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Highly ordered amphiphilic cyclopalladated arylimine self-assembly films for catalyzing Heck and Suzuki coupling reactions

Yaqing Zhao, Na Zhao, Meiling Zou, Tiesheng Li*, Guoping Li, Jinpeng Li and Yangjie Wu*

A series of new cyclopalladated arylimine compounds (3a–c, 4a–c) were synthesized and characterized. Their catalytic properties for Heck and Suzuki coupling reactions in a homogeneous system were preliminarily investigated using water as solvent, in which no ligands, air isolation or assistant solvents were needed in cross-coupling reactions. The optimization of the homogeneous system provided a basis for research on the heterogeneous catalytic reaction catalyzed by ordered self-assembly films. Organized monolayers of 3a–c were prepared and utilized as C–C coupling catalysts. Monolayers of 3a–c were deposited using Langmuir–Blodgett techniques and analyzed using π–A isotherms, UV–visible and X-ray photoelectron spectroscopies and atomic force microscopy, which showed near orientation on the surface and stability under the optimized experimental conditions suitable for exploring Heck and Suzuki coupling reactions. The activity of immobilized 3c monolayer is enhanced relative to homogeneous reaction, in which the ordered monolayers are efficient with a catalyst loading as low as 10^{-5} mol%, turnover number as high as 79 200 and turnover frequency as high as 2640 h^{-1}. The catalytic efficiency is 100 times higher than that in the homogeneous case using the same amount and ratio of reagent. The increased activity of immobilized 3c monolayer is due to a combination of its structure and changes in conformation when deposited onto the substrate. The topographic changes of catalyst films, stability of films and catalytic activity were investigated with atomic force microscopy, cyclic voltammetry, X-ray photoelectron spectroscopy and inductively coupled plasma atomic emission spectrometry, from which a heterogeneous catalytic mechanism for Suzuki coupling reaction is proposed. The study demonstrates that careful monolayer studies can provide useful models for the design and study of supported molecular catalyst systems.

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Keywords: cyclopalladated arylimines; Heck reaction; Suzuki reaction; Langmuir–Blodgett (LB) films; ordered monolayer

Introduction

C–C coupling reactions are versatile tools in synthetic chemistry and of practical interest in industry.[1–3] Heck and Suzuki coupling reactions are the most thoroughly investigated.[4,5] Catalytic procedures have been shown to be particularly attractive and versatile in numerous organic transformations because they usually offer high yields, good regio- and stereo-selectivity and excellent compatibility with many functional groups. Efficiency of these reactions has been elegantly and widely demonstrated in the synthesis of natural products, organic building blocks, pharmaceuticals and agricultural derivatives.[6–9] The mechanism in homogeneous systems has been well explored.[10–15] In recent years, much attention has been focused on aqueous and heterogeneous switching of organic transformations using amphiphilic material-supported transition metal complexes or metal nanoparticles.[16–19] Meantime, palladium supported on carbon,[20–24] mesoporous material (MCM-41), molecular sieves,[25–27] oxides (MgO, TiO_2, ZnO, Al_2O_3),[28–31] basic zeolites and sepiolites,[32–34] silica[35–39] and alumina[40,41] has been applied to cross-coupling reactions. Also, cyclopalladated complexes have been extensively studied because of advantages such as their high activity in various types of coupling reactions, stability in air, no need for ancillary ligands and simple synthetic methods.[42–46] Beller *et al.*[47] first reported the use of cyclopalladated complexes as catalysts for Heck and Suzuki coupling reactions, and since then various palladacycles have been reported. Milstein and co-workers described good performance from orthopalladated imines and CN palladacycles for Heck[48] and Suzuki[49] reactions.

Our group obtained a series of cyclopalladated ferrocenylimines which can be used for Heck, Suzuki, Sonogashira and Kumada reactions, among others, in homogeneous systems, in which they showed highly efficient catalytic ability, and their catalytic mechanisms were also investigated.[50–62]

However, homogeneous catalysts with traditional phosphine-based ligands are difficult to handle and remove from a reaction

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* *Correspondence to: Tiesheng Li or Yangjie Wu, College of Chemistry and Molecular Engineering, Key Laboratory of Biological Chemistry and Organic Chemistry of Henan Province, Key Laboratory of Advanced Nano-information Materials of Zhengzhou, Zhengzhou University, Kexuedadao 100, Zhengzhou 450001, PR China. E-mail: lts34@zzu.edu.cn*

College of Chemistry and Molecular Engineering, Key Laboratory of Biological Chemistry and Organic Chemistry of Henan Province, Key Laboratory of Advanced Nano-information Materials of Zhengzhou, Zhengzhou University, Kexuedadao 100, Zhengzhou 450001, PR China

mixture, and phosphorus ligands are often water- and air-sensitive, which limits their applications in heterogeneous catalysis.[28,63,64]

It is well known that there are difficulties in investigating mechanisms because active species cannot be determined in heterogeneous systems,[65–67] which makes general conclusions difficult to obtain in most cases because the mechanism of a certain reaction is strongly affected by the conditions. Therefore, contradictory results are sometimes reported.[68,69] Immobilized catalysts can mirror their homogeneous behavior or the process can alter a catalyst's activity perhaps even changing the mechanism whereby it operates. Detailed understanding of catalytic behavior at interfaces is clearly desirable, but studies of supported catalysts can be riddled with uncertainties. Typical high-surface-area supports are often not uniform, giving variation in catalyst binding sites, aggregation and orientation with respect to the surface. It is often difficult to determine if the structure of a molecular catalyst remains intact upon adsorbing it to a surface. If catalytic activity is observed with a supported system, it is frequently impossible to know what species is responsible for the catalysis. Therefore, procedures for studying molecular catalysts at a uniform and reproducible interface can enhance the understanding of their behavior in heterogeneous environments, which often provides a rational way to improve catalytic activity and selectivity.[70] For this proposal, we placed cyclopalladated catalysts on a substrate in the form of self-assembly films which have high catalytic activity and recyclability, but the orientation and density could hardly be controlled.[71–75]

The Langmuir–Blodgett (LB) technique is a simple method for assembling layers with well-defined molecular orientation and control over thickness at the molecular level to reproducibly produce highly ordered molecular arrays.[76–79] 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 applications have been studied using the LB technique and have generated considerable interest.[80] Töllner *et al.*[81] reported the hydrogenation of carbon–oxygen double bonds catalyzed by active LB films of a rhodium complex. Abatti *et al.*[82] used porphyrin LB films as catalysts for alkene epoxidation, and doubled yields compared with the homogeneous system. Benítez *et al.*[83] investigated the catalytic properties of irconium phosphonate LB films and self-assembled monolayers using the epoxidation of *cis*-cyclooctene. Park *et al.*[84] reported catalytic CO oxidation by LB films of Rh/Pt bimetallic nanoparticles, and Pasc-Banu *et al.*[85] used pincer Mn LB films to catalyze olefin oxidation.

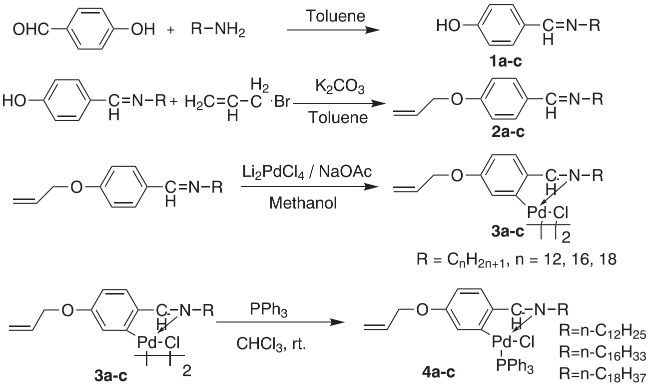
In order to gain an insight into the mechanism for heterogeneous systems, amphiphilic cyclopalladated ferrocenylimines were designed and synthesized.[4,5] The results indicated that these amphiphilic compounds exhibited good catalytic activity in homogeneous systems and their assembled films had higher catalytic efficiency due to the regular molecular orientation. In the research on heterogeneous mechanisms mentioned above, the amphiphilic cyclopalladated ferrocenylimine LB films desorbed from glass slides when they were placed in organic solvents, stirring or under heating conditions, which would affect the experimental results because of their lower molecular weight, and result in recycling only once.[5,86,87] To overcome this limitation, it is one of the key factors that a cyclopalladated complex should be strongly adsorbed on the substrate under experimental conditions. If a polymerizable group is introduced, catalytic activity and recycling could be improved.[88] That is to say, if the designed cyclopalladated imine LB films were used in pure water, or their polymers, they should well assemble on a substrate and would not be desorbed easily from the substrate.

In the study reported here, we took advantage of a well-understood surface modification process to compare the activity of surface-confined monolayer films of a series of polymerizable cyclopalladated arylimine (**3a–c**, **4a–c**; Scheme 1) catalysts with their homogeneous behavior. Their catalytic properties for Heck and Suzuki cross-coupling reactions in homogeneous systems were initially investigated to determine suitable experimental conditions for subsequent investigation of their assembled films in heterogeneous catalysis. Through careful molecular design and controlled deposition, monolayers with known surface coverage and molecular orientation to the interface were obtained. Using these controlled-orientation surfaces for the example of Suzuki coupling reaction, increased activity of the surface-confined catalyst relative to homogeneous reactions under the same conditions was observed. Their catalytic mechanism and recycling for Suzuki reaction were also investigated. In addition, to provide an insight into the specific example of immobilized cyclopalladated complexes, the results demonstrate the utility of studying well-characterized molecular monolayers which can be used as models for supported molecular catalyst systems.

Experimental

General methods

All solvents were obtained from commercial sources and used without purification. The experiment for monolayer spreading on water was performed with a LB system (KSV-5000-3, KSV Instruments, Helsinki, Finland) equipped with computer controls. Surface pressure was measured with a Pt Wilhelmy plate in air. Distilled and deionized water with a resistivity of 18.2 MΩ cm (Milli-Q Gradient, Millipore Co., USA) was used as a subphase. Melting points were measured using a WC-1 microscopic apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker DPX-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Elemental analyses were conducted with a varioEL III system (Elementar GmbH). Mass spectra were measured with an LC-MSD-Trap-XCT instrument. All Heck and Suzuki reactions were accomplished without the protection of inert gas. An SPM-9500 J3 (Shimadzu Corporation, Japan) was employed for atomic force microscopy (AFM) measurements in air at ambient temperature.



Scheme 1. Synthesis of cyclopalladated arylimine complexes (**3a–c**, **4a–c**).

HPLC was conducted with a Waters 600 liquid chromatograph. The content of Pd in LB films was measured with atomic absorption spectroscopy (AAS) using a Z-8000 polarized Zeeman atomic absorption spectrophotometer (Hitachi Corporation, Japan). Inductively coupled plasma atomic emission spectrometry (ICP-AES) was carried out with an ICAP 6000 Series (Thermo Scientific). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure was approximately 3×10^{-9} mbar. The binding energies were referenced to the C 1 s line at 284.8 eV from adventitious carbon. Crystal structures were determined using an X'Pert PRO (PANalytical) with graphite monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) at room temperature.

Preparation of compounds (1a–c, 2a–c, 3a–c, 4a–ac)

Compounds **1a–c** and **2a–c** were prepared according to the literature[5,56] and dimer compounds **3a–c**, i.e. $(PdCl(CH_2{=}CHCH_2OC_6H_6CH{=}NR))_2$, were prepared as follows. A mixture of dilithiumchloropalladate (10 ml, 0.1 mol l^{-1}), sodium acetate (1 mmol), compound **2** (1.1 mmol) and methanol (10 ml) was stirred at room temperature for 24 h. The mixture was then filtered, distilled and subjected to column chromatography using dichloromethane and petroleum ether (3:1), and yellow solid **3** was obtained. Compounds **3a–c** were decomposed with triphenyl phosphate to give monolayers **4a–c**. Crystals of **4a–c** were also obtained. Characterization of **1**, **2** and **3** and analysis of crystals of **3a–c** and **4a–c** are presented in the supporting information (content **1** and **2**).

Heck cross-coupling reactions

Aryl halide (0.5 mmol), styrene (1.5 mmol) and catalyst **3** (0.1 mol%) were combined with base (1 mmol) and dimethylformamide (DMF; 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 three times with ethyl acetate. The combined organic phase was dried with $MgSO_4$ and filtered, and the solvent was analyzed using gas chromatography.

Suzuki cross-coupling reactions

Aryl halide (0.25 mmol), arylboronic acid (0.6 mmol), catalyst **3** (0.1 mol%) and tetrabutylammonium bromide (0.3 mmol) were combined with base (0.3 mmol) and deionized water (1.5 ml) in a small round-bottom flask. The reaction mixture was stirred and then extracted three times with ethyl acetate. The combined organic phase was dried with $MgSO_4$ and filtered, and the solvent was analyzed using gas chromatography.

Preparation of Langmuir monolayer and LB films

A chloroform solution containing the catalyst was carefully spread onto an ultrapure water surface. After evaporation of solvent (30 min) and stabilization for 1 h, the Langmuir monolayer was compressed at a speed of 5 mm min^{-1} at 20 ± 1 °C. LB films were transferred onto indium tin oxide (ITO) glass substrates (for electrochemical study) and glass slides (for AFM and catalysis study). The glass slides were cleaned in boiling concentrated H_2SO_4 for 1 h and then washed with pure water. The ITO glass substrates were ultrasonically washed in acetone, ammonia, ethanol and pure water in sequence.

Hydrophilic treatment

Silicon and glass wafers were put into a mixed solvent of concentrated nitric acid and concentrated sulfuric acid (2:1 v/v) and heated to boiling for 1–1.5 h. Then, the wafers were washed with deionized water. The ITO glass substrates were ultrasonically washed in acetone, ammonia, ethanol and pure water in sequence.

ICP-AES analysis

After each reaction was over, the glass wafer was removed and the reaction mixture was centrifuged and broken down with nitrolysis, in which the Pd concentration was measured using ICP-AES.

AAS analysis

Glass wafers (2.5 × 2.5 cm^2) with **3c** monolayer were put into a mixed solvent of concentrated nitric acid and concentrated sulfuric acid (2:1 v/v) and heated to boiling for 1–1.5 h. The wafers were then washed with deionized water. The Pd concentration of the solution was found to be 45.7 mg ml^{-1} as measured using AAS. The Pd content of the catalyst was 2.0×10^{-10} mol cm^{-2}.

Results and discussion

Catalytic activity of complexes 3a–c in homogeneous systems

It is very important for selecting suitable system, for example, certain C-C coupling reaction as temple and using solvent to catalytic LB films. So, the catalytic activity of cyclopalladated arylmine complexes **3a–c** for homogeneous Heck and Suzuki coupling reactions was systematically investigated. An initial survey of bases (0.1 mol% catalyst, DMF as solvent, at 140°C for 24 h) reveals that K_3PO_4, NaOAc and KOAc are much better than other bases (Table S3, entries 1, 5–9, 11, 12). There are nearly no products when the temperature is decreased to 75°C with NaOAc and KOAc (Table S3, entries 10 and 13). The yields are obviously improved when the temperature is decreased from 140 to 75°C and the reaction time is reduced from 24 to 12 h with K_3PO_4 (Table S3, entry 2). But as the temperature decreased to 50°C or to room temperature, the yields decrease rapidly (Table S3, entries 3 and 4). There are no significant differences among the three catalysts with the same solvent (DMF), base (K_3PO_4), reaction temperature (140°C) and reaction time (24 h) (Table S3, entries 1, 14 and 15). Therefore, the optimum reaction conditions are as follows: base, K_3PO_4; reaction time, 12 h; reaction temperature, 75°C. Taking catalyst **3c** as an example, a wide range of electronically and structurally diverse aryl halides can be cross-coupled efficiently under these optimized reaction conditions. The results are summarized in Table S4.

The reaction of substrates with a strongly electron-donating group, such as *p*-substituted group of bromobenzene, with styrene gives low yields (Table S4, entries 4–6). On the contrary, high yields are obtained with strongly electron-withdrawing *p*-substituted group of bromobenzene (Table S4, entries 7, 9–12). For this reaction system, the yield of 4-bromobenzenecarboxylic acid is only 5.5% because there are many byproducts due to the carboxyl group (Table S4, entry 8). The yields are low with electron-withdrawing or electron-donating group in *m*-position (Table S4, entries 13–16). The yields using substrates with *o*-substituted electron-donating groups are also lower because of steric effects (Table S4, entries 18 and 19). By contrast, the yields are higher with *o*-substituted electron-withdrawing groups (Table S4, entries 17 and 20).

The results of Heck coupling with structurally diverse aryl halides with styrene in pure water are listed in Table S5. Different results are obtained, in which the catalytic efficiency of **3c** is higher and independent of the substrate structure except chlorobenzene (Table S5, entry 3). Cross-coupling reactions of 1-bromonaphthalene, 3-bromothiophene and 3-bromopyridine with styrene catalyzed by **3c** also proceed smoothly under the same reaction conditions to afford the cross-coupling products in high yields (Table S5, entries 12–14).

To investigate the activity of the catalysts **3a–c** for other cross-coupling reactions, the Suzuki reactions of arylboronic acid with aryl halides were employed. Our initial survey of bases for 4-bromotoluene with phenylboronic acid as the coupling partners using 0.1 mol% loading of **3c** with DMF as solvent reveals that K_3PO_4, $NaOAc{\cdot}3H_2O$ and K_2CO_3 are much better than other bases (Table S6, entries 1, 7 and 8). Considering economic factors, K_2CO_3 was adopted in subsequent research owing to its low cost.

Reaction temperature, solvent and reaction time for 4-bromotoluene with phenylboronic acid were also studied (Table S7) using the appropriate base (K_2CO_3) and catalyst **3c**. The results show that DMF, tetrahydrofuran, toluene and water are much better than other solvents (Table S7, entries 3–6) using 0.1 mol% of **3c** and K_2CO_3 as base. When water is selected as the solvent, *n*-Bu_4NBr is present. The yields are obviously decreased when the temperature is lowered from 80 to 60°C in DMF (Table S7, entries 7–9). With the appropriate solvent (water) and base (K_2CO_3), we set out to examine the scope and limitations of the protocol based on both aryl halides and arylboronic acids in the presence of 0.1 mol% of complex **3c**, at 80°C. The results are listed in Table S8.

The results of Suzuki coupling reaction with structurally diverse arylboronic acid and aryl halides are listed in Tables S8 and S9. For activated and inactivated aryl bromides, excellent yields are obtained (Table S8, entries 1–12). But the yields are lower when the substrates are heterocyclic compounds (Table S8, entries 13–15). For arylboronic acid, the conversion is excellent with *m*-substituted and *p*-substituted compounds (Table S9, entries 1–7). With heterocyclic substituents and alkyl substituents, moderate yields are obtained (Table S9, entries 9, 10 and 12). However, the yields are also low when aryl halides are *o*-substituted (Table S9, entries 8 and 11). These results show that the amphiphilic cyclopalladated arylimines are efficient catalysts for Suzuki coupling reaction of arylboronic acid with aryl halides in homogeneous systems under the optimized reaction conditions.

Characterization of 3a–c monolayer and LB films

In order to investigate the heterogeneous catalytic mechanism of **3a–c** LB films, the molecular arrangement at the air–water interface was first studied. Complex **3a–c** linked long alkyl chain was spread from a chloroform solution (200 μl, 0.5 mg ml^{-1}) to measure the π–A isotherms at a compression speed of 5 mm min^{-1} at 20 ± 0.5°C. Figure 1 shows the isotherms obtained by compression after evaporation of solvent for 30 min and stabilization for *ca* 1 h in the uncompressed state. The π–A isotherms of complexes **3a–c** exhibit collapse pressures of 58, 69 and 63 mN m^{-1}, respectively. All isotherms are reproducible.

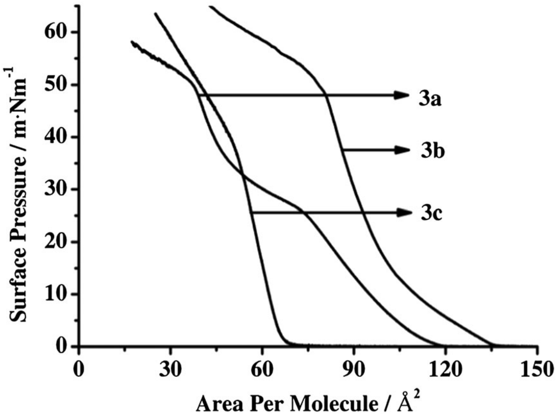


Figure 1. π–A isotherms of **3a–c** at water–air interface at room temperature.

The high collapse pressure can be attributed to the strong polar groups and chain–chain interactions.[89] The average surface areas occupied per molecule obtained by extrapolation of the liner part of the isotherms of complexes **3a–c** are 72, 106 and 67 $Å^2$, respectively. The isotherms show a gradual transition, indicating a slight structural alteration in the molecules. The static elasticity–surface pressure (E_s–π) curve is the differential form of the change of surface pressure during compression and would be better for determining the surface state of the monolayer than the integral form of the π–A isotherm. It is determined from the condensability of the arranged molecules. To directly select optimum surface pressure for Langmuir monolayer and LB film formation, the static elasticity of the monolayer was calculated from π–A isotherms (Fig. 1). A high static elasticity value is associated with a monolayer that has a strong cohesive structure at the interface and is the most stable and rigid.[90,91] The surface pressures obtained as 10–18, 25–40 and 10–20 mN m^{-1} are determined as optimum transfer pressures for **3a–c** deposition, respectively, from air–water interface onto substrates (Fig. S4).

UV–visible spectra can be used to verify whether the monolayer can be transferred ordered and densely onto substrates. Film-forming materials can be transferred with different surface configuration when different surface pressures are selected.[86] UV–visible absorption spectra of **3a–c** LB films with different layers and pressures were obtained and the best surface pressures were chosen for their LB film deposition from air–water interface. In the UV–visible spectra of complexes **3a–c** in $CHCl_3$ solution, the peak (200–230 nm) belongs to the benzene derivatives. Figure 2 shows the UV–visible spectra of **3a** LB films with different numbers of layers deposited at various surface pressures. When the surface pressure is 18 mN m^{-1}, the absorption peak of benzene is inconspicuous and the absorption is very weak (Fig. 2(A)). The absorption increases with increasing number of layers when the surface pressures are12 and 15 mN m^{-1}. The liner relationship between number of layers and absorbance at 12 and 15 mN m^{-1} indicates that the monolayer is successfully transferred onto solid substrates (Figs. 2(B) and (C)). In contrast, the absorbance does not vary linearly with the number of layers when the surface pressure is 18 mN m^{-1} (Fig. 2(D)). Similar results are obtained for the UV–visible spectra of complexes **3b** and **3c** (Figs S5 and S6). Although the absorbance is liner with the number of layers (Figs. 2(B) and (C), S2(B) and (D) and S3(B) and (C)), the orientation of the monolayer changes with a change in surface pressure.

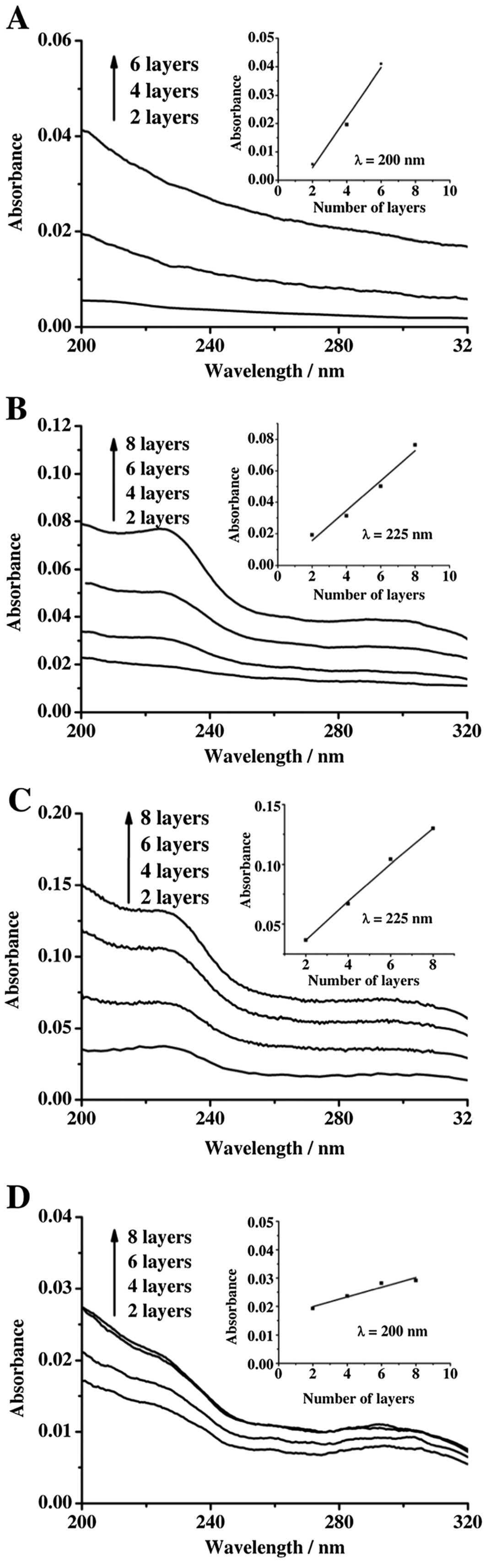


Figure 2. UV–visible spectra of complex **3a** LB films with different numbers of layers deposited at various surface pressures: (A) 10 mN m^{-1}; (B) 12 mN m^{-1}; (C) 15 mN m^{-1}; (D) 18 mN m^{-1}). Insets: number of layers deposited versus absorption at certain wavelength.

AFM can be used to provide topographic images of monolayers, giving a direct view of surface morphology with high spatial resolution, which is often indicative of film quality.[92] Figure 3 shows AFM images of the hydrophilic treated glass slides and one-layer LB films of complex **3c** transferred at surface pressures of 10, 15, 20, 25 and 30 mN m^{-1}. All scan ranges are 2.5 μm × 2.5 μm. The AFM images obtained after one-layer LB films of complex **3c** are transferred show obvious signs of cluster formation and exhibit a higher R_a than that observed after hydrophilic treatment (14.34 nm instead of 2.29 nm). The images obtained are smooth and homogeneous, indicating that well-ordered and uniform monolayer films had been fabricated.

The cyclic voltammetry curves of one-layer LB films of complex **3c** deposited on ITO glass are shown in Fig. 4. The experiments were carried out in 0.1 M HCl solutions versus Ag/AgCl electrode in three-electrode electrochemical cells. No redox peaks are observed between −0.6 and +1.0 V versus Ag/AgCl electrode in 0.1 M HCl solution (Fig. 4, dotted curve), suggesting that the ITO glass is hydrophilic treated. For LB films of complex **3c** transferred onto ITO glass, a pair of redox peaks is seen between −0.2 and +1.6 V versus Ag/AgCl electrode (Fig. 4, solid curve). There is a reduction peak at around +0.6 V corresponding to the reduction reaction from Pd^{2+} to Pd^0 and an oxidation peak at around +0.3 V corresponding to the oxidation reaction from Pd^0 to Pd^{2+}, suggesting that complex **3c** had been deposited onto ITO glass.

XPS measurements of **3c** LB films are shown in Fig. 5, in which the peaks of elements Pd, N and C in the XPS spectrum can be seen at 337.9, 399.8 and 284.8 eV, which is evidence that the complex **3c** is present in the LB films.

After pretreatment with piranha solution, the glass substrates become strongly hydrophilic, having extremely low water contact angle (6°), and then the water contact angles increase to 80° after deposition of **3c** monolayer (Fig. 6), which indicates that catalyst is deposited on the substrate, with which 99% yield can be obtained for Suzuki reaction (50°C, 24 h, water, K_2CO_3, n-Bu_4NBr). On the other hand, hydrophilic surface modified with dimethyldichlorosilane has higher water contact angle (101°) and has a contact angle of 65° after deposition of **3c** monolayer (Fig. 6), which indicates that catalyst is deposited on the substrate, with which 95% yield can be achieved in catalyzing Suzuki reaction (50°C, 24 h, water, K_2CO_3, n-Bu_4NBr). This is evidence that the orientation of the deposited cyclopalladated ferrocenylimine can be influenced by different surfaces. The changes of water contact angles on differently modified solid surfaces also indicate that the configuration of catalyst monolayer had significantly changed, which could clearly have an influence on the catalytic properties.

Catalytic activity of organized 3a–c monolayer and LB films in heterogeneous systems

The catalytic performance of LB films of cyclopalladated arylimine complexes **3a–c** for Suzuki coupling reaction was systematically investigated. Suzuki reaction was taken as an example to investigate the catalytic activity of complex **3a–c** Langmuir monolayers under mild reaction conditions (compared with the homogeneous case, such as lower reaction temperature and shorter reaction time). The results are summarized in Table 1. The yield of the reaction of 4-bromotoluene with phenylboronic acid is 92% in pure water when catalyzed by **3c** Langmuir monolayer prepared at 20 mN m^{-1} (Table 1, entry 5). The yield increases to 99% when the reaction

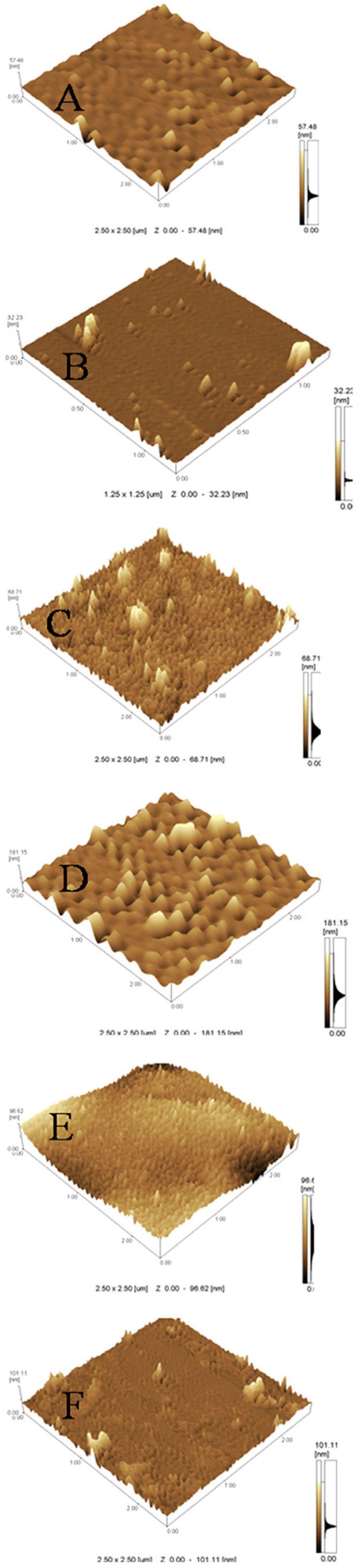


Figure 3. AFM images acquired from glass slides after (A) hydrophilic treatment, and monolayer of complex **3c** deposited at (B) 10, (C) 15, (D) 20, (E) 25 and (F) 30 mN m^{-1}.

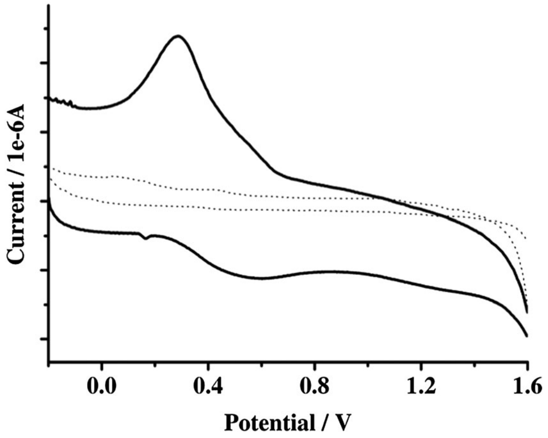


Figure 4. Cyclic voltammograms of pure ITO glass (dotted line) and one-layer LB films of complex **3c** transferred onto ITO glass (solid line).

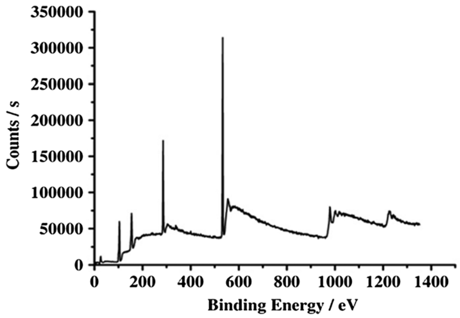


Figure 5. XPS spectrum of **3c** LB film.

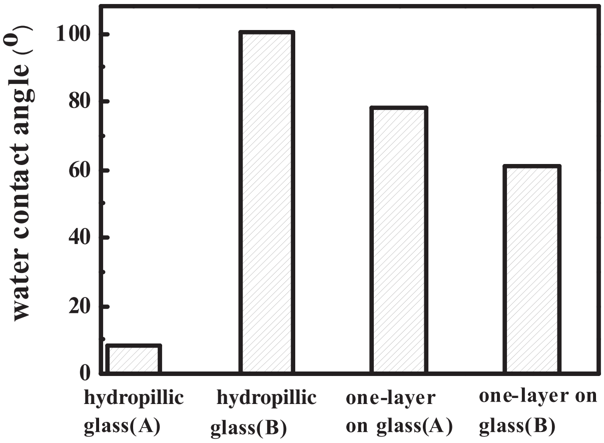
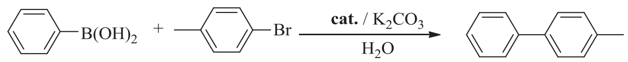


Figure 6. Water contact angle of **3c** monolayer transferred onto glass (surface pressure = 20 mN m^{-1}).

time is prolonged to 30 h (Table 1, entry 6) and changes when the Langmuir monolayer is obtained at different surface pressures (Table 1, entries 7–16). The results confirm that the catalyst **3a–c** Langmuir monolayers can effectively catalyze Suzuki reaction when the monolayers are obtained at 15 (**3a**), 35 (**3b**) and 20 mN m^{-1} (**3c**), respectively. For example, the π–A isotherm of **3c** shows an increase in surface pressure near a mean molecular area of 67 Å^2 per molecule. This indicates that the

Table 1. Data for the Suzuki coupling reaction catalyzed by **3c** monolayer[a]



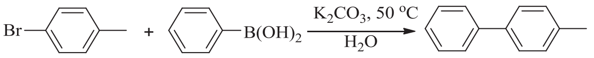
Entry	Solvent (H_2O/ C_2H_5OH)	Temperature (°C)	Catalyst/surface pressure (mN m^{-1})	Yield (%)[b]
1	1:1	50	**3c**/20	23
2	2:1	50	**3c**/20	13
3	1:1	60	**3c**/20	86
4	2:1	60	**3c**/20	30
5	H_2O	50	**3c**/20	92
6[c]	H_2O	50	**3c**/20	>99
7	H_2O	50	**3a**/10	12
8	H_2O	50	**3a**/12	88
9	H_2O	50	**3a**/15	90
10	H_2O	50	**3a**/18	5.4
11	H_2O	50	**3b**/25	53
12	H_2O	50	**3b**/30	79
13	H_2O	50	**3b**/35	93
14	H_2O	50	**3c**/10	3.0
15	H_2O	50	**3c**/15	55
16	H_2O	50	**3c**/25	4.8

[a] Reaction conditions: $PhB(OH)_2$ (0.3 mmol), 4-bromotoluene (0.25 mmol), catalyst **3a–c** Langmuir monolayer (2.5 cm × 1 cm), K_2CO_3 (0.3 mmol), solvent (2.5 ml), 24 h, *n*-Bu_4NBr (0.3 mmol), no stirring.

[b] Yield determined by HPLC based on products.

[c] 30 h.

Table 2. Amount of Pd in LB films after various recycling runs[a]



Entry	Solvent	Stir	Pd (×10^{-6} mmol)	TON	Yield (%)[b]
After first reaction	DMF	No	No		Trace
After first reaction	H_2O	Yes	No		28
After first reaction	H_2O	No	6.29	3676	99
After second reaction	H_2O	No	5.03	3308	95
After third reaction	H_2O	No	4.77	2573	87
After fourth reaction	H_2O	No	No		9.0

[a] Reaction conditions: $PhB(OH)_2$ (0.03 mmol), 4-bromotoluene (0.025 mmol), K_2CO_3 (0.03 mmol), *n*-Bu_4NBr (0.03 mmol), 50°C for 24 h under air.

[b] Yield determined by GC, based on product.

calculated catalyst loading of its LB film is as low as 2.5×10^{-10} mol cm^{-2} (measured as 2.0×10^{-10} mol cm^{-2}) from which its catalytic efficiency is 100 times higher than that in the homogeneous case, with a turnover number (TON) as high as 79 200 and turnover frequency (TOF) as high as 2640 h^{-1}. The catalytic results clearly demonstrate that ordered structures have a major influence on catalytic performance (Table 1). The observed increase in activity can be attributed to a combination of enhanced catalyst lifetime and the altered conformation that the molecule adopts upon adsorption. However, effects due to the local concentration of sites cannot be ruled out.

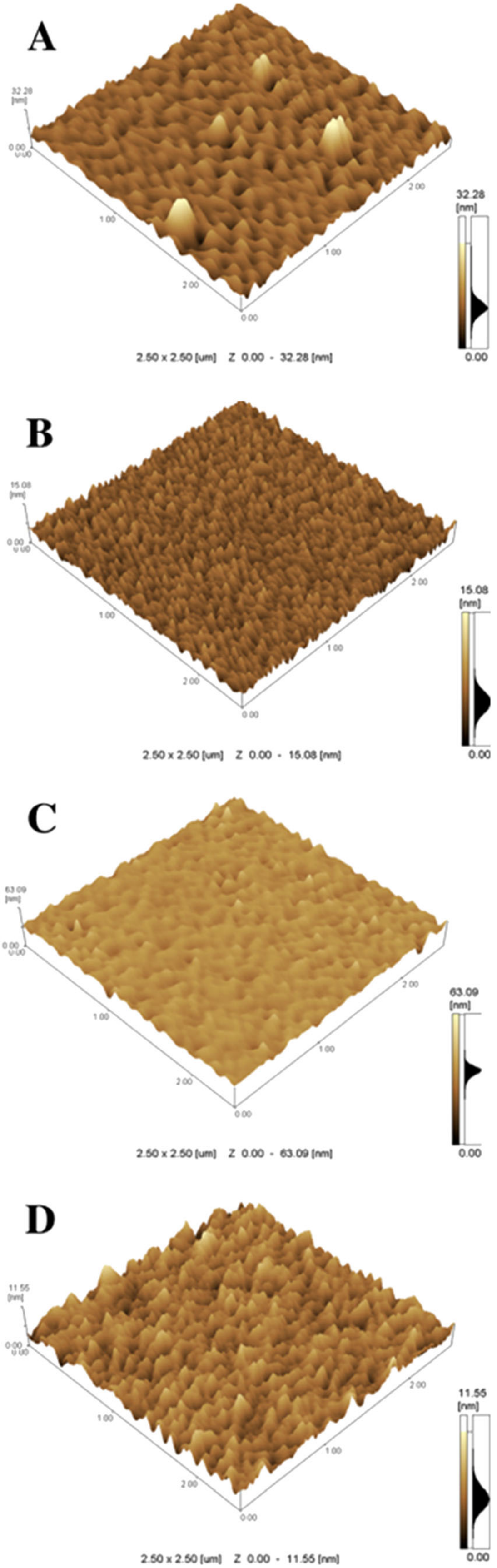


Figure 7. AFM images of monolayer of complex **3c** deposited on glass slides after (A) the first, (B) the second, (C) the third and (D) the fourth catalytic run.

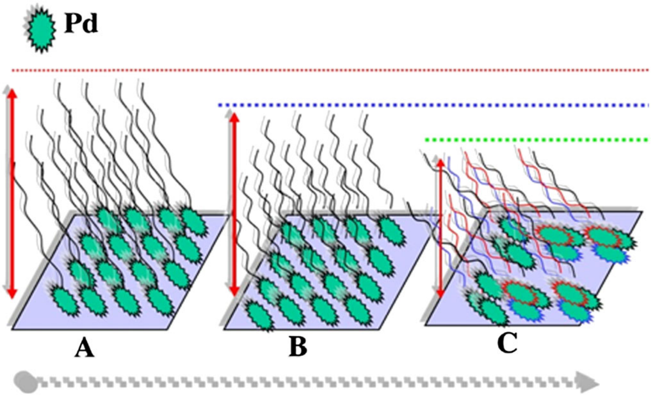


Figure 8. Schematic of the arrangement of LB films transferred onto solid slides (A) before catalytic reactions and after (B) the first and (C) the second catalytic run.

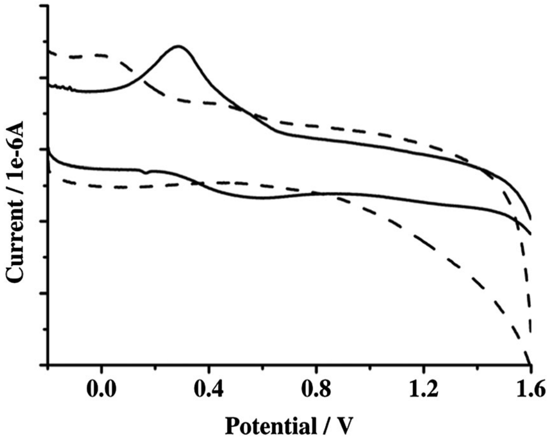


Figure 9. Cyclic voltammograms before (solid line) and after (dashed line) catalytic reactions of one-layer LB films transferred onto ITO glass.

Concerning the use of the catalyst for both industrial and pharmaceutical applications, its recyclability is important. Taking catalyst **3c** LB films as an example, these LB films deposited onto glass slides show great advantage in that Suzuki reaction can be conveniently carried out without ligand and the catalyst is easily separated. However, it is known that a disadvantage of LB films is easy desorption from the solid slides when stirred or in organic solution which go against recycling and elucidation of the mechanism in heterogeneous systems. The influence of stirring and solvent was investigated (Table 2). High yield can be obtained without stirring and using water as solvent.

We examined the reuse of the catalyst LB films in Suzuki coupling reaction between 4-bromotoluene and phenylboronic acid under various conditions. Recycling of one-layer LB film catalyst of **3c** shows that three runs can be performed without any significant loss of catalytic activity (99, 95 and 87%, respectively). However, there is almost no coupling product in the fourth and fifth runs (9 and 11%), which is probably because the LB film is no longer ordered as a result of heating or is coated by reagents or desorbed from the solid slides.

It should also be noted that new phenomena might arise from the ability to organize molecular catalysts into controlled assemblies to enhance catalytic activity. Changes in molecular design can also be used to improve the recycling ability compared to our previous research.[86]

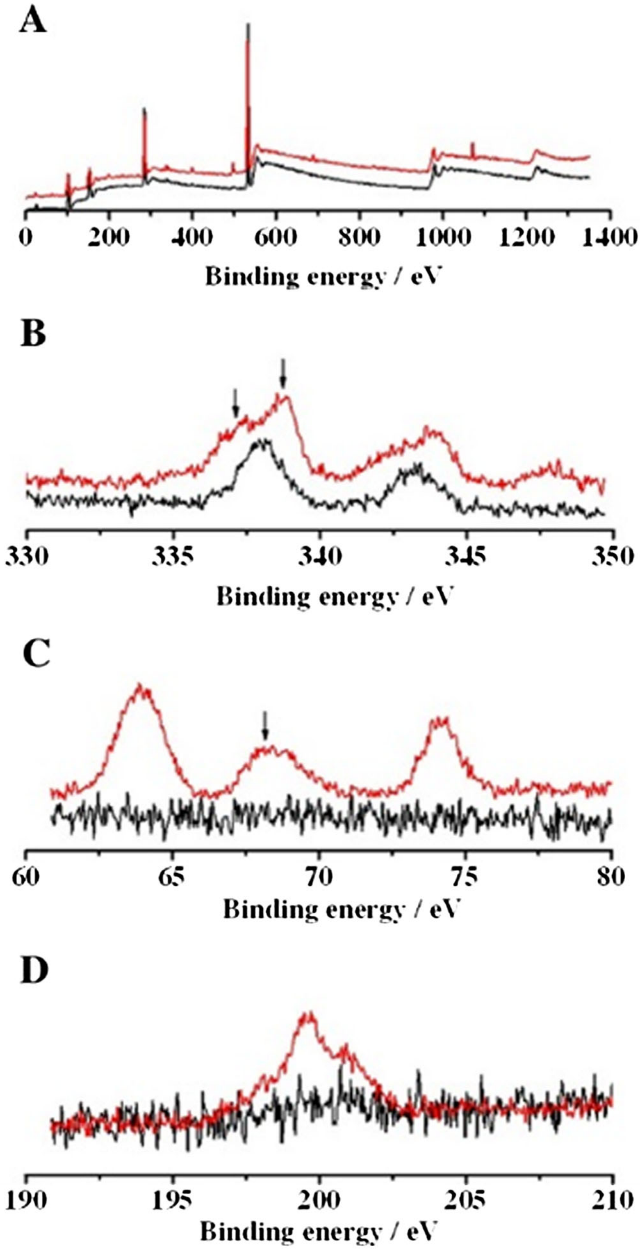
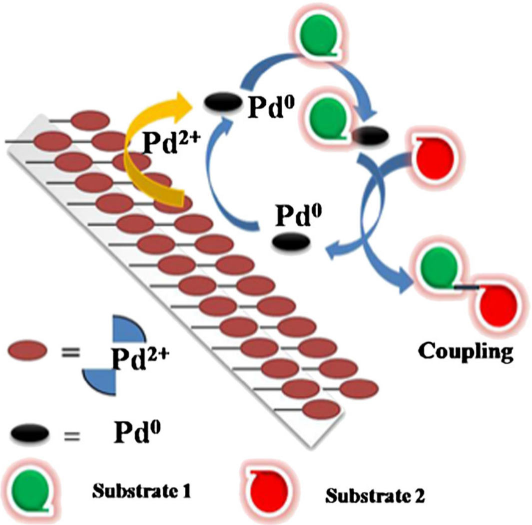


Figure 10. (A) XPS spectra of **3c** monolayer on silicon wafers before catalytic reaction (black curve) and after catalytic reaction (red curve). (B) Pd 3d, (C) Br 3d and (D) Cl 2p XPS spectra before (red curve) and after (black curve) catalytic reaction.

AFM images and cyclic voltammetry curves of LB films after catalytic runs were used to investigate the topographic and electrochemistry properties. Taking catalyst **3c** as an example, the surfaces were investigated using AFM before and after catalytic reactions. The AFM images of one-layer LB films of complex **3c** deposited onto glass slides after various reaction runs are shown in Fig. 7. All scan ranges are 2.5 μm × 2.5 μm. The images indicate the height of the clusters decreases from 10–11 nm (after the first two runs) to 1.6 nm (after the third run) and to 0.9 nm (after the fourth run), probably because the alkyl chains bind to each other or aggregate instead of forming an ordered arrangement (Fig. 8) resulting in a quick decrease in catalytic activity (in the fourth run).



Scheme 2. Proposed catalytic mechanism.

The cyclic voltammetry curve of LB films of complex **3c** deposited on ITO glass has obvious differences after the catalytic reactions (Fig. 9). Reduction peak is inconspicuous and oxidation peak decreases from +0.3 to −0.05 V. This indicates that the catalysts after catalytic reaction are harder to reduce and easier to oxidize, probably because the Pd catalysts change from oxidized state (Pd^{2+}) to reduced state (Pd^0) and the LB films are no longer ordered or are covered by reagents which are obstacles for the current.

XPS spectra of **3c** monolayer on silicon were also measured before and after catalysis to give an insight into the mechanism. The results are shown in Fig. 10. For the monolayer before catalysis, the peaks of elements Pd, N and C in the XPS spectrum (Fig. 10(A)) can be seen at 337.9, 399.8 and 284.8 eV, which show that the complex **3c** is present in the LB films. The ratio of *I*(Pd)/*I*(C 1 s) is very small, indicating that Pd catalyst is covered with native carbon element. However, peaks in the Br 3d spectrum (68.4, 188.3, 181.9, 168.6 eV; Fig. 10(C)) and Na 1 s spectrum (1071.7 eV) appear when the reaction is over, indicating the substrates and the base (Na_2CO_3) enter into the reaction. We suppose that the reagent coordinates with Pd to generate intermediate in LB films in the whole stage. Thus, we speculate that the reaction intermediates and products coexist in the LB films in this process. Shifts of Pd 3d$_{5/2}$ (from 337.9 to 338.6 eV) and Pd 3d$_{3/2}$ (from 343.2 to 344.1 eV) assigned to Pd2+ are observed in Fig. 10(B). The shoulder peak at 336.82 eV (Pd$^0_{3/2}$) is assigned to Pd(0).[93] The shifts of the binding energy indicate that the Pd catalyst changes from oxidized state (Pd^{2+}) to reduced state (Pd^0), but there is a certain amount of Pd^{2+} on the surface. There is an inconspicuous binding energy peak of Cl 2p detected before the catalytic reaction (Fig. 10(D)), suggesting that the Pd catalyst changes from oxidized state (Pd^{2+}) to reduced state (Pd^0). The Cl 2p peak appears at 197.1 eV after catalysis (Fig. 10(D)) indicating that P=Cl covalent bonds are present.

Supporting experiments were designed. The substrate with **3c** LB monolayer was taken from the reaction system which was filtered and new substrate was added. No coupling products are detected, indicating that the catalytic mechanism is of heterogeneous nature.

According to the results discussed above, a reasonable heterogeneous catalytic mechanism is proposed. First, an amount of Pd^{2+} on the surface of LB films generates Pd^0 precursor, and then bromo substrates combine with Pd^0 to form intermediates which is the key step. The intermediates react with another substrate in a synergic way to form coupling product and leaching Pd^0 at the same time. Finally, Pd^0 re-deposits onto the **3c** films and leaches again. This is not real surface catalysis, but a leaching and re-deposition mechanism.[68] The plausible mechanism is depicted in Scheme 2.

Conclusions

A series of cyclopalladated arylmine compounds **3a–c** were synthesized and characterized using infrared, UV–visible, ^{1}H NMR and mass spectroscopies. Their catalytic activity for Heck and Suzuki cross-coupling reactions was investigated in both homogeneous and heterogeneous systems.

For reactions of activated and inactivated aryl bromides with arylboronic acids, excellent yields were obtained in pure water, which showed that the catalytic efficiency was high in the homogeneous case. Especially, all the cross-coupling reactions need no ligands, air isolation and assistant solvents, which mean the catalysts are suitable for future research for their assembled films in heterogeneous catalysis.

Organized monolayer films of **3a–c** were prepared using LB techniques and used as C–C coupling catalysts. The results confirmed that the yields were changed when the Langmuir monolayers were obtained at different surface pressures. The immobilized **3c** monolayer showed an enhanced activity relative to homogeneous reaction, for which the results show that the ordered monolayers are efficient with a catalyst loading as low as 10^{-5} mol%, and TON as high as 79 200 and TOF as high as 2640 h^{-1}. The catalytic efficiency is 100 times higher than that in the homogeneous case using the same reagent amount and ratio. The increased activity of immobilized **3c** monolayer is a result of a combination of the cyclopalladated arylimine structure and a change in conformation when deposited onto the substrate. A heterogeneous catalysis mechanism for Suzuki coupling reaction was also proposed. In addition, to provide an insight into the specific example of immobilized cyclopalladated complexes, the results demonstrate that the utility of well-characterized molecular monolayers can be used as models for supported molecular catalyst systems.

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