12.71 %. ESI-MS: m/z 440; ¹H NMR (300 MHz, 295K, DMSO): δ 8.20-7.82 (m, ArH, 4H); 6.72 (s, ArH, 2H); 3.85 (s, ArCH₂, 2H); 2.50 (br s, (CH₂)₄ 8H). FT-IR: (CH₂)₂N-H 3225 cm⁻¹; ArCH₂ 1484 cm⁻¹; Ar (C-O) 1289 cm⁻¹.

2.5. General procedure for Suzuki-Miyaura cross-coupling reactions

Suzuki-Miyaura cross-coupling reactions were achieved with a procedure described [41]. An oven dried 25 mL flask equipped with a stir bar was charged with **1** (0.05 mmol) in DMF (1 mL). Phenylboronic acid (0.75 mmol), aryl halide (0.5 mmol) and K_2CO_3 (1.5 mmol) were dissolved separately each in 2 mL of methanol and added with the catalyst in the flask. The ensuing mixture was reacted at 65 °C for 9 h. Then the solvent was evaporated from the reaction mixture and the product was separated from the impurities using a mixture of diethyl ether (3×10 mL) and water (10 mL). The organic layer was collected, dried over anhydrous Na₂SO₄ and filtered. Then the solvent was removed under reduced pressure and the desired catalyst was confirmed using ¹H NMR.

2.6. General procedure for aryl Grignard coupling reactions

Kumada-Corriu cross-coupling reactions were carried out using the procedure described [42]. Catalyst **2** (0.05 mmol) in DMF (1 mL) was taken to a 50 mL round bottom flask. Aryl halide (1.0 mmol) and Grignard reagent (1.0 mmol) were dissolved separately each in 3 mL of Et_2O and

added dropwise under vigorous stirring. After stirring the resulting mixture at room temperature for 30 min, the reaction was quenched with HCl (aq) (2.0 M, 5 mL). The organic phase was extracted with ethyl acetate (5 mL) and dried using anhydrous MgSO₄. The crude mixture obtained was analyzed by thin layer chromatography and then purified by column chromatography on silica gel. Further, the isolated product was characterized by ¹H NMR.

3. Results and discussion

Ni(II), Cu(II) and Zn(II) complexes were synthesized using mixed-bidentate ligand systems (N,N-O,O) of 2,2'-methylenebis(4-nitrophenol) and 1,10-phenanthroline / piperazine (schemes 1 and 2). These metal(II) complexes were obtained as colored solids in 48-81% yield. The elemental analysis data is in agreement with the theoretical value for the synthesized complexes. Metal ions usually bind to 2,2'-methylenebis(4-nitrophenol), through dissociation of the bisphenolic protons, as bidentate oxygen-oxygen donors and 1,10-phenanthroline / piperazine as bidentate nitrogen-nitrogen donors forming eight-membered and five-membered chelate rings, respectively [43, 44].

$$2 \bigoplus_{OH}^{NO_2} + CH_2O \xrightarrow{H_2O \text{ with } H_2SO_4}_{\text{stirring with reflux}} \xrightarrow{NO_2 \\ OH OH OH}^{NO_2} \xrightarrow{OO_2}_{OH OH}$$

Scheme 1. Synthesis of 2,2'-methylenebis(4-nitrophenol).



Scheme 2. Synthesis of transition metal(II) complexes with mixed ligands.

The synthesis of methylene bis(4-nitrophenolate) is easy and it is stable in air. There are several aminobis(phenolate) ligand based complexes used for this kind of carbon-carbon cross coupling reactions [45, 46]. Rigidity of the complex favors these reactions [47]. Our goal was to increase the yield of the catalytic product by increasing the rigidity of the complex. Hence we used a bisbidentate ligand along with 1,10-phenanthroline / piperazine instead of small ligands *viz.*, chloride or acetate; we have found that the complexes with phenanthroline have more activity than the others.

3.1. IR spectra

Infrared spectra of the complexes show several bands from 400-4000 cm⁻¹. The spectrum of the uncoordinated ligand shows the phenolic O-H stretch at 3316 cm⁻¹ and phenolic C-O stretch at 1279 cm⁻¹; the ligand also displays a band at 1486 cm⁻¹ corresponding to the ArCH₂ stretch, indicating the formation of bisphenol through a CH₂ linkage. The coordination of metal ion through bisphenolic oxygens is affirmed by the disappearance of phenolic O-H band [43] with an increase in C-O stretching frequency from 1279-1282 cm⁻¹ for the Ni(II) complex (1). There is a band at 1487 cm⁻¹ corresponding to methylene (CH₂) stretch consistent with the methylene bridge [48]. The same trend is observed in **2-6**. The appearance of N-H stretch at 3217 cm⁻¹ indicates the non-deprotonation of the piperazine protons in **4-6** [49]. All the complexes show strong bands at 400-450 cm⁻¹ and 500-550 cm⁻¹ corresponding to M-N and M-O, respectively [50, 51].

3.2. Electronic spectra

The complexes are soluble in DMSO and DMF, sparingly soluble in dichloromethane, ethyl acetate, acetonitrile, ethanol, methanol, chloroform and benzene and slightly soluble in petroleum ether and hexane. Electronic spectra of the complexes have been recorded in DMSO solution. The complexes show intense absorptions in the ultraviolet region attributed to transitions within the ligand orbitals and those in the visible region are due to ligand to metal charge transfer transition and d-d transition. The electronic spectra of the complexes are shown in figure 1. All the complexes exhibit an intense absorption at 275-260 nm assigned to π - π * transitions and another band at 345-320 nm due to n- π * transitions of the ligand. They show an intense absorption at 450-360 nm due to LMCT. Ni(II) complexes (1 and 4) show a band at 515,

575 nm which may be assigned to d-d transitions ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ which supports square planar geometry around Ni(II). Spectra of **2** and **5** show a band at 545, 517 nm which is assigned to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition affirming square planar geometry of Cu(II) [51]. The Zn(II) complexes (**3** and **6**) do not show d-d transitions.

3.3.¹H-NMR spectra

The ¹H-NMR spectrum of 2,2'-methylenebis(4-nitrophenol) (H₂L) support the assigned structure. The NMR spectrum of the free ligand shows singlets at 11.26, 3.72 and 6.98-8.24 ppm which are due to phenolic protons (O-H), benzylic protons (ArCH₂) and aromatic protons (ArH), respectively. The peak due to phenolic O-H proton is absent in the NMR spectra of nickel(II) and zinc(II) complexes. This indicates coordination of phenolic oxygen. The NMR spectra of the nickel(II) and zinc(II) complexes showed peaks at 2.51, 3.85 and 6.72-8.49 ppm, indicating the presence of piperazine moiety, benzylic proton and aromatic moiety, respectively. The Ni(II) (1 and 4) and Zn(II) (3 and 6) complexes are diamagnetic [52].

3.4. EPR spectra

The solution EPR spectra of the mononuclear copper(II) complexes were recorded in the X-band region using DMSO at liquid nitrogen temperature. The copper(II) complexes display an anisotropic (S=1/2) signal with hyperfine splitting into four lines in the low field components [53]. This pattern arises from the interaction of the electron spin with the copper(II) nucleus ($I_{Cu}=3/2$). The observed g value for 2 and 5 are 2.04 and 2.00, indicating that the unpaired electron is in a $d_{x^2-y^2}$ orbital of d⁹ Cu(II) in a ground state doublet. The spectral features of these complexes are characteristics of axial symmetry [54]. The EPR spectral data are given in table 1 and the spectrum of 2 is shown in figure 2. EPR data reveal a square planar geometry for the d⁹ Cu(II) in the complexes [53].

3.5. Mass spectra

The expected mass value of the ligand is in agreement with the experimental $M^+ = 289 \text{ m/z}$ value of the molecular ion peak. The mass spectra of the metal complexes (**1-6**) show a molecular ion peak M^+ at m/z = 527, 531, 533, 515, 438 and 440, respectively. The mass spectrum of **6** is exhibited in figure 3.

3.6. Catalytic studies

In this paper, we report six new complexes and examined all as catalysts in C-C cross-coupling reactions. Two of these catalysts are quite active in the catalytic reactions. In both cases, the catalyst is dissolved in DMF. Then, the substrates are dissolved separately in methanol for Suzuki-Miyaura cross-coupling reaction and in diethyl ether for Kumuda-Corriu cross-coupling reactions. The substrate solutions are added slowly to the catalyst under optimized conditions. DMF is a well-known reductant for transition metals [55, 56]. Initially, the catalyst is reduced by DMF for 1 and 2 while undergoing oxidative addition with aryl halide under normal reaction conditions at or below room temperature. Our complexes have good stability against air, moisture and temperature. We used K_2CO_3 along with 2 in the Kumadu-Corriu catalytic reaction for activation of the catalyst and to increase the yield of the product [46]. The mechanism for the Suzuki-Miyaura coupling using 1 and Kumada-Corriu coupling using 2 (schemes 3a and 3b) includes three steps: oxidative addition (OA), transmetallation (TM), and reductive elimination (RE) [57, 58].



Scheme 3. Plausible mechanism for the catalytic conversion of C-C cross-coupling (a) and (b).

3.6.1. Suzuki-Miyaura cross-coupling catalytic studies. We have explored the reactions of a series of aryl halides with phenylboronic acid under different reaction conditions. Initially,

complexes **1-6** were used as catalysts for this reaction. From these observations, Ni(II) complex (**1**) showed better catalytic activity. Furthermore, we screened the above reaction with various solvents, acetonitrile, methanol and benzene, along with 1 mL dimethylformamide solution of catalyst. Methanol was the best solvent with better activity of electron-donating agents and providing more steric crowding compared to the piperazine group. The reactions using **1** as a catalyst furnished excellent yields, given in table 2. Among the various substrates used for catalytic activity, 4-bromoanisole, 2,6-dibromo pyridine and benzyl bromide have excellent activity in this coupling reaction (entries 2, 5 and 3). With 4-chlorophenol and 4-bromoaniline the conversions are good (entries 4 and 6) whereas the reaction of 4-chlorobenzaldehyde has moderate yield (entry 7). Reactions of chlorobenzene and 2-chloroaniline provided poor yields (entries 1 and 8). Complex **1** has comparable or better activity against previous reports as given in table 3.

3.6.2. Kumada-Corriu cross-coupling catalytic studies. All the complexes were used as catalysts for the reaction of aryl halides with Grignard reagent; copper(II) complex **2** is better than the other complexes. We used various solvents, tetrahydrofuran, acetonitrile, diethyl ether and benzene, along with 1 mL dimethylformamide solution of the catalyst; diethyl ether was best. The catalytic conditions, substrates and their products are given in table 4. The coupling with benzyl bromide has excellent conversion (entry 3) whereas bromobenzene, 2,6-dibromopyridine and 4-bromoanisole have good yields (entries 1, 4 and 5). 2-Bromopyridine and α,α' -meta dibromoxylene have moderate yields (entries 8 and 7) while 4-chlorobenzoic acid and chlorobenzene give poor yields (entries 6 and 2). Catalyst **2** has better or comparable activity to previous literature reports (table 5).

4. Conclusion

We reported a new series of (N,N-O,O) complexes of Ni(II), Cu(II) and Zn(II) using bisphenol and 1,10-phenanthroline / piperazine. Complexes 1 and 2 have good activity for Suzuki-Miyaura and Kumuda-Corriu C-C cross-coupling reactions. Overall, 1 has more activity than 2 in the C-C coupling reactions. As the catalytic activity of our complexes are competitive with others, new complexes of mixed ligands may provide a path to C-C cross-coupling reactions.

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Table 1. EPR data of the Cu(II) complexes with mixed ligands.

| Complexes | g _{xx} | g_{yy} | g _{zz} | <g></g> | |
|--------------------------------------------------------------|-----------------|----------|-----------------|---------|--|
| 2 | 2.04 | 2.03 | 2.06 | 2.04 | |
| 5 | 2.03 | 2.01 | 1.95 | 2.00 | |
| $\langle g \rangle = [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$ | | | | | |

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Table 2. Cross-coupling of substituted aryl halides with aryl boronic acid^a.

a. General conditions: arylboronic acid (1 mmol), aryl halide (1 mmol), catalyst (complex 1) (0.05 mmol) (5 mol %), K_2CO_3 ; X = Br and Cl; R = OCH₃, OH, NH₂ and CHO; b. Turnover number (TON) = (mmol of product) / (mmol of catalyst) after time t; c. Turnover frequency (TOF) = TON/time (h⁻¹); d. Isolated yield

| Entry | Catalyst | Conditions | Yield (%) ^{References^b} |
|-------|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|---------------------------------------------|
| 1 | Pd/MCM-41 (1 mol %) | KOH, H ₂ O, 80 °C, 4 h | 85 ^[59] |
| 2 | Pd(OAC) ₂ /PIC (0.01 mol %) | Na ₂ CO ₃ , H ₂ O, 100 °C, 2 h | >99 ^[60] |
| 3 | $[NiCl_2{(anisyl)_3P}_2] (5 mol \%)$ | Et ₃ N, aqueous TPGS-750-M, 45 °C, overnight | 86 ^[61] |
| 4 | [Ni(II)PNP] (2 mol %) | t-BuoK, Toluene, 120-135 °C, 16 h | 92 ^[62] |
| 5 | Fe ₃ O ₄ /Pd (Nps) (1 mol %) | K ₂ CO ₃ , H ₂ O, 80 °C, 3 h | 90 ^[63] |
| 6 | Fe ₃ O ₄ /SiO ₂ -NH ₂ /PC-PD (1.5 mol%) | K ₂ CO ₃ , MeOH-H ₂ O (2:1), 65 °C, 0.75 h | 90 ^[64] |
| 7 | Pd-Fe ₃ O ₄ /rGO (0.5 mol %) | K ₂ CO ₃ , C ₂ H ₅ OH-H ₂ O (1:1), 80 °C, 1 h | 89 ^[65] |
| 8 | [Ni(NHCS)] (1 mol %) | K ₃ PO ₄ , Toluene, 110 °C, 4 h | 95 ^[66] |
| 9 | $[PdCl(PPh_3)(L_1)] (0.1 mol \%)$ | K ₂ CO ₃ , Toluene, 80 °C, 5 h | 85 ^[67] |
| 10 | [Ni(L)(Phen)] (5 mol %) | K ₂ CO ₃ , DMF-MeOH, 65 °C, 9 h | 92 ^{This work} |

Table 3. Comparison of catalytic efficiency of 1 against the literature reports in Suzuki-Miyaura C-C coupling reactions^a.

a. Reaction conditions: arylboronic acid (1 mmol), 4-bromoanisole (1 mmol), catalyst (complex 1) (0.05 mmol) (5 mol %), K₂CO₃; b. Previous reports

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Table 4. Cross-coupling of substituted aryl halides with aryl Grignard reagents^a.

a. General conditions: ArMgCl (1 mmol), aryl halide (1 mmol), catalyst (complex 2) (0.05 mmol) (5 mol %); X = Br and Cl; R = OCH₃ and COOH; b. Turnover number (TON) = (mmol of product) / (mmol of catalyst) after time t; c. Turnover frequency (TOF) = TON/time (h^{-1}); d. Isolated yield

| Entry | Catalyst | Conditions | Yield (%) ^{References^b} |
|-------|--------------------------------------------------------------------|------------------------------------|---------------------------------------------|
| 1 | Ni(L) ₂ (0.2 mole %) | Ether, RT, 4 h | 81 ^[68] |
| 2 | CoCl ₂ /Ti(OC ₂ H ₄) (7.5 mol %) | THF, RT, 0.5 h | 56 ^[69] |
| 3 | NiCl ₂ (CNN) (1 mol %) | THF, RT, 24 h | 20 ^[70] |
| 4 | $CoCl_2(L1)_2(PF_6)$ (0.01 mol %) | THF, RT, 2 h | 71 ^[71] |
| 5 | Ni(iPr)Cl ₂ (1.0 mol %) | Et ₂ O-THF, 45 °C, 12 h | 88 ^[72] |
| 6 | FeCl ₂ (5 mole %) | Xylene, 140 °C, 12 h | 90 ^[73] |
| 7 | $NiBr_{2}(L) (0.03 mol \%)$ | THF, RT, 0.5 h | >99 ^[74] |
| 8 | Ni(CH ₃ CN) ₂ Cl ₂ (2 mol %) | THF, -20 °C, 10 h | 75 ^[75] |
| 9 | [Cu(L)(Phen)] (5 mol %) | DMF:Et ₂ O, RT, 0.5 h | 83 ^{This work} |

Table 5. Comparison of catalytic efficiency of our [Cu(L)(Phen)] catalyst (2) against the literature reports in Kumada-Corriu C-C coupling reactions^a.

a. Reaction conditions: phenylmagnesium chloride (1 mmol), 4-bromoanisole (1 mmol), catalyst (complex 2) (0.05 mmol) (5 mol %); b. Previous reports

