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Salen and half-salen palladium(II) complexes: synthesis, characteriztion and catalytic activity toward Suzuki–Miyaura reaction

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ABSTRACT

Salen and half-salen palladium(II) complexes (salden)Pd (**1**, salden=*N*,*N*′-bis(3,5-di- *tert*-butylsalicylidene)-1,2-dimethylethylenediamine), (hsalph)PdCl (**2**, hsalph=3,5-di-*tert*- butylsalicylidene-1-iminophenylene-2-amine), and (salph)Pd (**4**, salph=*N*,*N*′-bis(3,5-di-*tert*- butylsalicylidene)-1,2-phenylenediamine) were prepared and structurally characterized by X-ray crystallography. Complex **2** proved to exhibit high catalytic activity toward Suzuki–Miyaura reaction. Polyaromatic C_3-symmetric derivatives and various fluorinated biphenyl derivatives were readily achieved in good yields using Suzuki–Miyaura reaction catalyzed by complex **2**.

1. Introduction

Palladium-catalyzed Suzuki–Miyaura reaction has been used extensively for the synthesis of natural products, pharmaceutical intermediates, conducting polymers, pesticides, and liquid crystals.[1,2] By far, phosphine-based ligands remains to be the most popular selection in this reaction.[3–9] However, most of the phosphine ligands are air- and moisture-sensitive, and P–C bond degradation sometimes occurs at elevated temperatures, which leads to palladium aggregation and eventually affects the overall catalytic performance.[10] Recent application of phosphine-free ligands, such as *N*-heterocyclic carbenes,[11–24] *N*,*N*,*O*-chelate ligand,[25] *N*,*O*- or *N*,*N*-bidentate ligands,[9,26–32] aryloximes,[33,34] arylimines,[35–39] *N*-acylamidines,[40] guanidine[41] and simple amines[42–47] to Pd-catalyzed Suzuki–Miyaura reaction has opened new opportunities. The design of novel palladium complexes bearing phosphine-free ligands, which show high catalytic activity and selectivity toward C–C bond forming reactions is becoming increasingly important. In our previous work, bis(imino)pyridine palladium(II) complexes have been used successfully to catalyze Suzuki–Miyaura reaction in water.[48,49] Herein, we describe the synthesis and characterization of air- and moisture-stable palladium(II) complexes bearing Salen or half-salen ligands and their catalytic activity toward Suzuki–Miyaura reaction.

2. Results and discussion

2.1. Synthesis of complexes 1–4

(Salden)Pd (**1**, salden=*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-dimethylethylenediamine) was prepared by the reaction of ligand $\mathbf{L_1}$ with $PdCl_2(CH_3CN)_2$ in ethanol for 12 h at room temperature. However, the reaction of ligand $\mathbf{L_2}$ with $PdCl_2(CH_3CN)_2$ in the same condition afford product **5**, rather than the expected complex (salph)Pd (**4**, salph=*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine). We speculated that product **5** should consist of (hsalph)PdCl (**2**, hsalph=3,5-di-*tert*-butylsalicylidene-1-iminophenylene-2-amine) and **3**, which were formed by the reaction of $PdCl_2(CH_3CN)_2$ with ligand $\mathbf{L_3}$ and benzene-1,2-diamine derived from the hydrolyzation of ligand $\mathbf{L_2}$, respectively. To verify this hypothesis, complexes **2** and **3** were prepared by reaction of $PdCl_2(CH_3CN)_2$ with the corresponding ligands in EtOH. Comparative studies of ^{1}H NMR (Fig. 1), ^{13}C NMR, IR spectra, HRMS (EI), and element analysis indicated that product **5** surely consist of complexes **2** and **3** (molar ratio, **2**:**3**=4:1). Finally complex **4** was synthesized using another method that the $CHCl_3$ solution of ligand $\mathbf{L_2}$ reacted with the CH_3CN solution of $PdCl_2(CH_3CN)_2$ for 1 h at reflux condition (Scheme 1). The structures of complexes **1**, **2**, and **4** were further confirmed by X-ray crystallography. The crystal structures

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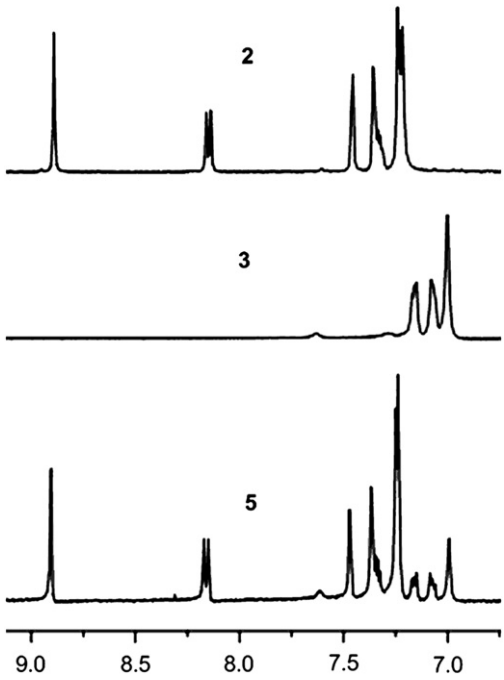


Figure 1. ^{1}H NMR spectra (aromatic region) of complexes **2**, **3**, and product **5** (400 MHz, DMSO-d_6).

of complexes **1**, **2**, and **4** are shown in Figures 2–4. Selected bond lengths and angles are summarized in Table 1. The geometries of **1**, **2** and **4** is a distorted square planar, and the Pd–N bond lengths (Pd(1)–N(1) 1.964(17) Å, Pd(1)–N(2) 2.025(19) Å) of **2** are slightly

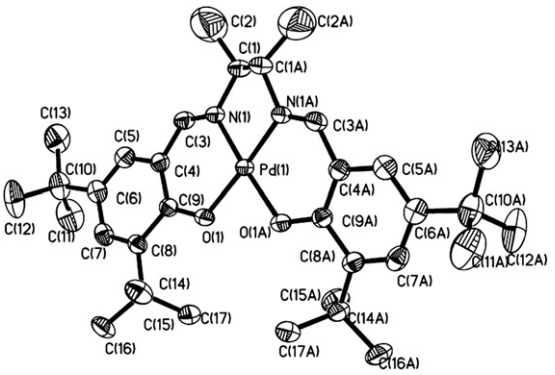


Figure 2. ORTEP drawing of complex **1**.

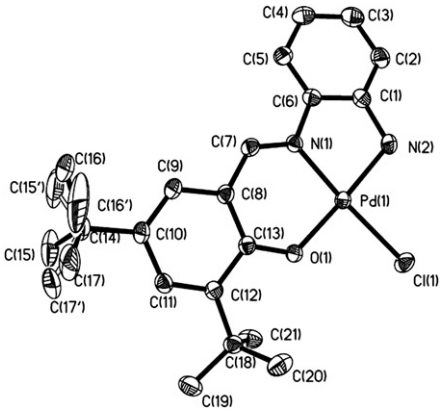
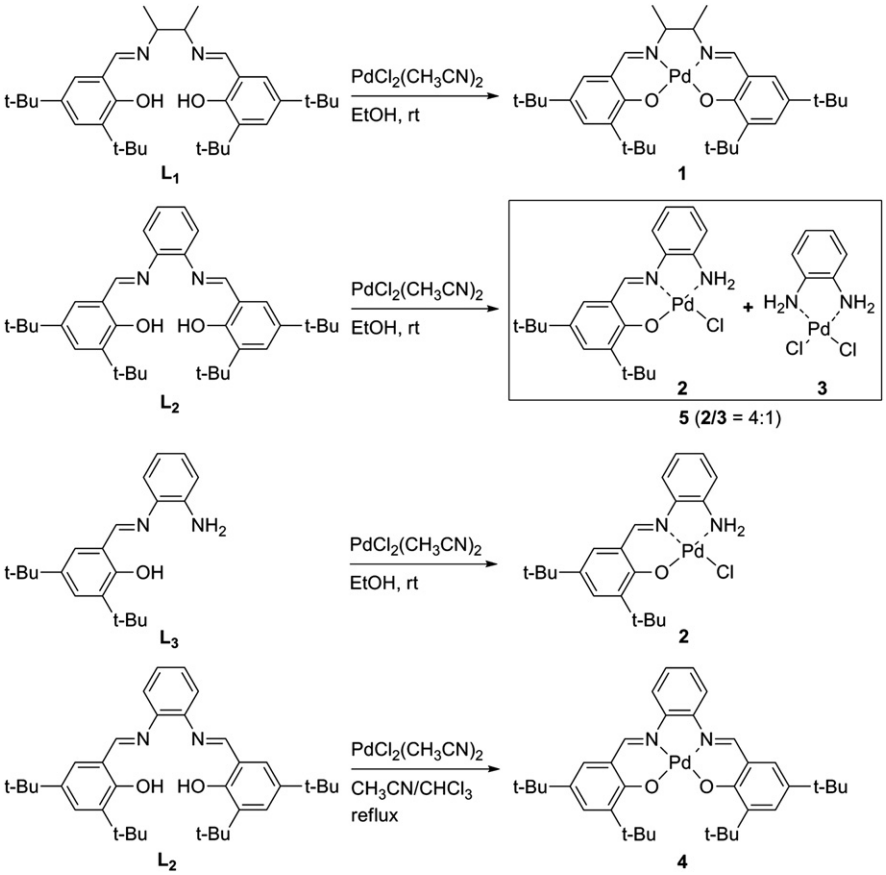


Figure 3. ORTEP drawing of complex **2**.



Scheme 1. Synthesis of complexes **1**–**4**.

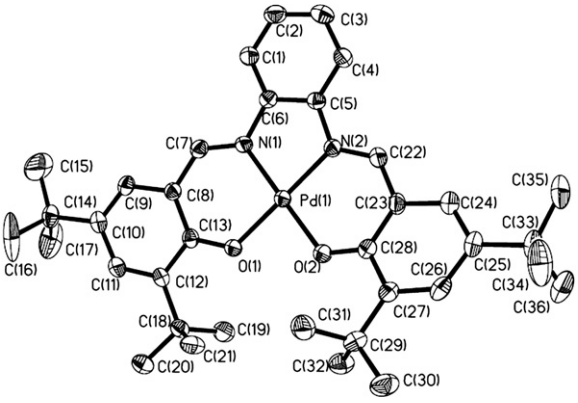


Figure 4. ORTEP drawing of complex **4**.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **1**, **2**, and **4**

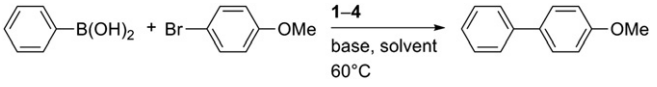
	1	2	4
Bond lengths			
Pd(1)–N(1)	1.949(3)	1.964(17)	1.950(3)
Pd(1)–N(2)	1.949(3)	2.025(19)	1.954(3)
Pd(1)–O(1)	1.987(2)	1.965(16)	1.986(2)
Pd(1)–O(2)	1.987(2)	—	1.978(2)
Pd(1)–Cl(1)	—	2.325(6)	—
Bond angles			
N(1)–Pd(1)–N(2)	84.29(18)	83.36(7)	83.77(11)
N(1)–Pd(1)–O(2)	175.69(10)	—	175.22(10)
N(2)–Pd(1)–O(2)	94.11(12)	—	94.58(10)
N(1)–Pd(1)–O(1)	94.11(12)	93.80(7)	94.38(10)
N(2)–Pd(1)–O(1)	175.69(11)	177.15(5)	176.12(9)
O(2)–Pd(1)–O(1)	87.77(14)	—	87.53(9)
N(1)–Pd(1)–Cl(1)	—	175.92(5)	—
O(1)–Pd(1)–Cl(1)	—	89.71(5)	—
N(2)–Pd(1)–Cl(1)	—	93.13(6)	—

longer than that of **1** and **4** (Pd(1)–N(1) 1.949(3) and 1.950(3) Å, Pd(1)–N(2) 1.949(3) Å and 1.954(3) Å), but the Pd(1)–O(2) bond lengths (1.987(2) Å and 1.978(2) Å) of **1** and **4** are obviously shorter than Pd(1)–Cl(1) bond lengths of **2** (2.325(6) Å).

2.2. Optimization of the Suzuki–Miyaura reaction conditions

Firstly, the Suzuki–Miyaura reaction of 4-bromoanisole and phenylboronic acid under different conditions was examined. The results are summarized in Table 2. Waghmode and co-worker reported that salen palladium complexes could catalyze Suzuki–Miyaura reaction of aryl iodides and bromides in DMF/H_2O at 100–110 °C.[50] In our experiment, complexes **1** and **4** showed no catalytic activity toward Suzuki–Miyaura reaction of 4-bromoanisole and phenylboronic acid in the presence of $K_3PO_4\cdot 3H_2O$ as base in EtOH at 60 °C under aerobic condition (entries 1 and 4). While the complex **2** was used as the precatalyst, the coupling product was obtained in excellent yield (96%, entry 2), and no palladium black was observed. However, the palladium black was obviously formed for the complex **4** as precatalyst (90%, entry 3). When the complex **2** catalyze the coupling reaction was run at room temperature, only 53% yield was obtained (entry 5). The base usually plays an important role in Suzuki–Miyaura reaction, because the addition of bases exerts a remarkable accelerating effect on the transmetalation between *R*–Pd–X and organoboronic acids.[51] The effect of bases and solvents on the Suzuki–Miyaura reaction catalyzed by complex **2** was then examined, which showed that $K_3PO_4\cdot 3H_2O$ was the best base and EtOH was the best solvent. Next, low catalyst loading test were performed. When the reaction was carried out in the presence of complex **2** with 0.1 mol % for 5.0 h, the 98% yield was obtained (entry 13), decreasing the loading of complex **2** to 0.01 mol % and 0.001 mol % also gave 96% and 90% yields, respectively in the same conditions (entries 14 and 15). Even though in the presence of 0.0001 mol % of complex **2**, 4-bromoanisole was also coupled with phenylboronic acid efficiently to give a 76% yield of the corresponding product, and the TONs could be up to 760,000 (entry 16).

Table 2
Optimization of the Suzuki–Miyaura reaction conditions[a]



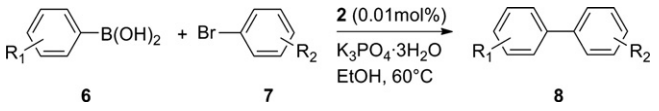
Entry	Complex (mol %)	Base	Solvent	Yield[b] (%)	TON
1	**1** (1.0)	$K_3PO_4\cdot 3H_2O$	EtOH	0	0
2	**2** (1.0)	$K_3PO_4\cdot 3H_2O$	EtOH	96	96
3	**3** (1.0)	$K_3PO_4\cdot 3H_2O$	EtOH	90	90
4	**4** (1.0)	$K_3PO_4\cdot 3H_2O$	EtOH	0	0
5[c]	**2** (1.0)	$K_3PO_4\cdot 3H_2O$	EtOH	53	53
6	**2** (1.0)	NaOAc	EtOH	10	10
7	**2** (1.0)	KOH	EtOH	70	70
8	**2** (1.0)	K_2CO_3	EtOH	63	63
9	**2** (1.0)	NEt_3	EtOH	52	52
10	**2** (1.0)	$K_3PO_4\cdot 3H_2O$	Toluene	50	50
11	**2** (1.0)	$K_3PO_4\cdot 3H_2O$	H_2O	32	32
12	**2** (1.0)	$K_3PO_4\cdot 3H_2O$	DMSO	0	0
13[d]	**2** (0.1)	$K_3PO_4\cdot 3H_2O$	EtOH	98	980
14[d]	**2** (0.01)	$K_3PO_4\cdot 3H_2O$	EtOH	96	9600
15[d]	**2** (0.001)	$K_3PO_4\cdot 3H_2O$	EtOH	90	90,000
16[d]	**2** (0.0001)	$K_3PO_4\cdot 3H_2O$	EtOH	76	760,000

[a] Reaction conditions: 0.50 mmol 4-bromoanisole, 0.75 mmol phenylboronic acid, 1.20 mmol base, 1 mol % complexes **1**–**4**, 2.0 mL solvent, 60 °C, reaction time 2.0 h.
[b] Isolated yields.
[c] The reaction was carried out at room temperature.
[d] Reaction time 5.0 h.

2.3. Scope and limitations of substrates

The cross-coupling reactions of various aryl bromides and arylboronic acids have been investigated in the presence of 0.01 mol % of complex **2** (Table 3). The electron-poor aryl bromide,

Table 3
Suzuki–Miyaura reaction of aryl bromides catalyzed by complex **2**[a]



6 **7** **8**

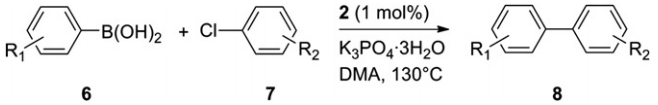
Entry	R_1	R_2	Product	Yield[b] (%)
1	H (**6a**)	4-OMe (**7a**)	**8a**	98
2	H (**6a**)	4-COMe (**7b**)	**8b**	99
3	H (**6a**)	4-Me (**7c**)	**8c**	96
4	H (**6a**)	2-Me (**7d**)	**8d**	83
5	H (**6a**)	4-F (**7e**)	**8e**	95
6	H (**6a**)	4-COOH (**7f**)	**8f**	92
7	H (**6a**)	4-OH (**7g**)	**8g**	93
8	4-F (**6b**)	4-OMe (**7a**)	**8h**	91
9	4-F (**6b**)	4-COMe (**7b**)	**8i**	93
10	4-F (**6b**)	4-F (**7e**)	**8j**	95
11	4-Me (**6c**)	4-OMe (**7a**)	**8k**	96
12	4-Me (**6c**)	4-COMe (**7b**)	**8l**	95
13	4-Me (**6c**)	4-Me (**7c**)	**8m**	98
14	4-Me (**6c**)	2-Me (**7d**)	**8n**	91
15	4-F (**6b**)	4,4′-Propyl-cyclohexyl (**7h**)	**8o**	98
16	4-F (**6b**)	4,4′-Pentyl-cyclohexyl (**7i**)	**8p**	90
17	4-F (**6b**)	4,4′-Pentyl-bicyclohexyl (**7j**)	**8q**	90
18	3,4-Difluoro (**6d**)	4,4′-Pentyl-cyclohexyl (**7i**)	**8r**	94
19	3,4,5-Trifluoro (**6e**)	4,4′-Pentyl-cyclohexyl (**7i**)	**8s**	93

[a] Reaction conditions: aryl bromide 0.50 mmol, arylboronic acid 0.75 mmol, $K_3PO_4\cdot 3H_2O$ 1.20 mmol, complex **2** (0.01 mol %), EtOH 2.0 mL, 80 °C, reaction time 5.0 h.
[b] Isolated yields.

such as 4-bromoacetophenone, reacted with different arylboronic acids to give excellent yield at 60 °C for 5.0 h (≥93%, entries 2, 9, 12). The electron-rich aryl bromide, such as 4-bromoanisole, also gave good yield at the same condition (≥95%, entries 1, 3, 8, 11,). And the aryl bromides containing *ortho* substituent also reacted effectively to prepare the desired sterically demanding biaryl products in good yields (≥90%, entries 4 and 14). The water-soluble aryl bromides, such as 4-bromophenol and 4-bromobenzoic acid reacted with phenylboronic acid to give excellent yields (entries 6 and 7). With this finding in hand, we next turned our attention toward the synthesis of liquid crystal compounds using Suzuki–Miyaura reaction of aryl bromide with fluorophenylboronic acid catalyzed by complex **2**. Liquid crystal products **8o–9s** can be obtained in excellent yields (≥90%, entries 15–19). Thus, this method provides a highly efficient way to prepare biphenyl derivatives used as liquid crystal compounds.

For the cross-coupling reactions of aryl chlorides and arylboronic acids, higher catalyst loading (1 mol % of complex **2**) should be used (Table 4). Initially an attempt to react 1-chloro-4-nitrobenzene with phenylboronic acid was not successful in EtOH at 60 °C, but we found the reaction could be carried out successfully in DMA at 130 °C and gave 98% yield (entry 6). The results showed that high temperature was required to improve the Suzuki–Miyaura reaction of aryl chloride. The coupling reaction of aryl chlorides bearing an electron-withdrawing group, such as 4-$COCH_3$, 4-CN, and 4-CHO, with phenylboronic acid gave biaryls in good yields ranging from 84–96% for 12 h (entries 2, 7, 8, 10). The electron-rich aryl chlorides reaction with arylboronic acids, such as 3- or 4-bromoanisole, also gave moderate yields (48%, 75%, 61%, and 80%, respectively, entries 1, 5, 9 and 13). But the aryl chlorides containing *ortho* substituent also reacted to prepare the desired biaryl products at the same condition in low to moderate yields (22% and 70%, respectively, entries 12 and 4).

Table 4
Suzuki–Miyaura reaction of aryl chlorides catalyzed by complex **2**[a]



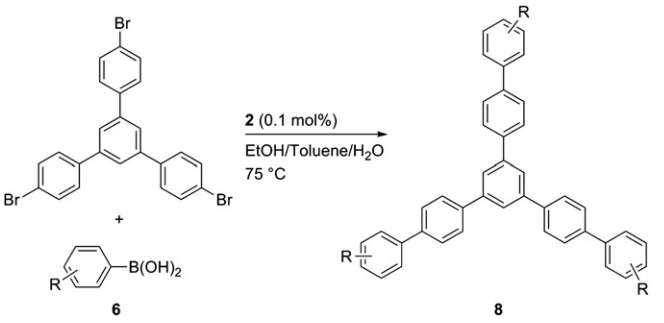
6 7 8

Entry	R_1	R_2	Product	Yield[b] (%)
1	H (**6a**)	4-OMe (**7k**)	**8a**	48
2	H (**6a**)	4-COMe (**7l**)	**8b**	84
3	H (**6a**)	4-Me (**7m**)	**8c**	76
4	H (**6a**)	2-Me (**7n**)	**8d**	70
5	H (**6a**)	3-OMe (**7o**)	**8t**	75
6	H (**6a**)	4-NO_2 (**7p**)	**8u**	98
7	H (**6a**)	4-CN (**7q**)	**8v**	96
8	H (**6a**)	4-CHO (**7r**)	**8w**	90
9	4-Me (**6c**)	4-OMe (**7k**)	**8j**	61
10	4-Me (**6c**)	4-COMe (**7l**)	**8k**	91
11	4-Me (**6c**)	4-Me (**7m**)	**8l**	60
12	4-Me (**6c**)	2-Me (**7n**)	**8m**	22
13	4-Me (**6c**)	3-OMe (**7o**)	**8x**	80

[a] Reaction conditions: aryl chloride 0.25 mmol, arylboronic acid 0.40 mmol, $K_3PO_4·3H_2O$ 0.75 mmol, complex **2** (1 mol %), DMA 2.0 mL, 130 °C, reaction time 12 h.
[b] Isolated yields.

It is worth mentioning that complex **2** proved to be an effective catalyst for the Suzuki–Miyaura reaction to prepare polyaromatic C_3-symmetric derivatives. For the consideration of solubility of 1, 3, 5-tris(4-bromophenyl)benzene, we select EtOH/toluene/H_2O (2.0 mL/1.0 mL/0.5 mL) as solvent, in the presence of 0.1 mol % of complex **2**, excellent yields were obtained for the reactions of various arylboronic acids with 1, 3, 5-tris(4-bromophenyl)benzene at 75 °C in air (90–96%, Table 5). Although synthesis of **8z** and **8z′** have been reported using Suzuki–Miyaura reaction in the presence of 30 mol % $Pd(PPh_3)_4$, THF/toluene/H_2O (3.0 mL/3.0 mL/1.0 mL) as solvent at 90 °C under N_2, the coupling products were obtained in only 53% (**8z**) and 47% (**8z′**) yields, respectively.[52]

Table 5
Synthesis of polyaromatic C_3-symmetric derivatives[a]



6 8

Entry	R	Product	Yield[b] (%)
1	H (**6a**)	**8y**	96
2	F (**6b**)	**8z**	90
3	Me (**6c**)	**8z′**	95
4	3,4-Difluoro (**6d**)	**8z″**	94

[a] Reaction conditions: aryl bromide 0.05 mmol, boronic acid 0.25 mmol, $K_3PO_4·3H_2O$ 0.40 mmol, complex **2** 0.1 mol %, EtOH/Toluene/H_2O (2.0 mL/1.0 mL/0.5 mL), 75 °C, reaction time 5.0 h.
[b] Isolated yields.

3. Conclusion

Air- and moisture-stable palladium(II) complexes **1**, **2**, and **4** bearing salen or half-salen ligand have been successfully prepared and their solid structures were confirmed by X-ray crystallography. Half-salen palladium(II) complex **2** proved to be a highly efficient catalyst for Suzuki–Miyaura reaction of arylboronic acids and aryl bromides, even activated aryl chlorides. Polyaromatic C_3-symmetric derivatives and fluorinated biphenyl derivatives used for liquid crystals could be readily prepared in good to excellent yields by the Suzuki–Miyaura reaction catalyzed by complex **2**.

4. Experimental section

4.1. General

All the Suzuki reactions were carried out under air using magnetic stirring unless otherwise noted. ^{1}H NMR spectral data were recorded on a Bruker DPX–400 spectrometers using TMS as internal standard and $CDCl_3$ or DMSO-d_6 as solvent. ^{13}C NMR spectra were recorded on the same spectrometer (100 MHz) in proton decoupled mode. EI–Mass spectra were measured on a LC/Q–TOF MS (Micromass, England). Acetonitrile and chloroform were dried over CaH_2, distilled and stored under nitrogen. Ethanol were dried and distilled from Mg. All other reagents were of analytical grade quality purchased commercially and used as received.

4.2. Synthesis of complex 1–4

*4.2.1. Synthesis of complex **1**.* To a solution of ligand $\mathbf{L_1}$ (2.0 mmol) in C_2H_5OH (20 mL) was added $PdCl_2(CH_3CN)_2$ (2.5 mmol). The resulting solution was stirred for 12 h at room temperature, the product was filtrated to afford a crude product. Further purification of the product was performed by a chromatography on silica gel column (CH_2Cl_2 as eluent), a yellow solid was obtained. Anal. Calcd for $C_{34}H_{50}N_2O_2Pd$: C, 65.32; H, 8.06; N, 4.48; Found: C, 65.14; H,

7.99; N, 4.52. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 2H), 7.44 (s, 2H), 7.00 (s, 2H), 3.97–3.85 (m, 2H), 1.49 (s, 18H), 1.43 (m, 6H), 1.28 (s, 18H).

*4.2.2. Synthesis of complex **2**.* To a solution of ligand $\mathbf{L_3}$ (2.0 mmol) in C_2H_5OH (20 mL) was added $PdCl_2(CH_3CN)_2$ (2.0 mmol). The resulting solution was refluxed for 4 h, stand a period time at room temperature, after the solid was filtrated and washed twice with $CHCl_3$, which was dissolved with larger ethanol, the filtrate was evaporated to give a yellow solid product in 60% yield. Anal. Calcd for $C_{21}H_{27}ClN_2OPd$: C, 54.20; H, 5.85; N, 6.02; Found: C, 53.95; H, 5.80; N, 5.93. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.91 (s, 1H), 8.17 (d, 1H, J_1=8.4 Hz), 7.48 (d, J=2.0 Hz, 1H), 7.37 (d, J=2.0 Hz, 1H), 7.34 (m, 1H), 7.26 (s, 2H), 7.24 (d, J=6.0 Hz, 2H), 1.35 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.93, 153.80, 147.88, 139.95, 138.42, 129.46, 127.54, 120.19, 116.75, 35.80, 34.12, 31.61, 29.86; HRMS (EI), m/z: $[M-Cl]^+$, calculated for: 429.1158; found, 429.1149.

*4.2.3. Synthesis of complex **3**.* To a solution of benzene-1,2-diamine (2.0 mmol) in C_2H_5OH (20 mL) was added $PdCl_2(CH_3CN)_2$ (2.0 mmol). The resulting solution was stirred for 5 h at room temperature, after the solid was filtrated and washed twice with EtOH give a yellow solid product in 90% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.17 (m, 2H), 7.08 (m, 2H), 7.01 (s, 4H).

*4.2.4. Synthesis of complex **4**.* To a solution of ligand $\mathbf{L_2}$ (2.0 mmol) in $CHCl_3$ (20 mL) was added in the CH_3CN solution of $PdCl_2(CH_3CN)_2$ (2.5 mmol), the resulting solution was stirred for 1 h at reflux. When the reaction completed, the mixture was cooled to room temperature, the solution was condensed to afford a crude product. Further purification of the product was performed by a chromatography on silica gel column (CH_2Cl_2 as eluent), a red solid was obtained. Anal. Calcd for $C_{36}H_{46}N_2O_2Pd$: C, 67.02; H, 7.19; N, 4.34; Found: C, 66.56; H, 7.04; N, 4.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 2H), 7.88 (dd, 2H, J_1=3.2 Hz, J_2=6.0 Hz), 7.54 (s, 2H), 7.30 (dd, 2H, J_1=3.2 Hz, J_2=6.0 Hz), 7.20 (s, 2H), 1.55 (s, 18H), 1.34 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.06, 152.25, 143.71, 141.17, 136.68, 131.65, 128.31, 126.97, 119.82, 115.35, 36.17, 34.00, 31.24, 29.55.

*4.2.5. Synthesis of product **5**.* To a solution of ligand $\mathbf{L_2}$ (2.0 mmol) in C_2H_5OH (20 mL) was added $PdCl_2(CH_3CN)_2$ (2.0 mmol). The resulting solution was stirred for 4 h at room temperature, the solid was filtrated and washed twice with $CHCl_3$ to give a yellow solid product **5** (**2**/**3**=4:1). Anal. Calcd. For $C_{90}H_{116}Cl_6N_{10}O_4Pd_5$: C, 50.53; H, 5.45; N, 6.52. Found: C, 49.44; H, 5.24; N, 6.84; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.91 (s, 1H), 8.17 (d, 1H, J=8.0 Hz), 7.48 (d, J=2.0 Hz, 1H), 7.37 (d, J=2.4 Hz, 1H), 7.34 (m, 1H), 7.26 (s, 2H), 7.24 (d, J=6.0 Hz, 2H), 7.17 (m, 2H), 7.09 (m, 2H), 7.00 (s, 4H), 1.35 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.93, 153.80, 147.88, 139.95, 138.42, 129.46, 127.54, 120.19, 116.75, 35.80, 34.12, 31.61, 29.86; IR (KBr, cm^{-1}): 3437, 3200, 3044, 2957, 1603 (C=N), 1583, 1519, 1492, 1421, 1360, 1227, 1166, 751, 540. HRMS (EI), m/z: [M(complex **2**)−Cl]$^+$, calculated for: 429.1158; found, 429.1149; [M(complex **3**)−2Cl]$^+$, calculated for: 213.9722; found, 213.9224.

4.3. General procedure for complex 2 catalyzed Suzuki–Miyaura reaction of aryl bromides

A mixture of aryl bromide (0.50 mmol), arylboronic acid (0.75 mmol), $K_3PO_4\cdot 3H_2O$ (1.20 mmol) and complex **2** (0.01 mol %, this is obtained by dilution with EtOH) in 2.0 mL of EtOH was stirred at 60 °C under the air condition for 5.0 h. The reaction mixture was filtered through a short pad of silica gel eluting with 5 mL of EtOAc. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with petroleum to give the corresponding coupling products.

*4.3.1. 4-Fluoro-4′-(4-propyl-cyclohexyl)-biphenyl (**8o**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J=7.2 Hz, 3H), 1.02–1.11 (m, 2H), 1.20–1.39 (m, 5H), 1.44–1.50 (m, 2H), 1.90 (t, J=6.4, 4H), 2.47–2.53 (m, lH), 7.07–7.12 (m, 2H), 7.27 (d, J=8.0 Hz, 2H), 7.46 (d, J=8.0 Hz, 2H), 7.50–7.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.61, 20.23, 33.77, 34.54, 37.23, 39.91, 44.47, 115.59, 115.80, 127.07, 127.49, 128.63, 137.95, 147.26. HRMS (EI), m/z: $C_{21}H_{25}F$, calculated: 296.1940; found, 296.1945.

*4.3.2. 4-Fluoro-4′-(4-pentyl-cyclohexyl)-biphenyl (**8p**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J=7.2 Hz, 3H), 1.02–1.11 (m, 2H), 1.20–1.39 (m, 5H), 1.44–1.50 (m, 2H), 1.90 (t, J=6.4, 4H), 2.48–2.54 (m, lH), 7.08–7.12 (m, 2H), 7.27 (d, J=8.0 Hz, 2H), 7.46 (d, J=8.0 Hz, 2H), 7.50–7.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.24, 22.87, 26.82, 32.40, 33.81, 34.55, 37.55, 37.57, 44.48, 115.56, 115.78, 127.04, 127.46, 128.77, 137.94, 147.24, 161.26, 161.40, 163.71, 163.86. HRMS (EI), m/z: $C_{23}H_{29}F$, calculated: 324.2253; found, 324.2256.

*4.3.3. 4-Fluoro-4′-(4′-pentyl-bicyclohexyl-4-yl)-biphenyl (**8q**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J=6.4 Hz, 3H), 0.97–1.33 (m, 18H), 1.73–1.96 (m, 9H), 2.49 (m, 1H), 7.08–7.12 (m, 2H), 7.27 (d, J=8.0 Hz, 2H), 7.46 (d, J=8.0 Hz, 2H), 7.50–7.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.33, 22.93, 26.88, 30.30, 30.54, 32.45, 33.84, 34.80, 37.68, 38.12, 43.11, 43.62, 44.50, 115.59, 115.81, 127.06, 127.48, 128.63, 137.48, 137.93, 147.28, 161.23, 163.68. HRMS (EI), m/z: $C_{29}H_{39}F$, calculated: 400.2566; found, 400.2576.

*4.3.4. 3,4-Difluoro-4′-(4-pentyl-cyclohexyl)-biphenyl (**8r**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J=8.0 Hz, 3H), 1.05–1.11 (m, 2H), 1.19–1.40 (m, 5H), 1.45–1.51 (m, 2H), 1.90 (t, J=12.0 Hz, 4H), 2.48–2.54 (m, lH), 7.16–7.23 (m, 1H), 7.28 (d, J=8.0 Hz, 2H), 7.34–7.38 (m, 1H), 7.44 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.28, 22.91, 26.85, 32.43, 33.81, 34.55, 37.57, 37.58, 44.53, 115.90, 116.07, 117.50, 117.68, 122.95, 127.03, 127.63, 136.89, 138.57, 147.94, 148.67, 149.56, 151.14, 151.26, 151.89, 152.02. HRMS (EI), m/z: $C_{23}H_{28}F_2$, calculated: 342.2159; found, 342.2155.

*4.3.5. 3,4,5-Trifluoro-4′-(4-pentyl-cyclohexyl)-biphenyl (**8s**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, J=8.0 Hz, 3H), 1.00–1.10 (m, 2H), 1.20–1.39 (m, 5H), 1.44–1.50 (m, 2H), 1.90 (t, J=12.0 Hz, 4H), 2.48–2.54 (m, lH), 7.15–7.18 (m, 2H), 7.28 (d, J=8.0 Hz, 2H), 7.42 (d, J=8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.14, 22.76, 26.70, 32.26, 33.58, 34.31, 37.34, 44.33, 110.64, 110.80, 126.72, 127.58, 128.62, 132.19, 135.68, 137.26, 148.39. HRMS (EI), m/z: $C_{23}H_{27}F_3$, calculated: 360.2065; found, 360.2063.

4.4. General procedure for complex 2 catalyzed Suzuki–Miyaura reaction of aryl chlorides

A mixture of aryl chloride (0.25 mmol), arylboronic acid (0.40 mmol), $K_3PO_4\cdot 3H_2O$ (0.50 mmol), and complex **2** (1 mol %) in 2.0 mL of DMA was stirred at 130 °C under the air condition for 12 h. The reaction mixture was quenched with water and extracted with EtOAc (2×5 mL). The solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with petroleum to give the corresponding coupling products.

4.5. Synthesis of polyaromatic C_3-symmetric derivatives

A mixture of aryl bromide (0.05 mmol), arylboronic acid (0.25 mmol), $K_3PO_4\cdot 3H_2O$ (0.40 mmol), and complex **2** (0.1 mol %)

in 3.5 mL of EtOH/toluene/H_2O=2:1:0.5 was stirred at 75 °C under the air condition for 5.0 h. The reaction mixture was quenched with water and extracted with EtOAc (2×5 mL). The solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with petroleum to give the corresponding coupling products.

*4.5.1. 1,3,5-Tris[4-(phenyl)phenyl]benzene (**8y**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 3H), 7.82 (d, J=8.0 Hz, 6H), 7.74 (d, J=8.0 Hz, 6H), 7.68 (d, J=7.6 Hz, 6H), 7.48 (t, J_1=7.2 Hz, J_2=7.6 Hz, 6H), 7.38 (t, J_1=7.2 Hz, J_2=7.6 Hz, 3H).

*4.5.2. 1,3,5-Tris[4-(4′-fluorophenyl)phenyl]benzene (**8z**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 3H), 7.80 (d, J=8.4 Hz, 6H), 7.68 (d, J=8.4 Hz, 6H), 7.63 (dd, J_1=J_2=8.4 Hz, 6H), 7.17 (t, J=8.4 Hz, 6H). HRMS (EI), m/z: $C_{42}H_{27}F_3$, calculated: 588.2065; found, 588.2075.

*4.5.3. 1,3,5-Tris[4-(4′-methylphenyl)phenyl]benzene (**8z′**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 3H), 7.80 (d, J=8.4 Hz, 6H), 7.72 (d, J=8.4 Hz, 6H), 7.58 (d, J=8.0 Hz, 6H), 7.29 (d, J=8.0 Hz, 6H), 2.42 (s, 9H). HRMS (EI), m/z: $C_{45}H_{36}$, calculated: 576.2817; found, 576.2825.

*4.5.4. 1,3,5-Tris[4-(3′,4′-bifluorophenyl)phenyl]benzene (**8z″**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 3H), 7.80 (d, J=8.0 Hz, 6H), 7.67 (d, J=8.0 Hz, 6H), 7.49–7.44 (m, 3H), 7.39–7.37 (m, 3H). HRMS (EI), m/z: $C_{42}H_{24}F_6$, calculated: 642.1782; found, 642.1802.

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Supplementary data

CCDC 675154, 686604, and 675153 contain the supplementary crystallographic data for complexes **1**, **2**, and **4**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version doi:10.1016/j.tet.2009.11.072.

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