PAPER

Nickel catalyzed one pot synthesis of biaryls under air at room temperature†

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A practical, room temperature catalytic system has been developed for the synthesis of biaryls in one step from the homocoupling of *in situ* generated Grignard reagents using a nickel(II) complex. The use of atmospheric oxygen as the oxidant makes the system environmentally friendly. The reaction system is compatible with diverse functionality to afford biaryls in appreciable yields.

1. Introduction

The synthesis of biaryls is of particular interest to industry as shown by their broad application in multidisciplinary fields.[1] These motifs increasingly turn up in materials that are important to society such as pharmaceuticals, biocides, and specialized engineering materials such as high strength rigid-rod polymers, molecular wires, liquid crystals and nonlinear optical materials, all attracting enormous interest both within the chemical community and outside.[2] The transition metal catalyzed homocoupling of Grignard reagents is one of the most efficient synthetic methods for the construction of a symmetrical biaryl backbone.[3] To date, various simple metal salts have been used as catalysts for the synthesis of biaryls.[4,5] Though, many nickel-catalyzed coupling reactions have been reported so far, the demand of a stoichiometric amount of an organic oxidant or an extra ligand limits their use in industrial scale applications.[6,7] This has led to a search for an alternative protocol, and environmentally benign molecular oxygen has been found to be a more attractive oxidant for these homocoupling reactions. Iron, manganese[8] and palladium[9] based catalysts have been well-reported for use in such homocoupling reactions. But the problem encountered with these later methods is their two step synthetic route, where the organometallic compounds are prepared first and then in a separate reaction converted into the biaryl product. The recently reported cobalt catalyzed homocoupling of Grignard reagents in one step by Chen *et al.*[10] did not discuss the catalytic mechanism and the system requires a higher amount of catalyst loading than the present system.

Though a variety of metallic reagents can be applied in the coupling reaction, the development of a ligand framework that is able to accommodate the changes during catalysis is highly desirable. 4-Aminoantipyrine Schiff base derivatives have received increasing interest for a variety of applications because of the their flexible complexing behavior due to the different possible types of coordination with metal ions.[11,12] But these have not been explored very much in homocoupling reactions. Triphenylphosphine-based ligands have become increasingly important to the systematic modification and tuning of catalytic activity.[13] The nickel complexes used for C–C coupling represent an attractive area of research mainly because of their wide scope covering a range of applications and excellent compatibility with many functional groups. Significantly, the low cost and excellent redox properties of nickel, make this objective economically as well as synthetically alluring, in part because of the utility of its heavy metal congener palladium.[14]

In our previous work, we reported a ruthenium(III) catalyst containing dmit(2-thioxo-1,3-dithiole-4,5-dithiolate) and triphenylphosphine ligands for the homocoupling reaction.[15] In continuation of our efforts to afford symmetrical biaryls, in this paper, the ligands and metal precursors are varied and their influence on the coupling reaction is studied. A tridentate Schiff base is introduced in place of the dmit ligand and nickel is used instead of ruthenium. Herein we report a one-pot synthesis of biaryls using an octahedral nickel(II) complex, as the catalyst. The nickel(II) complex was synthesized from the Schiff base 4-{[(E)-(2,4-dihydroxyphenyl)methylidene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one and triphenylphosphine ligands. The catalytic method adopted represents a simple pathway for the *in situ* formation of a Grignard reagent. The reaction proceeded at room temperature using atmospheric oxygen as the oxidant.

2. Experimental

2.1 Materials and methods

All chemicals used were of analytical grade. The C, H and N contents of the compounds were determined by using a

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Thermoflash EA1112 series elemental analyzer. Magnetic susceptibility measurements were 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^{-1}. The electronic spectrum of the complex was measured on a GBC Cintra 101 UV-Vis double beam spectrophotometer using DMF in the 200–800 nm range. FT-IR spectra were recorded on a Thermo Nicolet Avatar FT-IR spectrometer in the frequency range 400–4000 cm^{-1}. ^{1}H NMR (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded in a Bruker AV 400 instrument using TMS as the internal standard. Coupling reactions were monitored by gas chromatography, Shimadzu 2014.

2.2 Synthesis

2.2.1 Synthesis of 4-{[(E)-(2,4-dihydroxyphenyl)methyl-idene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (L$_1$). The Schiff base **L$_1$** was synthesized according to the reported procedure.[16] A solution of 4-aminoantipyrine (2.03 g, 10 mmol) in ethanol was added drop wise to a solution of 2,4-dihdroxybenzaldehyde (2,4-DHB) (1.38 g, 10 mmol) in ethanol. The mixture was stirred at room temperature for 15 minutes and then refluxed for 2 hours. The yellow colored solid product was filtered, washed, recrystallized with ethanol and dried *in vacuo*.

Ligand **L$_1$**: yield: (2.32 g, 72%); mp: 234 °C; elemental analysis calcd for $C_{18}H_{17}N_3O_3$ (%), C: 66.86, H: 5.30, N: 13.00. Found C: 66.85, H: 5.27, N: 12.98; FT-IR (cm^{-1}): 1605 (C=O), 1576 (–CH=N–), 1314 (C–O); ^{1}H NMR δ_H (400 MHz; DMSO; Me$_4$Si): 13.32 (br s, –OH), 9.56 (s, –CH=N–), 6.2–7.6 (m, Ar–H), 3.26 (s, N–CH$_3$), 2.38 (s, =C–CH$_3$); MS (ESI) (m/z) calcd for $C_{18}H_{17}N_3O_3$ [M + 1]: 323.34. Found: 324.3; UV-Vis λ_{max} (nm): 278, 315, 340, 390.

2.2.2 Synthesis of Ni(II) complex (NiL). The metal precursor $NiCl_2(PPh_3)_2$ was synthesized according to the previously reported procedure.[17] The nickel(II) complex, **NiL**, was obtained by refluxing a solution of **L$_1$** (1 mmol) and $[NiCl_2(PPh_3)_2]$ (1 mmol) in methanol for 3 hours with constant stirring (Fig. 1). The yellowish green coloured product obtained was filtered, washed with methanol and petroleum ether (60–80 °C) and dried *in vacuo*.
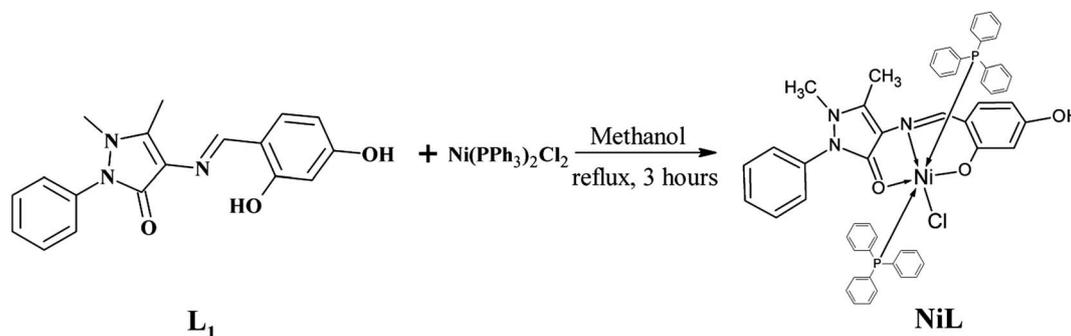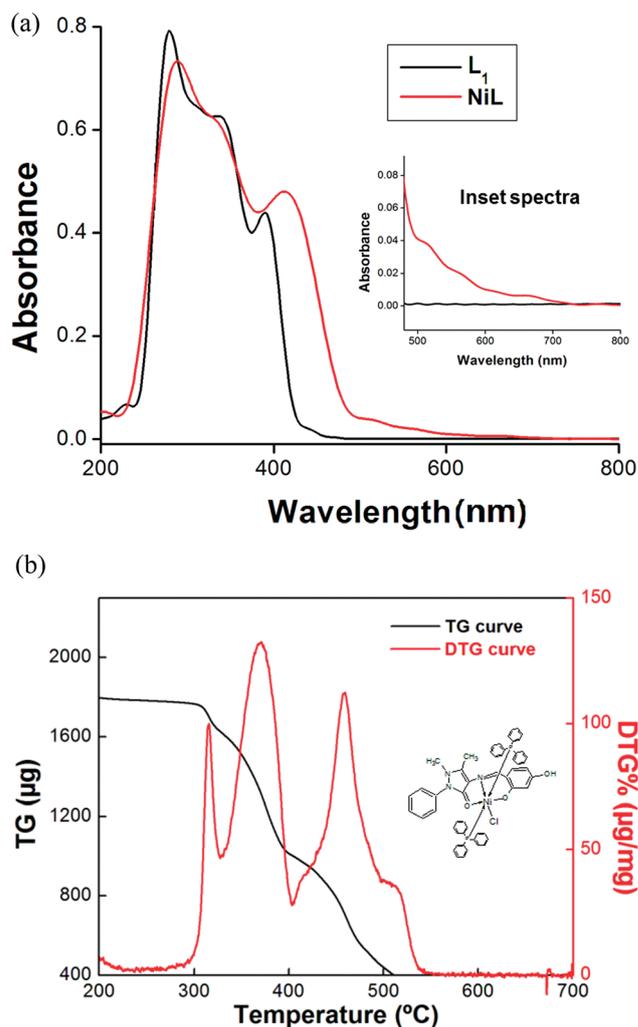

Fig. 2 (a) UV-Vis spectra of **L$_1$** and **NiL**, (b) TG analysis of **NiL**.

NiL: yield: (1.22 g, 65%); elemental analysis calcd for $C_{54}H_{46}ClN_3NiO_3P_2$ (%), C: 68.92, H: 4.93, N: 4.47. Found C: 68.84, H: 4.89, N: 4.42; FT-IR (KBr, cm^{-1}): 1618 (C=O), 1538 (–CH=N–), 1337 (C–O), 1071, 749, 693, 488 (M–O), 441 (M–N); ^{1}H NMR δ_H (400 MHz; DMSO; Me$_4$Si): 9.69 (s, –CH=N–), 7.18–8.83 (m, Ar–H), 3.24 (s, N–CH$_3$), 2.50 (s, =C–CH$_3$); ^{31}P NMR δ_P (H$_3$PO$_4$): 26.52; MS (ESI) (m/z) calcd for $C_{54}H_{46}ClN_3NiO_3P_2$ [M$^+$]:

L$_1$ **NiL**

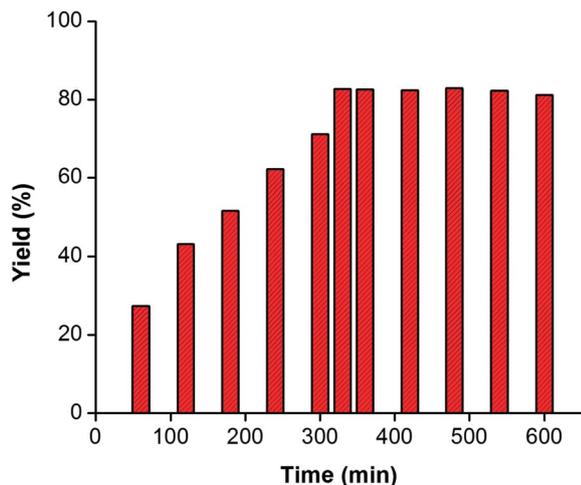Fig. 1 Reaction scheme for the synthesis of **NiL**.

Fig. 3 Dependence of the biaryl yield on reaction time in the presence of **NiL**.

941.1. Found: 941.4; UV-Vis λ_{max} (nm): 288, 334, 411, 511, 563, 658. μ_{eff}: 3.266.

2.3 Catalytic study

2.3.1 General procedure for the homocoupling of aryl Grignard reagents. In this procedure, magnesium turnings (13 mmol, 0.320 g atom) were placed in a two necked round bottom flask with a calcium chloride guard tube and a crystal of iodine was added. Aryl bromide (2 mmol of total 10 mmol) in 5 ml of anhydrous diethyl ether was added with constant stirring at room temperature. Initially, an increase in the temperature of the reaction mixture was observed and the appearance of turbidity after a few minutes indicated the initiation of the reaction. The remaining aryl bromide (8 mmol) in 5 ml of ether was added drop wise and the reaction mixture was stirred for 40 minutes. Then, to the reaction mixture, the catalyst **NiL** (0.03 mmol) was added. The reaction mixture darkened immediately

upon addition of the catalyst. Stirring was continued. After 5 hours the reaction mixture was cooled and hydrolyzed with a saturated solution of 10% aqueous ammonium chloride. After extraction with ether (3 × 50 ml), the combined organic layers were dried over anhydrous magnesium sulfate. All volatiles were removed under reduced pressure and the residue was chromatographed on silica gel to afford the respective biphenyl. The products obtained compared well with authentic samples using gas chromatography.

3. Results and discussion

The elemental analyses (C, H, N) were in good agreement with the molecular formulas proposed for L_1 and **NiL**. The FT-IR spectrum of the ligand exhibited intense bands at 1605 cm^{-1} and 1576 cm^{-1} corresponding to the antipyrine exocyclic ketone $\nu(C=O)$ and azomethine $\nu(CH=N)$, respectively. Coordination to the metal ion was confirmed by frequency shifts to 1618 and 1538 cm^{-1}, respectively.[18] The band in the region of 1314 cm^{-1}, which is assigned to the phenolic $\nu(C–O)$ in the free ligand, shifts to a higher wave number 1337 cm^{-1} in the complex suggesting its involvement in the coordination. Thus L_1 acts as a tridentate ligand with O, N, O coordination sites. The peaks at 1071, 749 and 693 cm^{-1} can be attributed to the presence of triphenylphosphine in the complex. The appearance of medium bands at 441 and 488 cm^{-1} could be attributed to $\nu(M–N)$ and $\nu(M–O)$, respectively. In the ^{1}H NMR spectrum of the complex,[19] the absence of a sharp singlet at 13.32 ppm shows that the phenolic oxygen coordinates after deprotonation. The presence of a peak at 9.67 ppm in the complex confirms the coordination of the azomethine nitrogen to the metal ion. The complex shows multiplets at 7.18–8.83 ppm due to the aromatic protons of the coordinated ligand. The ^{31}P{^{1}H} NMR spectrum exhibits a sharp singlet at 26.52 ppm indicating the presence of the triphenylphosphine groups in a trans configuration.[20] Mass analysis was used to further confirm the structures of L_1 and **NiL**. As shown in Fig. 2a, the electronic spectrum of the complex
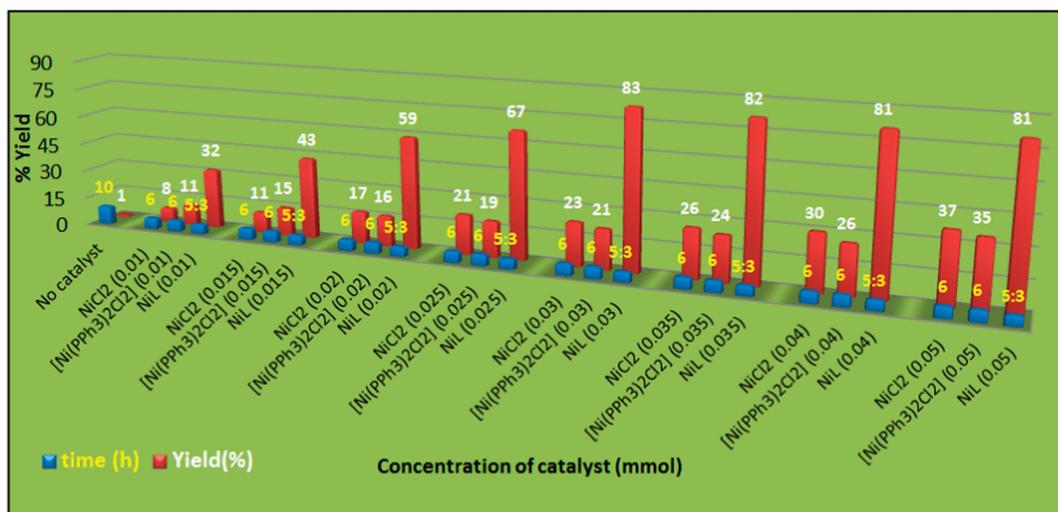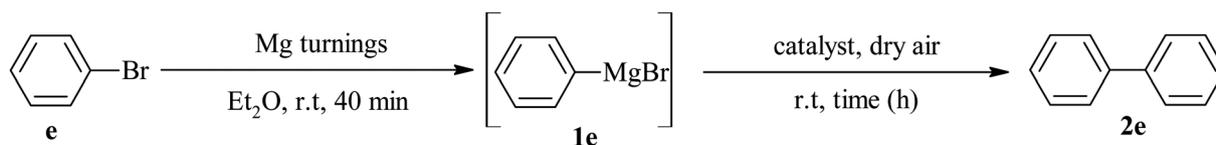

Fig. 4 Histogram of optimization of homocoupling of **1e** with respect to catalyst concentration.

Table 1 Optimization of homocoupling of **1e** with respect to catalyst concentration[a]

Entry	Catalyst (mmol)	Time (h)	Yield[b] (%)
1	No catalyst	10	01
2	$NiCl_2$ (0.01)	6	8
	$[Ni(PPh_3)_2Cl_2]$ (0.01)	6	11
	NiL (0.01)	5:30	32
3	$NiCl_2$ (0.015)	6	11
	$[Ni(PPh_3)_2Cl_2]$ (0.015)	6	15
	NiL (0.015)	5:30	43
4	$NiCl_2$ (0.02)	6	17
	$[Ni(PPh_3)_2Cl_2]$ (0.02)	6	16
	NiL (0.02)	5:30	59
5	$NiCl_2$ (0.025)	6	21
	$[Ni(PPh_3)_2Cl_2]$ (0.025)	6	19
	NiL (0.025)	5:30	67
6	$NiCl_2$ (0.03)	6	23
	$[Ni(PPh_3)_2Cl_2]$ (0.03)	6	21
	NiL (0.03)	5:30	83
7	$NiCl_2$ (0.035)	6	26
	$[Ni(PPh_3)_2Cl_2]$ (0.035)	6	24
	NiL (0.035)	5:30	82
8	$NiCl_2$ (0.04)	6	30
	$[Ni(PPh_3)_2Cl_2]$ (0.04)	6	26
	NiL (0.04)	5:30	81
9	$NiCl_2$ (0.05)	6	37
	$[Ni(PPh_3)_2Cl_2]$ (0.05)	6	35
	NiL (0.05)	5:30	81
10[c]	**NiL** (0.03)	5:30	5
11[d]	**NiL** (0.15)	8	80
12[e]	**NiL** (0.03)	5:30	37

[a] Reactions were carried out with 10 mmol of bromobenzene in the presence of atmospheric oxygen. [b] Isolated yield. [c] Inert atmosphere (argon). [d] With 50.0 mmol of bromobenzene in the presence of 0.150 mmol catalyst for 8 hours. [e] Reactions were carried out with 10 mmol of commercial phenylmagnesium bromide in the presence of atmospheric oxygen.

shows an intense absorption band in the region 292–409 nm, due to intra ligand charge transitions (ILCT) and a band in the region 411 nm that can be attributed to ligand to metal charge transfer transitions (LMCT). The characteristic d–d transition can be observed in the region 511–658 nm. The room temperature magnetic moment of 3.26 BM shows that the complex is octahedral in nature.[21] From the TG analysis (Fig. 2b), weight loss was observed at temperature ranges around 310–318, 335–393 and 450–524 °C corresponding to the loss of one chloride molecule, one ligand moiety and two molecules of triphenylphosphine respectively, which further confirms the assumed structure.

The present catalytic methodology involves an *in situ* formation of an aryl Grignard reagent. Iodine was used as a surface activator for commercially available magnesium turnings. The addition of aryl bromide during the formation of the Grignard reagent has a very important role. Various side products were observed with a fast addition, mainly ROH. When bromobenzene was added at a faster rate, we obtained phenol as the main side product.[22] The controlled addition of the aryl

bromides yielded the respective Grignard reagents with negligible amounts of side products. Thus, the formed Grignard reagent, on reaction with a catalytic amount of the nickel(II) complex, afforded the biaryl in moderate to good yield. The coupling reaction was successfully carried out in air at room temperature. Atmospheric oxygen was used as the oxidant, making the system energy efficient and environmentally friendly. No external oxidants were used. Optimization studies with respect to various parameters such as solvent, catalyst concentration and reaction time were carried out for the coupling of phenylmagnesium bromide (**1e**). The solvent effect on the coupling activity using **NiL** was analyzed in various solvents such as tetrahydrofuran, diethyl ether, benzene, *etc.*, in the presence of atmospheric oxygen. The best yield was obtained in diethyl ether, which can be attributed to its ability to coordinate with the Grignard reagent and thus stabilize the intermediate complex.[23] It was observed that the yield increases with reaction time (Fig. 3) and a total reaction time of 5:30 hours at room temperature gave a constant conversion of 83%.

Table 2 Nickel-catalyzed homocoupling of Grignard reagents using atmospheric oxygen as the oxidant[a]

$$\text{Ar-Br} \xrightarrow[\text{Et}_2\text{O, r.t}]{\text{Mg turnings}} \underset{\text{(intermediate)}}{\text{Ar-Mg-Br}} \xrightarrow[\text{Et}_2\text{O, r.t, 5:30 hours}]{\text{air, 0.03 mmol NiL}} \text{Ar-Ar}$$

Entry	Ar–Br	Product	Yield[b] (%)
1	a	2a	92
2	b	2b	79
3	c	2c	86
4	d	2d	75
5	e	2e	83
6	f	2f	76
7[c]	g	2g	65
8[c]	h	2h	61

Table 2   (Contd.)

$$\text{Ar-Br} \xrightarrow[\text{Et}_2\text{O, r.t}]{\text{Mg turnings}} \underset{\text{(intermediate)}}{\text{Ar-Mg-Br}} \xrightarrow[\text{Et}_2\text{O, r.t, 5:30 hours}]{\text{air, 0.03 mmol NiL}} \text{Ar-Ar}$$

Entry	Ar–Br	Product	Yield[b] (%)
9[d]	i	2i	68
10	j	2j	73

[a] *Reaction conditions*: Mg turnings (0.320 g), aryl bromide (10 mmol), catalyst (0.03 mmol), Et$_2$O (10 ml). [b] Isolated yield. [c] Reactions at −5 °C to rt. [d] In THF, 60 °C, 9 hours.
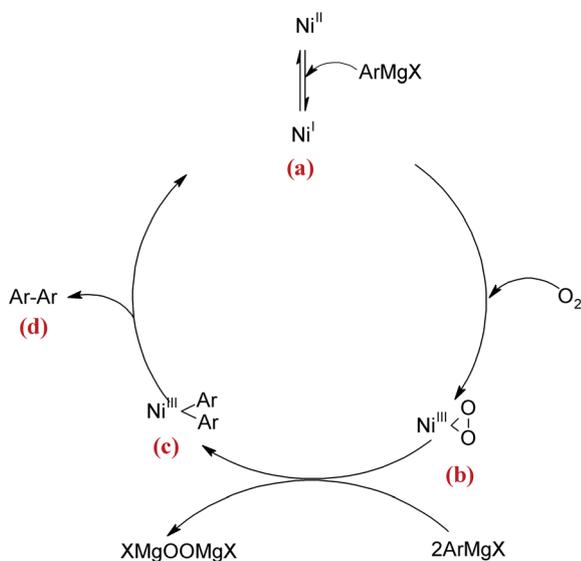

Fig. 5   Proposed mechanism.

Fig. 6   UV-Vis spectra for the confirmation of the peroxo-nickel(III) intermediate.

The effect of catalyst concentration on the yield of the coupling product (Fig. 4) was examined by varying the substrate to catalyst ratio from a total catalyst amount of 0.01 mmol to 0.05 mmol. Initially for a comparison study, we assessed the catalytic activities of simple nickel metal precursors, NiCl$_2$ and [Ni(PPh$_3$)$_2$Cl$_2$]. The results in Table 1 indicate that a better yield could be achieved by increasing the amount of NiCl$_2$ and [Ni(PPh$_3$)$_2$Cl$_2$] (entries 2–9). Next, we turned our attention to **NiL**. The yield increased with **NiL** loading and reached the highest value of 83% with 0.03 mmol of **NiL** at 5:30 hours
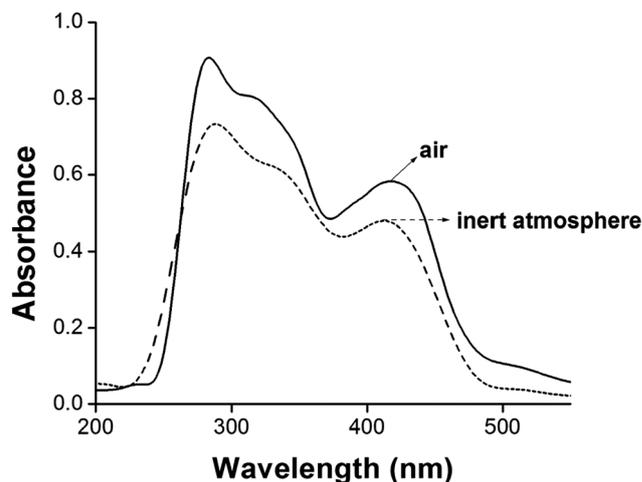
(entry 6). The influence of air is the key factor in the present catalytic system. A good yield was observed in the presence of atmospheric oxygen. The reaction was carried out in an inert atmosphere (argon) in the absence of air and resulted in a lower yield, which may be attributable to the lack of formation of the peroxo-nickel(III) active species (entry 10). In the absence of **NiL**, only traces of coupling products were obtained (entry 1) showing the effective catalytic role of **NiL**. The efficiency of the complex is so prominent that the present coupling can be readily scaled up to the reaction of 50.0 mmol of the aryl halide using 0.150 mmol of the catalyst, which yields 80% of the biaryl in 8 hours with a negligible amount of byproducts (entry 11). To exclude the effect of magnesium, the reaction was carried out

using commercial phenylmagnesium bromide as the starting material in the presence of air (entry 12). To our surprise the yield was lower (37%). This may be due to the difficulty in handling the commercial phenylmagnesium bromide.[10] Most of the reported Grignard reagent based catalytic systems[5,8] require a sophisticated set-up to handle the reagents in a moisture free environment in contrast to the present work.

This encouraging result led us to extend the scope of the reaction to various aryl Grignard reagents to synthesize simple functionalized biaryls in good yield (Table 2). It was observed that under similar reaction conditions high yields of **2a** and **2b** were obtained upon efficient coupling of 4-methoxy- and 2-methoxyphenylmagnesium bromide, respectively (entries 1 and 2). The presence of a methyl group at the *ortho*-position of the aryl Grignard reagent resulted in a somewhat lower yield of the homocoupling product (entry 4). It is noteworthy that the present reaction system is tolerant of an aryl chloride (entry 6). Nitro and nitrile groups were tolerated (entries 7 and 8), hence the reaction is chemoselective. Although, the sterically demanding substrate **1i** required a higher reaction temperature and longer reaction time, it gave the corresponding biaryl **2i** in moderate to good yield (entry 9). Also, the reaction allows the coupling of heteroaryl Grignard reagent **1j** successfully (entry 10). It was observed that when a Grignard reagent contains an electron donating group it enhances the yield of the coupling product compared to a reagent with an electron withdrawing group. The formation of cross-coupling products was found to be low in all of these experiments.

The proposed mechanism is depicted in Fig. 5 for the **NiL** catalyzed reaction. A low valent nickel species is generated by the Grignard reagent, which is a strong reducing agent, and is involved in the catalytic cycle.[24–26] The oxidative addition of atmospheric oxygen to the low valent nickel complex (a) forms a peroxo-nickel(III) intermediate (b), which is the key step of this catalytic cycle.[27] It then reacts with two equivalents of RMgX to give the biarylnickel(III) intermediate (c) and XMgOOMgX.[8,28] Thus, the formed biarylnickel(III) intermediate (c) undergoes a rapid reductive elimination, which eventually yields the homocoupling product Ar–Ar and nickel(I) is regenerated. It can be reasonably supposed that the formation of the unstable nickel(III) species (c) is required to achieve a very quick reductive elimination to give (d) and that the best way to favor the reductive elimination is to increase the oxidation state of the metal. The formation of the peroxo-nickel(III) intermediate was confirmed by UV-Vis spectrophotometer analysis (Fig. 6). The absorption peak of the catalytic reaction mixture that appears at 419 nm can be attributed to the peroxo-nickel(III) intermediate[27] and its absence from the reaction carried out under inert conditions further confirms the necessity of atmospheric oxygen for the present catalytic system. Various iron,[29] copper[30] and palladium[31]-catalyzed reactions are well established with such peroxo complexes as the catalytic intermediate.

The catalytic system reported herein shows an appreciable improvement of the yield of a biaryl in comparison with our previous work.[15] This can be attributed to the efficiency of **NiL**, which facilitates a faster reductive elimination reaction in the catalytic cycle. Hypothetically, it may be due to the presence of

more hindered ancillary ligands. The effect presumably arises from a relief in steric congestion upon generation of the free organic product and a resulting metal center with a reduced coordination number.[32]

4. Conclusions

In conclusion, we have developed an energy efficient nickel-catalyzed coupling methodology to couple aryl Grignard reagents at room temperature, using atmospheric oxygen as the oxidant. The reaction system is compatible with diverse functionality to afford biaryls in good to excellent yields. It is noteworthy that the reaction is chemoselective. The *in situ* preparation of the Grignard reagent, small amount of catalyst loading, and mild reaction conditions, make this catalytic methodology practicable to the large scale synthesis of symmetrical biaryls.

Acknowledgements

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