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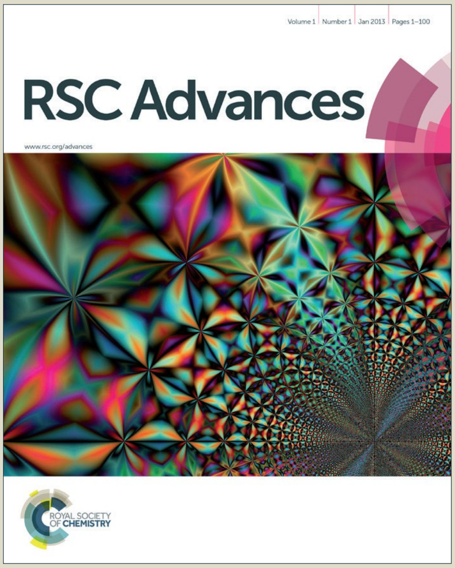

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Enhancing catalytic activity towards Heck-reaction by using 4,5,9,10-tetra(arylimino)pyrenylidenyldipalladium tetrachlorides

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Abstract: A series of binuclear 4,5,9,10-tetra(arylimino)pyrenylidenyldipalladium(II) tetrachloride complexes (**Pd1–Pd4**) was synthesized and characterized by the FT-IR and NMR spectroscopy as well as elemental analysis. The molecular structures of representative complexes **Pd1** and **Pd2** were determined by single crystal X-ray diffraction to reveal the square planar geometry around the palladium centre. The complex **Pd1** dissolved in the presence of ethanol to form mono-palladium complex **C1**, whose structure was also confirmed by single crystal X-ray diffraction. All binuclear palladium complexes promote the Heck cross-coupling reactions with high activities; the reaction can be carried out for various substrates and activators (basic compounds) and also in various solvents. The binuclear palladium complexes exhibit significantly higher efficiency than did its mono-palladium complexes bearing 4,5-bis(arylimino)pyrenylidenes.

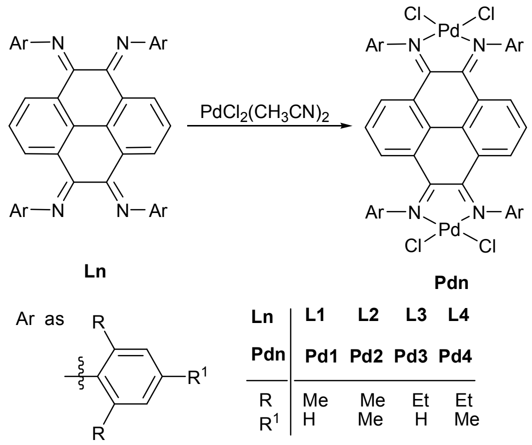
Introduction

Cross-coupling reactions promoted by transition metal catalysts have become powerful and versatile methods in organic syntheses.[1] Due to the high efficiency, mild reaction conditions and the tolerance of most functional groups, the palladium complex catalysts are especially useful in the coupling reaction between aryl or vinyl halides with activated alkenes,[2,3] called the Heck reaction. The scope and versatility of this reaction is extensively reviewed.[4–8] More importantly, the Heck reaction catalysts are currently applied to synthesize fine chemicals and monomers for functional polymers.[9–12] Frustratingly, high demand for any material results in gradually increasing price. Therefore the catalytic efficiency of palladium catalysts in the Heck reaction have been enhanced through the modification of the substituents within the ligands used,[13–15] which in turn affect the electronic and steric influences. Meanwhile, new palladium catalysts are obtained to promote the coupling reactions of less active haloarenes or alkenes.[16–20] There are a few of binuclear palladium catalysts explored,[21,22] with the observation of the positive synergetic performances;[22] however, the ligands used are difficult to synthesize. Design of binuclear palladium catalysts is still an interesting topic in the perspective of easily ligand preparation. The *N,N*-bidentate ligands are commonly incorporated into efficient palladium catalysts.[23] In addition to our efforts of designing late-transition metal pre-catalysts in ethylene polymerization,[24] some palladium complexes were synthesized as active catalysts towards Heck reactions.[25] The palladium complexes bearing newly designed 4,5-bis(arylimino) pyrenylidenes[26] exhibited not only high activity but also good thermostability in the Heck reaction.[27] In order to enhance ethylene polymerization by binuclear nickel complex pre-catalysts,[28] the 4,5,9,10-tetra(arylimino)pyrenylidene derivatives were synthesized. Extensively the title binuclear palladium complexes are also synthesized, and show high activities towards the Heck reaction, indicating activities better than their mono-palladium analogues[27] and other catalysts.[25] The current system with loading amount as one quarter molar ratio achieves the same TOF efficiency by the mono-palladium analogues.[27] Herein the synthesis and characterization of the title binuclear palladium complexes are reported in detail, and their catalytic performances towards Heck reaction are investigated and discussed.

Results and discussion

Synthesis and characterization of palladium complexes

The 4,5,9,10-tetra(arylimino)pyrenylidene derivatives, prepared according to the literature,[28] react with $PdCl_2(CH_3CN)_2$ in chloromethane to form the corresponding binuclear palladium complexes (Scheme 1). These palladium complexes were characterized by the FT-IR spectroscopy and the NMR measurements illustrating distinctive signals of all protons and carbons, and their components of C, H and N elements well coincide with the analytic observations. The palladium complexes are stable in solid state and also maintain good stability for several hours in their solutions of haloalkane and toluene, dimethylacetamide, dimethylformamide, acetone and acetonitrile. However, the dissociation can take place in the presence of ethanol. For example, the re-crystallization of complex **Pd1**, dissolved in the mixture solution of dichloromethane and ethanol and layered with diethyl ether, results in the mono-palladium complex bearing 4,5,9,10-tetra(2,6-dimethylphenylimino) pyrenylidene; the mono-palladium complex (**C1**) was also characterized by the FT-IR and NMR measurements. In addition, the molecular structures of mono-palladium (**C1**) and binuclear palladium complexes (**Pd1** and **Pd2**) were confirmed by single crystal X-ray diffraction.



Scheme 1 Synthetic procedure of binuclear palladium complexes

X-ray crystallography

The crystals of **C1** were obtained by layering diethyl ether on the solution of **Pd1** in the mixture of dichloromethane and ethanol at room temperature, meanwhile the crystals of complexes **Pd1** and **Pd2** were grown from their dichloromethane (DCM) solutions when covered with diethyl ether at room temperature, respectively. The mono-palladium complex **C1** and the binuclear palladium complexes **Pd1** and **Pd2** are all exhibit similar structure with distorted square planar geometry around the cationic palladium. There were free solvent molecules incorporated in the crystals of these palladium complexes, ethyl ether in **C1** and dichloromethane for both **Pd1** and **Pd2**, but these solvent molecules were disordered. Therefore the Platon Squeeze procedure was used to kill the free ethyl ether and dichloromethane molecules when refining structures of **C1**, **Pd1** and **Pd2**,[29] such option made no influence on their structures. The corresponding molecular structures are shown in Figures 1–3, and the selected bond lengths and bond angles are listed in Table 1.

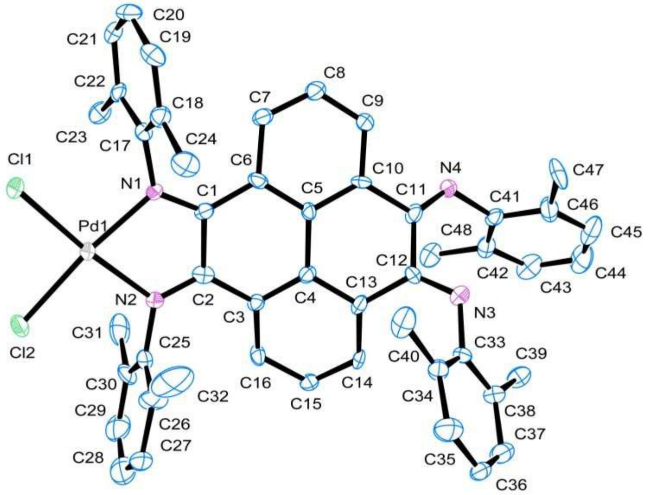


Figure 1 ORTEP drawing of **C1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths and angles for **C1, Pd1** and **Pd2**

	C1	Pd1	Pd2
	Bond lengths (Å)		
N(1)–C(1)	1.294(11)	1.297(10)	1.312(4)
N(2)–C(2)	1.282(11)	1.328(10)	1.302(4)
N(3)–C(12)	1.284(10)	1.309(10)	1.304(5)
N(4)–C(11)	1.224(10)	1.361(10)	1.307(5)
Pd(1)–N(1)	2.041(7)	2.045(7)	2.020(3)
Pd(1)–N(2)	2.030(7)	1.994(6)	2.017(3)
Pd(1)–Cl(1)	2.278(2)	2.272(2)	2.2909(10)
Pd(1)–Cl(2)	2.289(3)	2.317(2)	2.2874(11)
Pd(2)–N(3)		2.051(6)	2.026(3)
Pd(2)–N(4)		1.981(6)	2.015(3)
Pd(2)–Cl(3)		2.341(2)	2.2967(10)
Pd(2)–Cl(4)		2.253(2)	2.2781(10)
	Bond angles (°)		
C(1)–N(1)–Pd(1)	116.4(6)	116.2(5)	116.8(2)
N(2)–Pd(1)–Cl(1)	174.7(2)	170.85(19)	173.99(9)
C(1)–N(1)–C(17)	124.6(7)	123.0(7)	124.2(3)
C(17)–N(1)–Pd(1)	118.9(5)	120.7(5)	119.1(2)
C(2)–N(2)–Pd(1)	116.5(6)	115.6(5)	116.6(2)
C(12)–N(3)–Pd(2)		116.1(5)	116.5(2)
C(11)–N(4)–Pd(2)		114.4(5)	116.3(2)
N(3)–Pd(2)–Cl(3)		175.07(18)	174.89(9)

All the molecular structures indicate the adoption of distorted square planar geometry at palladium, consistent with the classical *N,N*-bidentate palladium complexes.[23,25] The C=N bonds of N1−C1 and N2−C2 bonds are of almost equal lengths within the structures of **C1** and **Pd2**, but a slight difference within **Pd1** for the N2−C2 (1.328(10) Å) and N1−C1 (1.297(10) Å). Within complex **C1**, there are functional C=N groups acting either free or coordination with palladium, the bonds involved in coordination as N(1)–C(1) (1.294(11) Å) and N(2)–C(2) (1.282(11) Å) are lengths longer than those free in coordination as N(3)–C(12) (1.284(10) Å) and N(4)–C(11) (1.224(10) Å), indicating that the effective coordination results weaker double-cationic palladium centres withdraw more electrons and elongate the bond lengths of coordinated C=N groups around 1.3 Å or longer (Table 1).

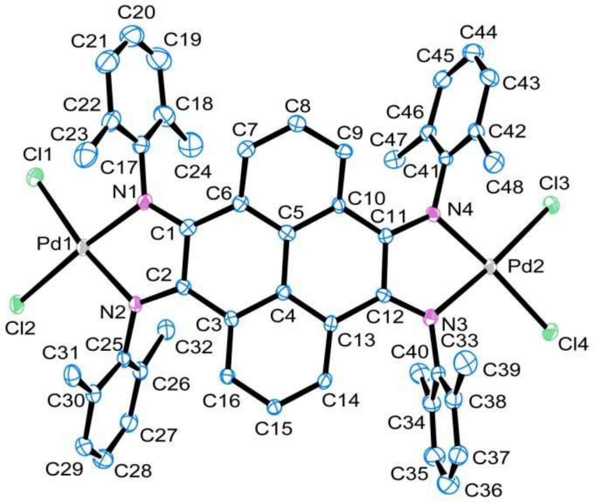


Figure 2 ORTEP drawing of **Pd1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

The coordination features are generally consistent to their mono-nuclear (palladium[27] and nickel[26]) and binuclear nickel analogues.[28]

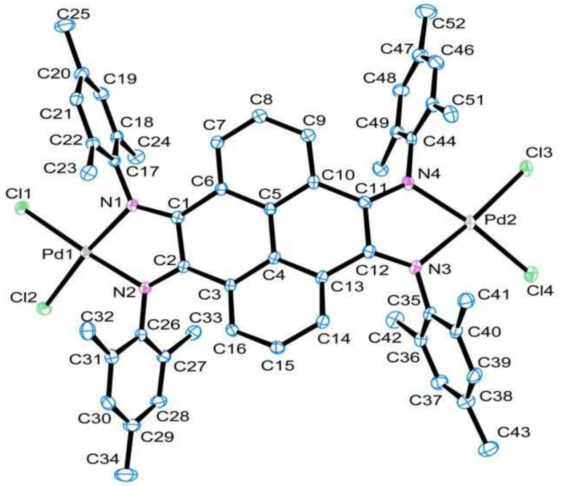
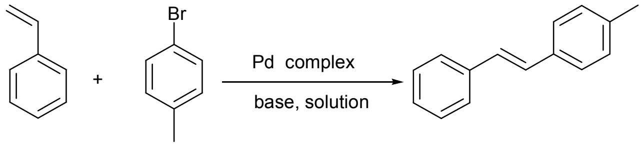


Figure 3 ORTEP drawing of **Pd2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Heck Coupling Reaction

The complex **Pd2** was used to optimize conditions for the typical Heck reaction of *p*-bromotoluene with styrene. In addition to palladium complex catalysts, in principle, the inorganic base and organic solvent significantly affect the catalytic activity. With a amount of **Pd2** loading of 0.001 mol% with respect to *p*-bromotoluene, a slight excess of (1.2 equivalent) styrene and 1.1 equivalents of inorganic base were conducted, the conversion of *p*-bromotoluene was monitored and tabulated in Table 2.

Table 2 Optimization of *p*-bromotoluene and styrene using complex **Pd2**[a]



Entry	Base	Solution	Temp (°C)	Time (h)	Conversion[b] (%)	TOF[c]
1	Na_2CO_3	DMA	60	8	nd	nd
2	Na_2CO_3	DMA	100	8	4.7	293
3	Na_2CO_3	DMA	150	2	88	22000
4	Na_2CO_3	DMA	150	4	94	11750
5	Na_2CO_3	DMA	150	8	96	6000
6	Na_2CO_3	DMA	150	12	96	4000
7	Na_2CO_3	DMF	150	8	60	3750
8	Na_2CO_3	Toluene	100	8	nd	nd
9	Na_2CO_3	CH_3CN	60	8	nd	nd
10	$NaHCO_3$	DMA	150	8	5.8	362
11	K_2CO_3	DMA	150	8	20	1250
12	NaOAc	DMA	150	8	11	688
13	NaOH	DMA	150	8	1.3	81

[a] Reaction conditions: 2×10^{-5} mmol **Pd2** as the catalyst, 2.0 mmol *p*-bromotoluene, 2.4 mmol styrene, 2.2 mmol base, 4.0 mL solution; [b] Determined by GC; [c] TOF: mol *p*-bromotoluene /mol Pd·h.

The reaction temperature was changed within different period for the selected solvent of *N,N*-dimethylacetamide (DMA) along with the base Na_2CO_3, (entries 1–6, Table 2). In these conditions, high catalytic efficiency was achieved for 150 °C (entries 3 and 4, Table 2). The coupling reaction did not occur at 60 °C (entry 1, Table 2), and it slowly began to process at 100 °C (entry 2, Table 2). DMA turned out to be the best solvent than other solvents, such as *N,N*-dimethylformamide (DMF) (entry 7, Table 2), toluene (entry 8, Table 2) or acetonitrile (entry 9, Table 2). Moreover, using other bases such as $NaHCO_3$ (entry 10, Table 2), K_2CO_3 (entry 11, Table 2), NaOAc (entry 12, Table 2) and NaOH (entry 13, Table 2) did not enhance the catalytic reactions.

For the catalytic observations on the basis of **Pd2**, the optimum conditions are 1.2 equivalent of styrene and 1.1 equivalent of Na_2CO_3 with the palladium loading of 0.001 mol% to *p*-bromotoluene in DMA at 150 °C for 8 h. The remaining palladium complexes were also investigated and the results are listed in Table 3, indicating the almost quantitative conversions (entries 1–4, Table 3). Therefore the title palladium complexes efficiently promote the Heck reaction with a good thermostability. With comparison with the literature of binuclear palladium catalysts,[21,22] the current palladium complexes showed higher activities, and were also easily synthesized. There were slight variations observed for different complexes, confirming the influences of the ligands used; however, it is difficult to a conclusion of a general tendency. All four binuclear palladium complexes (entries 1–4, Table 3) exhibited activities better than their mononuclear analogues, 4,5-bis(arylimino)pyrenylidenyl palladium complexes.[27] In addition, all investigated palladium compounds are applicable as catalysts towards the Heck reaction. The requisite amounts of $PdCl_2$ and $Pd(OAc)_2$ were also investigated for the purpose of comparison, but they achieved only low conversions of *p*-bromotoluene in 22 % and 41 % (entries 5 and 6, Table 3). Therefore the title palladium complexes are efficient catalysts towards Heck reaction.

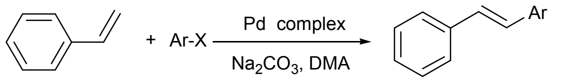
Table 3 Heck reaction of *p*-bromotoluene and styrene by Pd complexes [a]

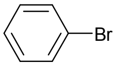
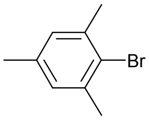
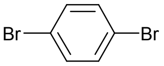
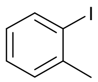
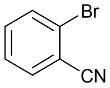
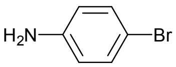
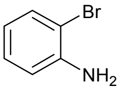
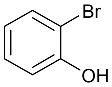
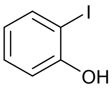
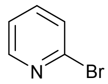
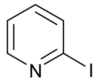
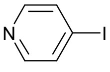
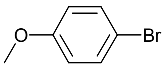
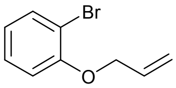
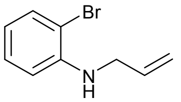
Entry	Pd complex	Conversion[b] (%)	TOF[c]
1	Pd1	90	5625
2	Pd2	96	6000
3	Pd3	92	5750
4	Pd4	95	5936
5[d]	$PdCl_2$	22	28
6[d]	$Pd(OAc)_2$	41	51

[a] Reaction conditions: 2×10^{-5} mmol Pd complex as the catalyst, 2.0 mmol *p*-bromotoluene, 2.4 mmol styrene, 2.2 mmol Na_2CO_3, 4.0 mL DMA, 150 °C for 8 h; [b] Determined by GC; [c] TOF: mol *p*-bromotoluene /mol Pd·h. [d] 2×10^{-3} mmol [Pd].

Furthermore, the catalyst **Pd2** was also used to study the Heck coupling reaction with other aryl halides, and the results are summarized in Table 4. Relatively high activity was achieved with bromobenzene (entry 1, Table 4); however, low activity was observed with 2-methylbromobenzene (entry 2, Table 4), which is consistent with the literature.[23] For 1,4-dibromobenzene (entry 3, Table 4), the conversion at the first step was 72 %, while only 14 % at the second step. Regarding 2-iodotoluene (entry 4, Table 4), the good activity was also achieved. In comparison with the mono-palladium complexes bearing 4,5-bis(arylimino) pyrenylidene derivatives,[27] the binuclear palladium catalysts exhibited lower activities when using haloarenes containing active amino or hydroxyl groups (entries 6–9, Table 4). Substances having electron-withdrawing substituents (entries 8 and 9, Table 3) enhanced the efficiency of the Heck reaction. However, the Heck reaction could not occurred by using the substance of chloro-arenes due to low active chloro-arenes.

Table 4 Heck reaction of aryl bromides and styrene using complex **Pd2** [a]



Entry	Ar-X	Conversion [b] (%)	Yield [c] (%)	TOF [d]
1		98	92	6125
2		56	44	3500
3		72 (14)	57 (6)	4500 (875)
4		92	83	5750
5		54	41	3375
6		12	7.2	750
7		11	6.8	688
8		21	13	1313
9		30	19	1875
10		18	12	1125
11		20	15	1250
12		5.0	3.8	313
13		37	24	2313
14		13	9.8	813
15		11	9.3	688

[a] Reaction conditions: 2×10^{-5} mmol complex **Pd2** as the catalyst, 2.0 mmol Ar-X, 2.4 mmol styrene, 2.2 mmol Na_2CO_3, 4.0 mL DMA, 150 °C for 8 h; [b] Determined by GC; [c] Isolated yield; [d] TOF: mol Ar-X /mol Pd·h.

Extensively the halo-arenes including other functional groups such as the halopyridine derivatives were also explored and indicated the activities (entries 10–13, Table 4). Moreover, the vinyl-substituted bromobenzene compounds were exposed to self-coupling without styrene, and the cyclic products were obtained (entries 14 and 15, Table 4), which indicates the potential for some complicated synthesis. In addition to the isolated yields of products, all conversion yields were calculated with respect to isolated products and confirmed by the ^1H and ^{13}C NMR measurements according to the literature data.[30–32] Therefore binuclear palladium catalysts towards the Heck coupling reaction are still worth investigating.

Conclusions

A series of binuclear complexes of 4,5,9,10-tetra(arylimino)pyrenylidenyldipalladium tetrachlorides was synthesized and fully characterized. The binuclear palladium complexes are stable in its solid state and major solvents. However, in presence of ethanol, the dissociation takes place to form mono-palladium complex. The molecular structures of both mononuclear and binuclear palladium complexes show the distorted square planar geometry around the palladium cation. All binuclear palladium complexes exhibit activities towards Heck coupling reactions higher than mono-palladium analogues bearing 4,5-bis(arylimino)pyrenylidene derivatives.[27] Both mono- and binuclear palladium catalysts showed high thermal stability. Further study of the binuclear palladium complexes in order to enhance the catalytic activities and application would be interesting.

Experimental section

General considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on the Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard. FT-IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using an HPMOD 1106 microanalyzer.

Synthesis and characterization

A series of 4,5,9,10-tetra(arylimino)pyrenylidene derivatives used as ligands (**L1–L4**) was prepared using our previous procedure.[28] 4,5,9,10-Tetra(2,6-dimethylphenylimino) pyrenylidene (**L1**, 0.67 g, 1 mmol) and $PdCl_2(CH_3CN)_2$ (0.51 g, 2 mmol) were mixed in 5 ml CH_2Cl_2 and the mixture was stirred for 12 h at room temperature. The precipitate was collected by filtration and washed with diethyl ether (3×5 mL), then dried under vacuum. The 4,5,9,10-tetra(2,6-dimethylphenylimino)pyrenylidenyl dipalladium tetrachloride (**Pd1**) was obtained as brown solid in 0.93 g (90.2 %). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (d, J = 13.2 Hz, 4H, Ph-H), 7.08 (d, J = 12.8 Hz, 6H, Ph-H), 6.90–6.70 (m, 8H, Ph-H), 2.32 (s, 6H, 2×CH_3), 2.18 (s, 6H, 2×CH_3), 1.91 (s, 6H, 2×CH_3), 1.32 (s, 6H, 2×CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 165.9, 165.0, 155.7, 154.6, 148.2, 146.5, 146.0, 133.5, 132.8, 131.5, 131.0, 130.6, 129.3, 128.7, 128.2, 127.9, 125.8, 125.0, 124.4, 123.3, 18.8, 18.5, 17.3, 17.1. FT-IR (KBr, cm^{-1}): 2908.9 (w), 1616.6 ($\nu_{C=N}$, w), 1588.1 (w), 1463.6 (s), 1377.2 (w), 1347.9 (s), 1287.2 (m), 1165.7 (m), 1088.2 (m), 922.3 (w), 766.2 (s), 707.2 (s). Anal. Calcd for $C_{48}H_{42}Cl_4N_4Pd_2$ (1029): C, 56.00; H, 4.11; N, 5.44. Found: C, 56.13; H, 4.22; N, 5.20.

4,5,9,10-Tetra(2,6-dimethylphenylimino)pyrenylidenylpalladium dichloride (**C1**): The mono-nuclear palladium complex was isolated as a results of our effort to obtain single crystals of binuclear palladium complex **Pd1**. The 4,5,9,10-tetra(2,6-dimethylphenylimino)pyrenylidenyldipalladium tetrachloride (**Pd1**) was solved in the mixture solution of dichloromethane and ethanol, then being layered with diethyl ether. The crystals collected from the surface of the Schlenk tube were characterized as 4,5,9,10-tetra(2,6-dimethylphenylimino)pyrenylidenyl palladium dichloride (**C1**). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.67 (d, *J* = 6.8 Hz, 1H, Ph-*H*), 7.38–7.20 (m, 5H, Ph-*H*), 6.99 (d, *J* = 7.6 Hz, 4H, Ph-*H*), 6.91–6.83 (m, 6H, Ph-*H*), 6.64 (t, *J* = 7.6 Hz, 2H, Ph-*H*), 2.41 (s, 6H, 2×C*H*$_3$), 2.31 (s, 6H, 2×C*H*$_3$), 1.98 (s, 6H, 2×C*H*$_3$), 1.36 (s, 6H, 2×C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 165.9, 165.1, 155.8, 154.7, 148.3, 146.6, 133.6, 133.4, 132.8, 132.6, 131.6, 131.0, 130.6, 130.1, 129.4, 129.3, 128.7, 128.6, 128.4, 128.3, 127.9, 127.8, 125.9, 125.1, 124.4, 124.2, 123.3, 18.8, 18.6, 18.4, 17.4, 17.3. FT-IR (KBr, cm^{-1}): 2909.2 (w), 2361.6 (w), 1623.3 ($\nu_{C=N}$, w), 1588.5 (w), 1464.8 (s), 1438.4 (m), 1374.7 (w), 1339.2 (s), 1283.6 (m), 1204.4 (w), 1089.1 (m), 1031.2 (w), 956.5 (w), 921.3 (m), 761.4 (s), 711.6 (s).

4,5,9,10-Tetra(mesitylimino)pyrenylidenyldipalladium tetrachloride (**Pd2**). Using the same procedure as for **Pd1**, **Pd2** was obtained as a brown solid in 0.90 g (83.3 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.05 (s, 4H, Ph-*H*), 7.01–6.97 (m, 4H, Ph-*H*), 6.80–6.76 (m, 3H, Ph-*H*), 6.69–6.53 (m, 3H, Ph-*H*), 2.38 (s, 6H, 2×C*H*$_3$), 2.37–2.19 (m, 24H, 8×C*H*$_3$), 1.30 (s, 6H, 2×C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 165.7, 165.0, 155.7, 154.6, 139.5, 137.4, 136.9, 136.5, 136.4, 134.9, 133.7, 132.6, 131.4, 131.0, 130.4, 130.3, 128.8, 128.2, 127.7, 124.4, 21.4, 20.2, 18.9, 18.8, 17.6, 16.4. FT-IR (KBr, cm^{-1}): 2911.1 (w), 1610.2 ($\nu_{C=N}$, w), 1587.3 (w), 1464.4 (s), 1376.0 (w), 1345.8 (s), 1288.0 (m), 1166.3 (w), 1090.0 (m), 1031.0 (w), 763.4 (s), 708.2 (s). Anal. Calcd for $C_{52}H_{50}Cl_4N_4Pd_2$ (1085): C, 57.53; H, 4.64; N, 5.16. Found: C, 57.14; H, 4.31; N, 4.81.

4,5,9,10-Tetra(2,6-diethylphenylimino)pyrenylidenyldipalladium tetrachloride (**Pd3**). Similarly **Pd3** was obtained as a brown solid in 0.68 g (59.6 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.46 (d, *J* = 7.2 Hz, 1H, Ph-*H*), 7.34 (d, *J* = 6.0 Hz, 3H, Ph-*H*), 7.25–7.22 (m, 3H, Ph-*H*), 7.08–7.02 (m, 2H, Ph-*H*), 6.99 (d, *J* = 8.0 Hz, 2H, Ph-*H*), 6.96–6.92 (m, 4H, Ph-*H*), 6.79 (t, *J* = 8.0 Hz, 2H, Ph-*H*), 6.53 (d, *J* = 7.6 Hz, 1H, Ph-*H*), 3.12–2.81 (m, 6H, 2×C*H*$_3$), 2.62–2.41 (m, 6H, 2×C*H*$_3$), 1.61 (s, 6H, 2×C*H*$_3$), 1.35 (t, *J* = 7.2 Hz, 6H, 2×C*H*$_3$), 1.26–1.17 (m, 12H, 4×C*H*$_3$), 0.79 (t, *J* = 7.2 Hz, 6H, 2×C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 165.5, 165.3, 153.0, 145.7, 145.6, 145.2, 142.2, 136.0, 133.5, 133.0, 132.7, 131.9, 128.9, 128.4, 127.5, 126.7, 126.2, 125.4, 125.0, 121.5, 24.9, 24.7, 24.6, 23.4, 13.5, 13.3, 13.1, 12.9. FT-IR (KBr, cm^{-1}): 2964.2 (m), 1583.2 (w), 1449.9 (m), 1344.6 (m), 1301.1 (m), 1167.4 (w), 1058.3 (m), 967.0 (w), 805.7 (m), 756.2 (s). Anal. Calcd for $C_{56}H_{58}Cl_4N_4Pd_2$ (1141): C, 58.91; H, 5.12; N, 4.91. Found: C, 58.87; H, 5.18; N, 4.94.

4,5,9,10-Tetra(2,6-diethyl-4-methylphenylimino) pyrenylidenyldipalladium tetrachloride (**Pd4**). Similarly **Pd4** was obtained as a brown solid in 0.75 g (62.6 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.20 (d, *J* = 8.0 Hz, 4H, Ph-*H*), 7.04 (s, 8H, Ph-*H*), 6.79 (t, *J* = 8.0 Hz, 2H, Ph-*H*), 2.37 (s, 12H, 4×C*H*$_3$), 2.23 (s, 24H, 8×C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 166.4, 165.7, 155.3, 147.5, 145.6, 143.7, 143.0, 138.3, 135.7, 135.5, 134.1, 133.2, 132.7, 132.1, 128.7, 127.4, 126.4, 125.1, 24.8, 24.6, 23.2, 21.7, 21.6, 21.5, 21.0, 13.3, 13.1, 13.0. FT-IR (KBr, cm^{-1}): 2968.7 (s), 1580.3 (w), 1449.9 (m), 1455.2 (m), 1303.3 (w), 1169.9 (m), 1063.7 (m), 1036.7 (m), 861.0 (m), 784.0 (s). Anal. Calcd for $C_{60}H_{66}Cl_4N_4Pd_2$ (1197): C, 60.16; H, 5.55; N, 4.68. Found: C, 59.74; H, 5.20; N, 4.97.

Table 5 Crystal data and structure refinement details for **C1, Pd1** and **Pd2**

Identification code	**C1**	**Pd1**	**Pd2**
CCDC	1036470	1036471	1036472
Empirical formula	$C_{48}H_{42}Cl_2N_4Pd$	$C_{48}H_{42}Cl_4N_4Pd_2$	$C_{52}H_{50}Cl_4N_4Pd_2$
Fw	852.16	1029.46	1085.56
T (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/n	P2(1)/n
a (Å)	18.764(4)	14.249(3)	14.458(3)
b (Å)	12.137(2)	12.729(3)	12.382(3)
c (Å)	21.618(4)	27.486(6)	30.667(6)
α (°)	90	90	90
β (°)	106.27(3)	90.50(3)	90.15(3)
γ (°)	90	90	90
V (Å^3)	4726.2(16)	4984.8(17)	5490.0(19)
Z	4	4	4
D_{calcd} (mg m^{-3})	1.198	1.372	1.313
μ (mm^{-1})	0.539	0.970	0.884
F(000)	1752	2072	2200
Crystal size (mm)	0.22 × 0.12 × 0.08	10.10 × 0.20 × 0.12	0.50 × 0.43 × 0.31
θ range (°)	1.13–25.00	1.48–25.00	1.56–27.52
Limiting indices	$-22 \leq h \leq 19$ $-14 \leq k \leq 14$ $-25 \leq l \leq 25$	$-16 \leq h \leq 13$, $-15 \leq k \leq 15$ $-32 \leq l \leq 25$	$-18 \leq h \leq 18$ $-16 \leq k \leq 16$ $-39 \leq l \leq 39$
No. of rflns collected	26306	28115	34189
No. unique rflns [R(int)]	8255(0.1035)	8751(0.0696)	12032(0.0422)
Completeness to θ (%)	99.0 (θ=25.00)	99.7 (θ=25.00)	95.4 (θ=27.52)
Goodness of fit on F^2	1.072	1.140	1.040
Final R indices [$I > 2\sigma(I)$]	R1 = 0.1000 wR2 = 0.2662	R1 = 0.0800 wR2 = 0.2385	R1 = 0.0548 wR2 = 0.1499
R induces (all data)	R1 = 0.1265 wR2 = 0.2883	R1 = 0.0926, wR2 = 0.2530	R1 = 0.0584 wR2 = 0.1534
Largest diff. peak and hole(e Å^{-3})	0.740 and − 0.952	1.222 and − 1.498	1.083 and − 1.116

X-ray Crystallographic Studies

The single crystals of complex **C1** suitable for X-ray diffraction analysis were obtained by laying ethyl ether on the solution of complex **Pd1** in the mixture of dichloromethane and ethanol mixed at room temperature; and the single crystals of complexes **Pd1** and **Pd2** suitable for X-ray diffraction analysis were individually grown by layering diethyl ether onto the corresponding dichloromethane solutions at room temperature. Data collections for **C1** and **Pd2** were carried out on the Rigaku MM007-HF Saturn 724 + CCD diffractometer with confocal mirror monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(3) K, whilst those for **Pd1** were carried out on the Rigaku Saturn 724 + CCD diffractometer with graphite-monochromated

Mo Kα radiation (λ = 0.71073 Å) at 173(2) K. The cell parameters were obtained by the global refinement of the positions of all collected reflections, and the intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by the full-matrix least squares on F^2, meanwhile all hydrogen atoms were placed in the calculated positions. The structure solution and refinement were performed by using the SHELXL-97 package.[33] Moreover, together with the structure refinements, the SQUEEZE option of the program PLATON was conducted to remove free solvent molecules,:[9] diethyl ether out of the structure of **C1** and dichloromethane out of both structures of **Pd1** and **Pd2**; such option had no influence on the structures. Crystal data and refinement details are collected in Table 5.

Heck reaction

General procedure for the Heck reaction of styrene with haloarenes was conducted in the presence of palladium complex. In a typical procedure, **Pd2** was used as indicated in entry 5 of Table 2. A 50 mL oven-dried Schlenk flask was charged under nitrogen with 2.0 mmol p-bromotoluene (342 mg), 2.4 mmol styrene(254 mg), 2.2 mmol anhydrous Na_2CO_3 (233 mg) and 4.0 mL DMA. The 2×10^{-5} mmol complex **Pd2** in DMA solution was added via syringe to the mixture solution, and then the reactor was kept stirred for 8 h under 150 °C. After cooling to room temperature, the reaction mixture was diluted with water and EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. The residue was separated by flash chromatography on silica gel to obtain the desired 1-methyl-4-styrylbenzene.

Acknowledgements

This work is supported by National Natural Science Foundation of China (Nos. 21476060 and U1362204).

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