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Article

Preparation, characterization and catalytic activity of amphiphilic cyclopalladated aryl imines and their Langmuir-Blodgett films

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ABSTRACT

A series of novel amphiphilic cyclopalladated aryl imines were synthesized and characterized. These catalysts showed high activity for Heck and Suzuki reactions in homogeneous systems. Heterogeneous Langmuir-Blodgett films of the catalysts also demonstrated high catalytic activity for these coupling reactions.

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1. Introduction

Palladium-catalyzed coupling reactions are an important method for generating C–C bonds in organic synthesis. Palladium catalysts tolerate a wide range of functional groups, can be used in a small amount, and also have low toxicity [1–5]. However, traditional catalysts such as PdCl_2 , $\text{Pd}(\text{AcO})_2$, $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, and $\text{PdCl}_2(\text{PPh}_3)_2$ have a number of drawbacks and limitations including air-sensitivity and high cost [6–8]. In recent decades, cyclopalladated complexes have been extensively studied because of their high activity in various types of coupling reactions, stability in the air, no need for ancillary ligands, and simple synthetic methods [9–13]. Beller et al. [14] first reported the use of cyclopalladated complexes as catalysts for Heck and Suzuki coupling reactions, and various palladacycles have been reported since. Ohff and Weissman et

al. described good performance from orthopalladated imines and CN-palladacycles for Heck [15] and Suzuki [16] reactions, respectively. In our previous work, we have focused on cyclopalladated ferrocenyl imines for Heck, Suzuki, and Sonogashira coupling reactions, and for C–H activation chemistry [17–20].

The Langmuir-Blodgett (LB) technique is a simple, low cost method for assembling layers with well-defined molecular orientation and control over thickness at the molecular level to reproducibly produce highly ordered molecular arrays. One advantage of LB films is that various experimental techniques can be used to study reaction mechanisms. Recently, amphiphilic transition metal catalysts on substrates for catalytic application were studied by LB technique and have generated considerable interest. Töllner et al. [21] reported the hydrogeneration of carbon-oxygen double bonds catalyzed by active LB

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Scheme 1. Synthesis of arylimine cyclopalladated catalysts.

films of a rhodium complex. Abatti et al. [22] used porphyrin LB films as catalysts for alkene epoxidation, and doubled yields were obtained compared with the homogeneous system. Benítez et al. [23] investigated the catalytic properties of the zirconium phosphonate LB films and self-assembled monolayers using the epoxidation of *cis*-cyclooctene. Park et al. [24] reported catalytic CO oxidation by LB films of Rh/Pt bimetallic nanoparticles.

In our previous studies, we synthesized a series of amphiphilic cyclopalladated ferrocenyl imines and investigated the activity of the LB films in Suzuki coupling reactions. However, the LB films presented with weak thermal stability and poor resistance to organic solvents, which prevented the investigation of the heterogeneous catalytic mechanism [25–27]. In order to overcome these limitations, a series of novel amphiphilic cyclopalladated arylimines (**2a–2c** and **3a–3c**, Scheme 1) were prepared and characterized. Their catalytic properties for Heck and Suzuki cross-coupling reactions were initially investigated in homogeneous systems to determine suitable experimental conditions for studies into heterogeneous catalytic activity of the self-assembled films. The catalyst **2b** was found suitable for formation of monolayers and LB films on solid slides, and its catalytic activity in Suzuki coupling reactions was also investigated.

2. Experimental

2.1. Synthesis of 4-[(alkyl imino)methyl]phenol (**1a–1c**)

A mixture of 4-hydroxybenzaldehyde (10 mmol), amine (10 mmol), 4 Å molecular sieve (4 g), and toluene (150 ml) was refluxed under a nitrogen atmosphere at 115 °C for 7 h. The reaction mixture was then filtered and a small amount of petroleum ether was added to the filtrate. The mixture was cooled and recrystallized at 0 °C to give the ligands **1a–1c** as white crystals. The products were confirmed by ¹H NMR, ¹³C NMR, and MS.

2.2. Synthesis of [PdCl(HOC₆H₄CH=NR)]₂ (**2a–2c**)

A mixture of dilithium chloropalladate (1.0 mmol), sodium acetate (1.0 mmol), **1a–1c** (1.1 mmol), and methanol (10 ml) was stirred at room temperature for 24 h. The mixture was then filtered, concentrated, and purified by silica column chro-

matography using dichloromethane and methanol (6:1) to give compounds **2a–2c** as yellow solids. The products were confirmed by ¹H NMR, ¹³C NMR, and MS.

2.3. Synthesis of [PdCl(CH₂=CHC(=O)C₆H₄CH=NR)]₂ (**3a–3c**)

A mixture of potassium carbonate (3 g), **2a–2c** (1.0 mmol), and dichloromethane (80 ml) was cooled by an ice bath under the nitrogen with stirring, and acryloyl chloride (1.2 mmol) was added. The resulting mixture was stirred on ice for a further 2 h. The ice bath was removed and the mixture was stirred at room temperature for 4 h. A NaOH solution was added and the mixture was stirred for a further 30 min. The mixture was then filtered, concentrated, and purified by silica column chromatography using dichloromethane and methanol (10:1) to give compounds **3a–3c** as light yellow solids. The products were confirmed by ¹H NMR, ¹³C NMR, and MS.

2.4. Preparation of the Langmuir monolayer and LB films

Chloroform solutions of the complexes were carefully spread onto an ultrapure water surface. After evaporation of solvent (30 min) and stabilization of the films for 1 h, the so formed Langmuir monolayers were compressed at a speed of 5 mm/min at 20 ± 1 °C. LB films were transferred onto silicon slides and glass slides (for atomic force microscopy (AFM) and catalytic studies). The solid slides were cleaned in a boiling mixture of concentrated H₂SO₄ and concentrated HNO₃ (1:1) for 1 h and then washed with pure water.

2.5. Heck cross-coupling reactions

Aryl halide (0.5 mmol), styrene (1.5 mmol), and catalyst **3a–3c** (0.1 mol%) were combined with K₃PO₄ (1.0 mmol) and dimethylformamide (1.5 ml) or deionized water (1.5 ml) in a small round-bottom flask. The reaction mixture was stirred and then quenched. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The organic phases were combined, dried with MgSO₄, and filtered, and the resulting solution was analyzed by gas chromatography.

2.6. Suzuki cross-coupling reactions

Aryl halide (0.25 mmol), aryl boronic acid (0.60 mmol), catalyst **3a–3c** (0.001 mol%), and *tetra-n*-butylammonium bromide (TBAB, 0.30 mmol) were combined with K₂CO₃ (0.3 mmol) and deionized water (1.5 ml) in a small round-bottom flask. The reaction mixture was stirred and then extracted with ethyl acetate three times. The organic phases were combined, dried with MgSO₄, and filtered, and the resulting solution was analyzed by gas chromatography.

3. Results and discussion

3.1. Catalytic properties for the homogeneous Heck coupling of bromobenzene and styrene

An initial survey of bases, including Et₃N, Na₂CO₃, K₂CO₃, NaHCO₃, NaOAc, K₃PO₄, and K₃PO₄·3H₂O, used for Suzuki reaction of bromobenzene and styrene using 0.1 mol% of catalyst **2b** was investigated, and K₃PO₄ was found to give the best result (>99% conversion determined by GC). From the experiments, it was found that 100 °C was the optimal reaction temperature, and using dimethylformamide as the solvent gave the best conversion. Using dimethylformamide as solvent, K₃PO₄ as base, and TBAB as co-catalyst at 100 °C, the activity of the catalysts for the Heck coupling of bromobenzene and styrene was investigated. The results are listed in Table 1.

Table 1 shows that all the catalysts gave high activity for this coupling reaction with 0.1 mol% catalyst loading. Using catalyst **2b**, the cross-coupling of different kinds of aryl halides with styrene was shown to be efficient under the optimized reaction conditions. The results in Table 2 show that various substituted aryl bromides gave high yields of coupled products (entries 1–7). A number of heteroaromatic substrates such as bromonaphthalene also gave high conversion (entries 8–10).

To investigate the capability of the catalysts for other cross-coupling reactions, the Suzuki cross-coupling reaction of 4-bromotoluene (0.5 mmol) and phenylboronic acid (0.6 mmol) was carried out with various bases and solvents in the presence of 0.001 mol% of **2b** without a blanket of inert gas. The reaction proceeded in ethanol-water solutions (2:1, 3 ml) with >99% conversion determined by GC. While several bases are suitable for this reaction, NaOH was chosen for its low cost. Using these conditions, the relative activity of several palladacycles **2a–2c** and **3a–3c** for the same model reaction was then studied. As shown in Table 3, **2a** and **2b** showed good activity toward the reaction and were chosen for further investigation.

Using the same protocol and 0.001 mol% loading of catalyst **2b**, a variety of aryl bromides were able to be coupled efficiently with phenylboronic acid. The results are shown in Table 4. For activated and inactivated aryl bromides, excellent yields were obtained (entries 1–5 and 8–11). 1-Bromonaphthalene and 3-bromopyridine also exhibited high conversion of 97% and 77%, respectively (entries 6 and 7). The amphiphilic cyclopalladated aryl imines were found to be efficient catalysts for Suzuki coupling of aryl bromides with phenylboronic acid.

Table 1

The relative activity of the catalysts on the Heck coupling of bromobenzene and styrene.

Entry	Catalyst	Yield ^a (%)
1	2a	>99
2	2b	>99
3	2c	>99
4	3a	98
5	3b	97
6	3c	98

Reaction conditions: PhBr 0.5 mmol, styrene 1.0 mmol, catalyst 0.1 mol%, K₃PO₄ 1.0 mmol, *n*-Bu₄NBr 0.5 mmol, DMF 2 ml, 6 h.

^a Determined by GC based on the products.

Table 2

Heck coupling of aryl halides with styrene using **2b** as a catalyst.

Entry	Aryl halide	Product	Yield ^a (%)
1	C ₆ H ₅ Br		94
2	<i>p</i> -CH ₃ O-C ₆ H ₄ Br		19
3	<i>p</i> -CF ₃ -C ₆ H ₄ Br		95
4	<i>p</i> -CHO-C ₆ H ₄ Br		93
5	<i>p</i> -COOCH ₃ -C ₆ H ₄ Br		84
6	<i>p</i> -NO ₂ -C ₆ H ₄ Br		94
7	<i>m</i> -CHO-C ₆ H ₄ Br		76
8	1-bromonaphthalene		80
9	3-bromopyridine		92
10	3-bromothiophene		77

Reaction conditions: aryl halide 0.5 mmol, styrene 1.0 mmol, catalyst 0.1 mol%, base 1.0 mmol, *n*-Bu₄NBr 0.5 mmol, DMF 2 ml, 6 h, 100 °C.

^a Isolated yield based on aryl halides.

Table 3

The relative activity of the catalysts for the Suzuki coupling of 4-bromotoluene and phenylboronic acid.

Entry	Catalyst	Yield ^a (%)
1	2a	>99
2	2b	>99
3	2c	87
4	3a	93
5	3b	93
6	3c	92

Reaction conditions: 4-bromotoluene 0.5 mmol, PhB(OH)₂ 0.6 mmol, NaOH 1.0 mmol, catalyst 0.001 mol%, ethanol-water (2:1) 3 ml, 8 h, rt.

^a Determined by GC based on the products.

3.2. Amphiphilic cyclopalladated arylimines LB films for Suzuki coupling reaction

LB films of compounds **2a–2c** and **3a–3c** were prepared, and their catalytic performance in Suzuki coupling reactions was investigated in heterogeneous systems. Compounds **2a–2c** and **3a–3c** were spread over a water surface at room temperature to measure surface pressure (π)–area (*A*) isotherms (Fig. 1). The isotherms show a gradual transition, indicating a slight structural alteration in the monolayer structure of the molecules. The π –*A* isotherms of catalysts **2a–2c** and **3a–3c** clearly show high collapse pressure, suggesting the formation of a

Table 4

Suzuki coupling of aryl halides with phenylboronic acid using **2b** as a catalyst.

$\text{R}-\text{C}_6\text{H}_4-\text{Br} + \text{C}_6\text{H}_5-\text{B}(\text{OH})_2 \xrightarrow[\text{Solvent, rt}]{\text{Catalyst, base}} \text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$			
Entry	Aryl halide	Product	Yield ^a (%)
1	<i>p</i> -CH ₃ -C ₆ H ₄ Br		>99
2	<i>p</i> -CH ₃ O-C ₆ H ₄ Br		99
3	<i>p</i> -CF ₃ -C ₆ H ₄ Br		98
4	<i>p</i> -NH ₂ -C ₆ H ₄ Br		82
5	<i>p</i> -NO ₂ -C ₆ H ₄ Br		>99
6	1-bromonaphthalene		97
7	3-bromo-pyridine		77
8	<i>o</i> -CH ₃ -C ₆ H ₄ Br		85
9	<i>o</i> -CN-C ₆ H ₄ Br		99
10	<i>m</i> -CN-C ₆ H ₄ Br		99
11	<i>p</i> -CN-C ₆ H ₄ Br		99

Reaction conditions: ArX 0.5 mmol, PhB(OH)₂ 0.6 mmol, NaOH 1.0 mmol, catalyst **2b** 0.001 mol%, ethanol-water (2:1) 3 ml, rt.

^a Determined by GC.

subphase of the condensed monolayers. Monolayers of **2b** could be transferred onto hydrophilic or hydrophobic glass slides as a Z-type film with a transfer ratio of almost unity under surface pressure of 20 mN/m using Langmuir-Blodgett technique, indicating that the LB films were stable and uniform. An isotherm of **2b** showed an increase in surface pressure near a mean molecular area of 65 Å²/molecule. This indicates that the content of catalyst in the LB films was $\sim 1 \times 10^{-5}$ mol%.

AFM was used to study the topography of the LB films and confirm the homogeneity and quality of the films transferred onto mica substrates. The AFM images of the LB films formed from complex **2b** are shown in Fig. 2. The AFM image obtained after the hydrophilic treatment (Fig. 2(a)) does not show any sign of cluster formation and exhibits a low root mean square surface roughness (*R*_{RMS}) of 0.40 nm. After the assembly of complex **2b**, clusters appear with increasing density as the number of layers increases. This results in an increase of *R*_{RMS} to 0.84, 1.01, and 2.92 nm for 1, 5, and 10 layers, respectively (Fig. 2(b)–(d)). This indicates that the LB films were successfully transferred onto the solid substrates.

We investigated the activity of LB films of complex **2b** in a

Fig. 1. π -A isotherms for **2a–2c** and **3a–3c** on pure water subphase. Compression rate: 20 mN/m.

Suzuki reaction between 4-bromotoluene and phenylboronic acid using the optimized conditions used previously in the heterogeneous systems. The films exhibited high catalytic activity and the yields increased with the number of LB layers (Table 5, entries 1–4). The LB films also exhibited high catalytic activity in water (entry 5). To confirm that the catalysis was indeed heterogeneous, an auxiliary catalytic experiment was added. The catalyst **2b** LB films were removed after $\sim 40\%$ conversion. The reaction mixture was then allowed to continue without the catalyst film, and no further conversion was observed in the following 36 h, strongly suggesting that catalyst did not dissolve into solution from the substrate and that the reaction was heterogeneous. The heterogeneous catalyst LB films of **2b** obtained about 25 times more active than its homogeneous coun-

Fig. 2. AFM images of the silicon wafers after hydrophilic treatment (a), 1-layer (b), 5-layers (c), and 10-layers (d) LB films of complex **2b** formed at surface pressure of 20 mN/m. All the scan ranges were $2.5 \times 2.5 \mu\text{m}^2$.

Table 5

Suzuki coupling of aryl halides with phenylboronic acid catalyzed by **2b** LB films.

Entry	Catalyst content (10 ⁻⁵ mol%)	Layer	Yield ^a (%)
1	6.17	2	21
2	12.34	4	58
3	18.52	6	73
4	24.69	6	87
5 ^b	12.34	4	46

Reaction conditions: 4-bromotoluene 0.1 mmol, PhB(OH)₂ 0.12 mmol, NaOH 0.125 mmol, ethanol-water (2:1) 3 ml, rt, 48 h, in weighing bottle (15 mm × 40 mm).

^a Determined by HPLC based on the products.

^b H₂O 3 ml, 72 h, *n*-Bu₄NBr 0.12 mmol.

terpart. The catalytic results clearly demonstrated that ordered structures have a major influence on catalytic reactions.

4. Conclusions

A series of novel amphiphilic aryl imines and their cyclopalladated complexes (**2a–2c** and **3a–3c**) were synthesized and characterized by ¹H NMR, ¹³C NMR, MS, IR, and elemental analysis. The palladacycles are thermally stable and insensitive to oxygen and moisture. The complexes exhibited good activity in the Heck reaction of aryl halides with styrene. Furthermore, they were also found to be very efficient for the Suzuki coupling of aryl bromides with phenylboronic acid. The catalyst **2b** showed suitability for Langmuir monolayer and LB film formation on solid slides. The catalytic activity of the catalyst films for the Suzuki coupling reaction was also investigated. The LB films of the catalyst **2b** show significantly higher homogeneous catalytic activity for the Suzuki reaction than the other catalysts. This may indicate that ordered structure has a major influence on a catalytic reaction. The reusability of the LB films and the catalytic mechanism will be investigated in future studies.

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Graphical Abstract

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Preparation, characterization and catalytic activity of amphiphilic cyclopalladated aryl imines and their Langmuir-Blodgett films

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The amphiphilic cyclopalladated aryl imine catalysts were successfully transferred on the solid slides and can be used for the Suzuki reactions.

两亲性芳香亚胺环钯化合物及其Langmuir-Blodgett膜的制备、表征及催化活性

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摘要: 合成并表征了一系列新型两亲性芳香亚胺环钯化合物. 结果显示, 该系列环钯催化剂可高效催化均相条件下的Heck和Suzuki偶联反应. 将两亲性芳香亚胺环钯二聚体制成LB膜, 其在异相条件下的催化活性是均相条件下的25倍.

关键词: 芳香亚胺; 环钯催化剂; Langmuir-Blodgett膜; Suzuki反应; Heck反应

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