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Sathya Munusamy, Premkumar Muniyappan & Venkatachalam Galmari

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Synthesis and structural characterization of palladium(II) 2-(arylazo)naphtholate complexes and their catalytic activity in Suzuki and Sonogashira coupling reactions

Sathya Munusamy, Premkumar Muniyappan and Venkatachalam Galmari

PG & Research Department of Chemistry, Government Arts College, Dharmapuri, India

ABSTRACT

A family of five palladium(II) 2-(arylazo)naphtholate complexes, [PdCI(PPh₃)(L)] (L = O, N-donor of bidentate 2-(arylazo)naphtholate ligands), have been synthesized and characterized by elemental analysis and spectral (FT-IR, UV–Vis, ¹H-NMR and ¹³C-NMR) methods. Further, the catalytic efficiency of all the complexes have been investigated for Suzuki and Sonogashira coupling reaction of various aryl halides.



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Palladium(II) complexes; azo ligands; characterization; catalyst; Suzuki; Sonogashira coupling reaction

1. Introduction

Coordination chemistry has traditionally emphasized the design and preparation of ligands which are able to control the electronic as well as steric properties of transition metal ions. There has been considerable interest in palladium complexes largely because of their potential catalytic and biological applications [1, 2]. As properties of such complexes depend primarily on the coordination environment around palladium, complexation by ligands of selected types is important.

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CONTACT Galmari Venkatachalam 🔯 gvchem@gmail.com 🗈 PG & Research Department of Chemistry, Government Arts College, Dharmapuri, Tamilnadu 636 705, India



Scheme 1. Major classes of metal-catalyzed cross coupling reactions.

The chemistry of azobenzene derivatives has stimulated research directed towards their use as materials for digital storage, as building blocks in supramolecular devices and polymer materials [3–5]. Special attention has been paid to complexes with nitrogen donors such as amines, imines, azo, and heterocyclic compounds as catalysts [6]. Several studies have been published on the synthesis and spectral properties of azodyes [7–9], reflecting their important applications in polyester fibers [10], disperse dyes [11] as well as their involvement in many biological reactions and in analytical chemistry [12].

Arylazo ligands provide a great platform in coordination/organometallic chemistry for development of ligand systems [13]. Most azo ligands are easily accessible using simple synthetic procedures with selection of an amine and substituted phenol. These ligands can potentially stabilize metals in different oxidation states which is particularly useful in catalytic reactions [14]. Metal complexes derived from arylazo ligands have found applications in catalysis [15].

The palladium-catalyzed Suzuki cross coupling of aryl halides with arylboronic acids is a powerful tool for preparation of unsymmetrical biaryl compounds [16] and has been applied to many areas, including herbicides [17] and natural product synthesis [18]. The value of the Suzuki reactions stems from using low-cost and non-toxic chemicals, vide substrate tolerance, mild reactions conditions, and easy separation of products from the reaction media [19, 20]. The use of non-flammable inexpensive and abundant green solvents such as water or water solutions is an important area of research for the Suzuki reaction [21-23]. Cross coupling reactions involve metal-catalyzed coupling of an organic electrophile with an organic nucleophile (Scheme 1). A variety of name reactions have been developed using organometallic carbon nucleophiles. Examples with nearly every metal in the periodic table have been demonstrated, but the most common organometallic species used include organotin (Stille), organoboron (Suzuki), Grignard reagents (Kumada), organosilicon (Hiyama), organozinc (Negishi) and in situ generated acetylide anions (Sonogashira). Key steps in these cross-coupling reactions include oxidative addition of the organic halide, trans metalation of the nucleophilic carbon, and reductive elimination to form the products.

The employment of hydrophilic ligands such as N-heterocyclic carbenes (NHCs) or phosphine ligands is another method of improving the efficiency of Suzuki catalysis in water. Palladium triaryl phosphine complexes have been the most commonly employed as catalysts for the Suzuki reactions. Sterically demanding, electron-rich phosphines, such as tri-*t*-butylphosphines and its analogs [24], di(*t*-butyl)aryl and dicyclo-hexylarylphosphines [25] have excellent activities in the Suzuki reactions phosphines.



Scheme 2. Synthesis of Pd(II) 2-(arylazo)naphtholate complexes.

have several disadvantages, including toxicity, sensitivity to air and moisture, and difficult separation from the products. As a result, NHCs have emerged as an alternative to phosphine ligands [26–32]. The unique steric and electronic properties of NHCs as well as their specific coordination chemistry (strong O-donor and weak π -acceptor properties) contribute to the generation of highly active and stable metal centers in the key catalytic steps of the Suzuki reaction.

Steric bulk of the ligand is believed to increase the rate of reductive-elimination to regenerate the active catalyst. Despite the bulky ligand increasing the reductive elimination rate, the rate of the oxidative addition step can be dramatically affected by the increasing size of the ligand. According to these points a balance between the steric and electronic properties of the ligand is an essential requirement. Though many reports are available on azo ligands with ruthenium and osmium, less research has been reported for palladium(II) arylazo complexes. We are therefore interested in continuing our studies on synthesis of catalysts derived from inexpensive and easily synthesized ligand sets.

As a continuation of our work [33] in designing new O, N donor based ligands for exploring their organometallic chemistry and catalytic activity in organic transformations [34], herein we report the synthesis and structural characterization of palladium(II) complexes containing 2–(arylazo)naphtholate ligands and their catalytic activity in Suzuki and Sonogashira coupling reactions of various aryl halides.

2. Experimental methods

2.1. Materials

All chemicals used were chemically pure and AR grade. Solvents were purified and dried according to standard procedure. $PdCl_2(PPh_3)_2$ was purchased from Arora Matthey and used without purification. Triethylamine, aniline, *p*-substituted aniline and 2-naphthol were purchased from Sigma Aldrich. Other chemicals (used in catalytic studies) were purchased from Merck and Aldrich. The 2-(arylazo)naphtholate ligands were prepared according to literature methods [35].

2.2. Physical measurements

Analyses of carbon, hydrogen and nitrogen were performed on elementary system model vario EL111 at Sophisticated Test and Instrumentation Center, Cochin, India. ¹H- and ¹³C-NMR spectra were recorded in the Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Kochi. FT-IR spectra of the complexes were recorded in a CARY 360, Agilent resolution pro spectrophotometer from 4000 to 400 cm⁻¹. Electronic spectra of the complexes were recorded in CHCl₃ solution with a Cary 300 Bio UV–Vis Varian spectrophotometer from 800 to 200 nm using cuvettes of 1 cm path length. Melting points are uncorrected and were determined in capillary tubes on a Boetius micro heating apparatus.

2.3. Synthesis of Pd(II) 2-(arylazo)naphtholate complexes

All the new complexes were prepared by the following general procedure. To an ethanol solution of 1:1 ratio of 2-(*p*-arylazo)naphtholate ligands (1 mmol, 0.037–0.047 g) was added [Pd(PPh₃)₂Cl₂] (1 mmol, 0.1 g) in CHCl₃. The resulting reaction mixture was then heated at reflux for 4 h to yield a reddish-purple solution. The solid mass thus obtained was subjected to purification by thin layer chromatography on a silica plate. Chloroform was used as eluent and a reddish purple band separated which was extracted with 1:1 dichloromethane–chloroform and evaporation of this extract gave [PdCl(PPh₃)(L₁₋₅)] as dark pink crystalline solids.

2.4. General procedure for coupling reactions of aryl halides with boronic acid (Suzuki coupling reaction)

In a two-necked flask under an atmosphere of nitrogen was placed palladium complexes (1–5) (1 mol%), bromobenzene (0.5 mmol), aryl boronic acid (0.75 mmol) and K_2CO_3 (1 mmol). The mixture was then refluxed at 80 °C for 2 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure and the resulting product was diluted with water (10 ml) and Et₂O (10 ml), followed by extraction twice (2 × 6 ml) with Et₂O. The combined organic fraction was dried over MgSO₄. The crude product was purified by column chromatography by using hexane as eluent.

2.5. General procedure for Sonogashira coupling reactions

To a slurry of aryl halide (0.5 mmol) palladium catalyst (0.3 mol%) in an appropriate solvent (5 ml), phenylacetylene (0.75 mmol) and K₂CO₃ (1.25 mmol) were added and heated at required temperature. After completion of the reaction (monitored by TLC), the flask was removed from the oil bath and water (20 ml) added, followed by extraction with ether (4 × 10 ml). The combined organic layers were washed with water (3 × 10 ml), dried over anhydrous Na₂SO₄ and filtered; solvent was removed under vacuum. The residue was dissolved in hexane and analyzed by GC–MS using Elite-5 columns, which are fused silica capillary columns coated with 5% diphenyl and 95% dimethyl polysiloxane.

	Elemental analysis found (calculated)%			IR (cm ⁻¹)			UV–Vis (nm)		
Complexes	С	Н	Ν	$\upsilon N = N$	υPPh ₃	υ C-0		λ_{max}	
[PdCl(PPh ₃)(L ₁)] (1)	72.00 (72.48)	4.12 (4.35)	5.25 (5.20)	1409	1455	1298	460 ^a	340 ^b	235 ^c
$[PdCl(PPh_3)(L_2)]$ (2)	72.68 (72.85)	4.63 (4.62)	4.98 (4.95)	1408	1465	1300	470 ^a	335 ^b	240 ^c
$[PdCl(PPh_3)(L_3)]$ (3)	68.76 (68.91)	4.38 (4.42)	4.71 (4.70)	1436	1460	1296	465 ^a	345 ^b	230 ^c
$[PdCl(PPh_3)(L_4)]$ (4)	55.54 (55.88)	2.89 (3.02)	4.05 (4.09)	1433	1474	1335	450 ^a	330 ^b	230 ^c
$[PdCl(PPh_3)(L_5)]$ (5)	59.01 (59.13)	3.07 (3.22)	12.90 (12.94)	1401	1479	1307	455 ^a	350 ^b	225 ^c
al MCT the mainting									

Table	1. Elemental	analyses,	IR	and	UV–Vis	spectral	data	of	Pd(II)	2-(arylazo)naphtho-
late co	mplexes.									

aLMCT transition.

bn–π*

сπ-π*.

3. Results and discussion

The reaction of 2-(*p*-arylazo)naphtholate ligands (HL_{1-5}) with $[Pd(PPh_3)_2Cl_2]$ proceeds smoothly in refluxing ethanol/chloroform in the presence of triethylamine to afford the expected mixed-ligand palladium complexes $[PdCl(PPh_3)(L)]$ (L = bidentate 2-(arylazo)naphtholate ligands) as shown in Scheme 2. The choice of substituents (R-groups) in 2-(arylazo)naphtholate ligands allows for fine tuning of electronic properties which may influence the resulting metal complex properties.

All the new palladium(II) complexes are highly colored, stable in air, non-hygroscopic and highly soluble in common solvents such as dichloromethane, chloroform, etc., The analytical data are listed in Table 1 and are in agreement with general molecular formulas proposed for all the complexes.

3.1. IR spectra

The IR spectral data of HL₁₋₅ and their metal complexes are given in Table 1. Infrared spectra of the complexes show multiple bands of varying intensities from 4000 to 400 cm⁻¹. No attempt has been made to assign each individual band to a specific vibration. However, the infrared spectra of all the ligands exhibit bands around 1444–1480 cm⁻¹ and 1242–1264 cm⁻¹ corresponding to azo v(N = N-) and phenolic v(C-O) stretching frequencies, respectively. On complexation v(N = N-) appears at lower frequency (1401–1436 cm⁻¹) and this red shift supports the coordination of N(azo) to palladium ion [36]. The band corresponding to phenolic v(C-O) stretch is shifted to higher frequency (1296–1335 cm⁻¹) in all the complexes, confirming that the other coordination site is the phenolic oxygen [15]. The complexes exhibit a band around 1490–1465 cm⁻¹ due to triphenylphosphine ligands (see Figures S1–S10, in supplementary materials).

3.2. Electronic spectra

The electronic spectra of the complexes have been recorded in $CHCl_3$ and display four intense absorptions from 800 to 200 nm. The electronic spectral data of all the complexes are listed in Table 1 and a representative spectrum is shown in Figure 1 (all other spectra are provided in the Figures S11–S14, in supplementary materials). The absorption bands around 550 nm have been assigned to ligand to metal charge



Figure 1. UV-Vis spectrum of [PdCl(PPh₃)(L₂)] (2).

transfer transitions taking place from the filled ligand (HOMO) orbital to the singly occupied palladium t₂ orbital (HOMO). The bands at 320–390 nm are due to $n-\pi^*$ transitions of non-bonding electrons present on the nitrogen of the arylazo group in the palladium(II) complexes. The band observed around 220–240 nm is assigned to $\pi-\pi^*$ transitions of the ligands. The patterns of the electronic spectra of all the complexes indicate the presence of square planar palladium(II) [37].

3.3. ¹H- and ¹³C-NMR spectra

¹H-NMR spectra of the complexes were recorded in CDCl₃ at room temperature. The characteristic signals in the ¹H-NMR spectra are given in Table 2 and a representative spectrum is given in Figure 2 (all the other spectra are in the Figures S15–S17, in supplementary materials). The signal as a multiplet in the spectra of all the complexes observed at 6.2–8.4 ppm have been assigned to the aromatic protons of triphenyl-phosphine and 2-(arylazo)naphtholate ligands. Methyl protons are singlets at δ 2. 49 ppm and the methoxy protons are singlets at 3.93 ppm, due to **2** and **3**, respectively. ¹³C-NMR spectra of **1** and **2** were recorded. The –CH₃ carbon peak appeared at δ 15.01 ppm for **1**. The methoxy carbon signal (OCH₃) was observed for **2** at δ 55. 34 ppm. The ¹³C-NMR spectra are shown in Figures S18 and S19 (see Supplementary materials).

3.4. Catalytic Suzuki cross coupling reactions

The palladium(II) complexes were screened for their catalytic activity in C–C coupling reactions. The results obtained are given in Table 3. We have also investigated the effects of catalyst loading on the coupling of bromobenzene with phenylboronic acid in order to optimize the reaction conditions. It is significant to accomplish good yields using minimum amounts of catalysts 0.01 mmol and K_2CO_3 as base and methanol as

 Table 2. The ¹H-NMR spectral data of Pd(II) 2-(arylazo)naphtholate complexes.

Complexes	¹ H-NMR data (δ; ppm)
[PdCl(PPh ₃)(L ₁)] (1)	7.06–8.36(Ar, m)
$[PdCl(PPh_{3})(L_{2})]$ (2)	6.61–8.44(Ar, m), 2.49(CH ₃ , s)
$[PdCl(PPh_3)(L_3)]$ (3)	6.66–8.43(Ar, m), 3.93(OCH ₃ , s)
$[PdCl(PPh_3)(L_4)] (4)$	6.23–8.36(Ar, m)
$[PdCI(PPh_{3})(L_{5})] (5)$	6.53–8.23(Ar, m)



Figure 2. ¹H-NMR spectrum of $[PdCl(PPh_3)(L_2)]$ (2).

solvent. The obtained results were promising and all the complexes have good activity.

To optimize the catalyst loading, it is preferable to use a small amount of catalyst and achieve a high yield in the Suzuki cross coupling reactions. Recently, it was reported that high catalyst loading leads to active black Pd formation and also inhibits catalytic cycles. Our reaction worked well with different catalyst ratios and the reaction of bromobenzene with phenyl boronic acid furnished good yield when 1 mol% of catalyst was loaded. We have chosen (1 mol %) catalyst [PdCl(PPh₃)(L₁) loading as the best conditions for further coupling reactions (see Supporting Information: effect of catalyst loading Table S1, in supplementary materials). To select the most suitable solvents in our catalytic system, we chose the reaction between bromobenzene with boronic acid in the presence of various solvents MeOH, CH₃CN, DMF/H₂O (2:1) and (1:2), CH₂Cl₂ and ethanol. Methanol gives an excellent yield of 82% and the poor one is acetonitrile with yield of 52%. In DMF/H₂O (2:1), MeOH/H₂O (2:1), CH₂Cl₂ and ethanol, the yields are 79%, 81%, 54%, and 70%, respectively.

The catalytic activity of the Pd(II) 2-(arylazo)naphtholate complexes were investigated under the same reaction conditions. To survey the generality of the catalytic protocol, we investigated the reaction using various aryl halides coupled with 8 🕢 M. SATHYA ET AL.



Table 3. Suzuki carbon-carbon coupling reaction of aryl bromides with phenylboronic acid^a.

aReaction conditions: 0.5 mmol of bromobenzene, 0.75 mmol of phenylboronic acid, 1 mmol of K_2CO_3 , 1 mol% of catalyst. blsolated yield after column chromatography.

bisolated yield after column chromatography.

arylboronic acids under the optimized conditions. The results are summarized in Table 3. When benzene boronic acid was coupled with aryl bromides containing both electron-donating and electron-withdrawing groups in the para position, the corresponding products were obtained in moderate yields. The ortho substituted aryl bromide (2-



Scheme 3. Probable mechanism for the observed Suzuki cross coupling reaction by [PdCl(PPh₃)(L)].

Table 4. Optimization of reaction conditions ^a .								
Br +	Complex 2 Solvent, Base							

|--|

Entry Solvent Base		Temp. °C	Catalyst loading (complex mol%)	Time (h)	Yield ^b (%)	
1	Toluene	K ₂ CO ₃	80	0.3	9	35
2	Acetone	K ₂ CO ₃	100	0.3	8	46
3	MeCN	K ₂ CO ₃	80	0.3	10	40
4	DMSO	K ₂ CO ₃	100	0.3	8	58
5	DMF	K ₂ CO ₃	78	0.3	8	66
6	Ethanol	Et₃N	78	0.3	6	70
7	Ethanol	K ₂ CO ₃	80	0.3	6	85
8	Ethanol	Pyrolidine	80	0.2	6	64
9	Ethanol	K ₂ CO ₃	78	0.1	6	79
10	Ethanol	K ₂ CO ₃	78	0.4	6	92

aReaction conditions: bromobenzene (0.5 mmol), phenylacetylene (0.75 mmol), base (1.25 mmol), solvent (5 ml), catalyst (0.3 mol%), temperature (80 °C).

blsolated yield after column chromatography.

bromotoluene, Table 3; entry 5) gave the corresponding products in slightly lower yield, perhaps due to steric effects.

The coupling reactions of two electron rich arylboronic acids with various aryl bromides (Table 3, entries 1-4) afforded the corresponding products in lower yields than 10 👄 M. SATHYA ET AL.



Table 5. Sonogashira reaction of aryl bromide with phenylacetylene^a.

aAryl bromide (0.5 mmol), phenylacetylene (0.75 mmol), catalyst complex **2** (0.3 mol%), ethanol (5 mL), K_2CO_3 (1.25 mmol), temperature 80 °C. blsolated yield based on column chromatography.

those of the benzene boronic acid. Also, coupling reactions of aryl chlorides with benzene boronic acid gave good conversions for all the substrates in 2 h. As expected, satisfactory results were obtained for all electron deficient substrates in the boronic acid (entry 6). Further, chlorobenzonitrile can also react with phenylboronic acid with good conversions. The catalytic activity of the present complexes is good and although several catalytic systems have been reported, a catalyst of this type is new for its bidentate O, N-donor environment with the palladium center (Scheme 3).

3.5. Catalytic Sonogashira cross coupling reactions

Our first approach was to optimize reaction conditions for the reaction between bromobenzene and phenylacetylene as a model reaction. The results are summarized in Table 4. We used a variety of solvents (Table 4, entries 1–6). All the solvents gave good conversion but excellent results were obtained with ethanol.

Ethanol also helped in decreasing the leaching of **2** (Table 4, entry 7). Toluene or acetonitrile gave lower product yields (Table 4, entries 1–3). Sonogashira coupling is strongly influenced by the nature of the base. We applied several bases (Table 4) among which K_2CO_3 gave maximum conversion and selectivity (Table 4, entry 7). Increase in Pd content from 0.3 mol% to 0.4 mol% did not show any significant

increase in product yield (Table 4, entries 7 and 10). Therefore, 0.3 mol% Pd loading at 80 °C for 6 h were the optimized reaction parameters for the model reaction (Table 4, entry 7).

Under these optimized conditions, we carried out substrate study using various substituted bromobenzene derivatives and phenylacetylene as starting materials. We tried reaction of both electron-donating as well as electron-withdrawing substituents of bromobenzene with substituted phenylacetylene which exhibits excellent reactivity towards **2**. The electron-withdrawing substituents (Table 5, entries 2, 5, and 7) gave greater yield compared to electron-donating groups (Table 5, entries 3, 4, and 6). The electron-withdrawing groups facilitate the removal of bromo group. The catalyst showed good activity for electron-donating groups compared to electron-withdrawing groups (Table 5, Entries 1–7).

4. Conclusion

The present work describes a simple and convenient route to synthesize a new family of palladium(II) complexes incorporating O, N donors of 2-(arylazo)naphtholate ligands. The prepared compounds have been characterized by spectroscopic techniques. All the complexes catalyze Suzuki and Sonogashira type C–C cross coupling reactions of aryl halides with phenyl boronic acid and phenylacetylene. All the catalytic reactions proceed under ligand free conditions.

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