

Dichloropalladium complexes ligated by
4,5-bis(arylimino)pyrenylidenes: Synthesis, characterization, and
catalytic behavior towards Heck-reaction

Kuifeng Song,^{†,‡} Shaoliang Kong,[‡] Qingbin Liu,^{*,†} Wen-Hua Sun^{*,‡} and Carl Redshaw^{*,§}

[†] Institute of chemistry and Chemical Engineering, Hebei Normal University,
Shijiazhuang 050091, China; [‡] Key laboratory of Engineering Plastics and Beijing
National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy
of Sciences, Beijing 100190, China; [§]Department of Chemistry, University of Hull, Hull,
HU6 7RX, UK

Abstract: A series of 4,5-bis(arylimino)pyrenylidenes palladium(II) chloride complexes (**C1-C4**) were synthesized and characterized by FT-IR and NMR spectroscopy, elemental analysis as well as by single crystal X-ray diffraction for the representative complexes **C1** and **C3**, which revealed a square planar geometry at the palladium centre. All palladium complexes exhibited high activity for the Heck cross-coupling reaction, which were effective when conducted in various solvents. Furthermore, the *in-situ* mixture of palladium dichloride and the ligand (**L1**) provided an effective catalytic system for the Heck-reaction.

Keywords: palladium complex; α -diimine ligand; molecular structure; Heck reaction.

1. Introduction

The arylation and vinylation of alkenes with aryl or vinyl halides, known as the Heck reaction, was discovered independently by Heck¹ and Mizoroki² in the early 1970s, and has subsequently gained popularity in carbon-carbon formation in synthetic organic syntheses promoted by palladium compounds.²⁻⁸ Moreover, palladium-mediated organic

synthesis is also extended to the reactions of Sonogashira-Hagihara^{9,10} and Suzuki-Miyaura.¹¹⁻¹⁴ In order to improve the catalytic efficiency of the palladium system, various complexes have been developed and indications into the electronic and steric influences exerted by the nature of the substituents on the ligands employed have been reported.¹⁵⁻¹⁷ Moreover, some palladium complex pre-catalysts could promote the coupling reaction of less active haloarenes or alkenes.¹⁸⁻²¹ These palladium complex pre-catalysts have often employed ligands derived from phosphine compounds,²²⁻²⁵ for which the toxicity in the application is commonly a concern. Further explorations into other potentially flexible (and efficient) ligands have suggested that palladium complex pre-catalysts bearing *N,N*-bidentate ligands such as diimine,²⁶ dipyridine²⁷⁻³² and hydrazine are useful.³³ Interestingly, reports on olefin polymerization by *N,N*-bidentate palladium complexes have been published,³⁴⁻³⁸ of which a few were also explored for their application in the Heck reaction.^{39,40} During our search for highly active pre-catalysts of α -diiminonickel complexes in ethylene polymerization,⁴¹⁻⁴⁷ a number of catalytic systems exhibited high activities and enhanced thermal stabilities.⁴⁵⁻⁴⁷ In addition, the 1,2-bis(arylimino)acenaphthylenylpalladium chlorides were found to be highly active and thermal stable in the Heck reaction.⁴⁸ More recently, a series of 4,5-bis(arylimino)pyrenylidenes was developed and successfully used as ligands for their nickel complex pre-catalysts in ethylene polymerization.⁴⁹ To broaden the scope of such compounds acting as ligands in catalysis, their palladium complexes have been prepared and were found to be highly active in promoting Heck coupling. Herein, the synthesis and characterization of the title palladium complexes and their catalytic behavior in the Heck reaction are reported.

2. Results and discussion

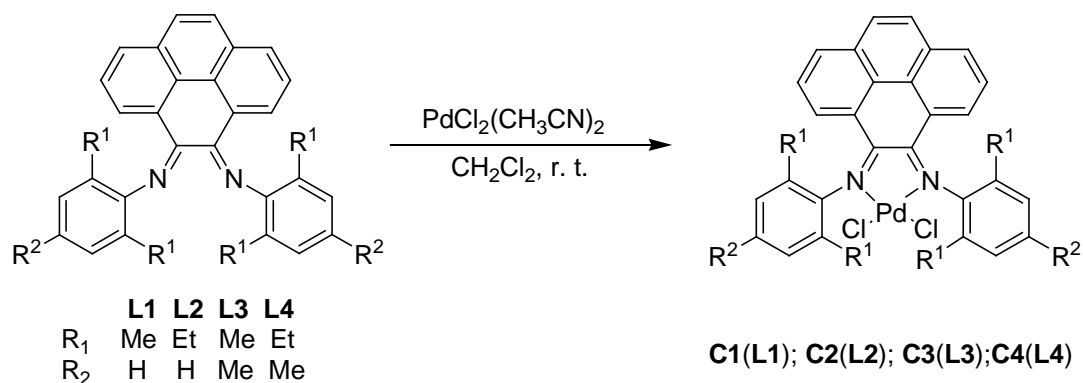
2.1. Synthesis and characterization of ligands and complexes

The 4,5-bis(arylimino)pyrenylidenes (**L1-L4**) were prepared according to the reported method.⁴⁹ α -Diiminopalladium (II) dichlorides (**C1-C4**) were obtained by the reaction of the corresponding ligands with $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ in dichloromethane at room

© 2014, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International <http://creativecommons.org/licenses/by-nc-nd/4.0/>

temperature (Scheme 1). All complexes tended to precipitate from the reaction solution, and optimized yields were obtained by adding excessive amount of Et₂O to the reaction solution. The elemental analysis data confirmed their composition as LPdCl₂, which were further identified by FT-IR and NMR spectroscopic measurements.

The stoichiometric reaction of PdCl₂(CH₃CN)₂ with the α-diimino ligands (**L1-L4**) in dichloromethane afforded the corresponding palladium chloride complexes (**C1-C4**) in reasonable isolated yields. The elemental analysis data confirmed their composition as LPdCl₂, which were further identified by FT-IR and NMR spectroscopic measurements. Due to the efficient coordination of N_{imino} to Pd, the absorption of the νC=N vibration became quite weak in the IR spectra of the palladium complexes, which is consistent with the observation of the infrared inactive C=N vibration in the palladium complexes.⁵⁰ The ¹³C NMR peaks for the C=N groups in the palladium complexes were shifted to lower field, for example δ 167.1 ppm for **C3** vs 159.1 ppm for **L3**, and were indicative of the strong coordination between the N_{imino} atom and the Pd center.⁵¹ To confirm the structures of the palladium complexes, single crystals of complexes **C1** and **C3** were obtained and the molecular structures were determined by single crystal X-ray diffraction.



Scheme 1. Synthetic procedure for the palladium complexes (**C1-C4**).

2.2. Crystal and molecular structures

Single crystals of the representative complexes **C1** and **C3** were obtained by slow diffusion of diethyl ether into dichloromethane solutions at ambient temperature. The molecular structures of each are shown in Figures 1 and 2, respectively, with selected

bond lengths and angles tabulated in Table 1. As shown in Figures 1 and 2, the complexes **C1** and **C3** possess similar structures, that is, with a square planar geometry at the palladium centre comprised of two nitrogen atoms (of the chelate) and two chloride atoms. For the complexes **C1** and **C3**, the double bonding features are illustrated by N1-C1 1.301(5) Å and N2-C14 1.310(5) Å in **C1** and 1.306(6) Å and 1.308(6) Å in **C3**, whilst the single bonds for N1-C17 and N2-C23 are 1.431(5) Å and 1.448(5) Å in **C1** and 1.439(6) Å and 1.433(6) Å in **C3**. The dihedral angles formed by the two imino-phenyl rings connected to the nitrogen atoms are 24.8 ° in **C1** and 18.6 ° in **C3**, respectively. Compared to the crystal structure of **L3**,⁴⁹ there are obvious changes of the dihedral angles involving the two imino-phenyl rings at 72.67 ° in **L3** and 18.6 ° in **C3**, the difference being attributed to more efficient coordination to the palladium center in **C3**.

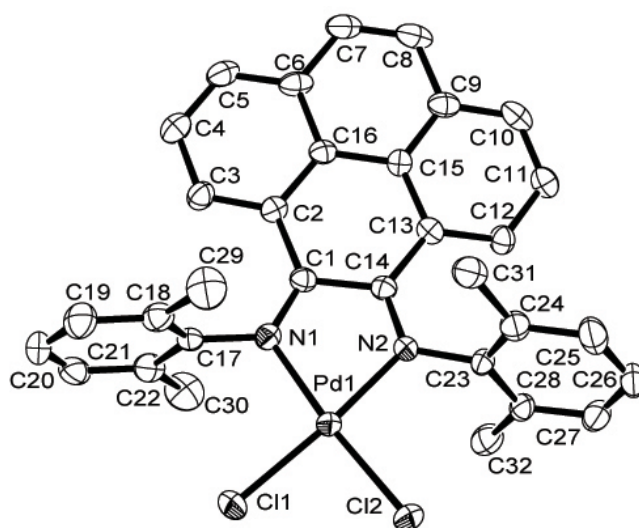


Figure 1. ORTEP drawing of **C1**. Thermal ellipsoids are shown at the 30 % probability level. Hydrogen atoms have been omitted for clarity.

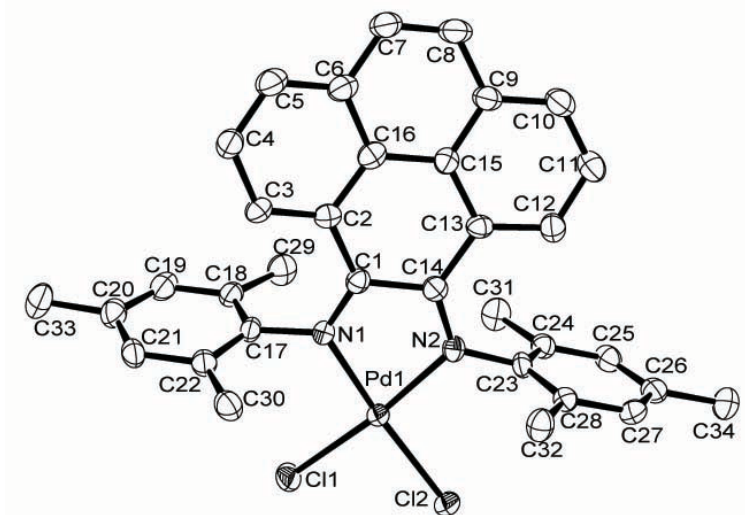


Figure 2. ORTEP drawing of **C3**. Thermal ellipsoids are shown at the 30 % probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for complexes **C1** and **C3**.

	C1	C3
Bond lengths (Å)		
Pd(1)-N(1)	2.024(3)	2.018(4)
Pd(1)-N(2)	2.003(3)	2.023(4)
Pd(1)-Cl(1)	2.2753(12)	2.2910(13)
Pd(1)-Cl(2)	2.2859(12)	2.2866(13)
N(1)-C(1)	1.301(5)	1.306(6)
N(1)-C(17)	1.431(5)	1.439(6)
N(2)-C(14)	1.310(5)	1.308(6)
N(2)-C(23)	1.448(5)	1.433(6)
Bond angles (°)		
N(1)-Pd(1)-N(2)	78.20(13)	78.18(16)
N(1)-Pd(1)-Cl(1)	96.56(10)	96.79(12)
N(2)-Pd(1)-Cl(1)	174.07(10)	172.92(12)
N(1)-Pd(1)-Cl(2)	174.28(10)	173.05(12)
N(2)-Pd(1)-Cl(2)	96.76(9)	96.54(12)
Cl(1)-Pd(1)-Cl(2)	88.60(4)	88.86(5)

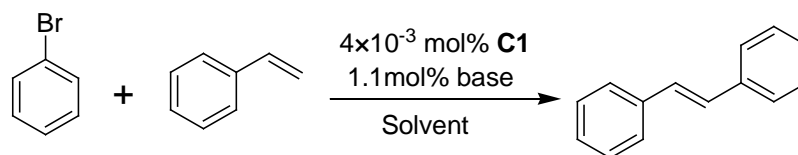
2.3. Catalytic behavior

With regard to the use of these palladium complexes as pre-catalysts in ethylene polymerization, the complexes **C1-C4** exhibited poor catalytic activities in the range $10^3 \text{ g(PE) mol}^{-1}(\text{Pd}) \text{ h}^{-1}$, with the assistance of MAO with Al/Pd ratio as 2000.

Therefore, trials of their potential in Heck coupling became the focus of our studies here.

The complex **C1** was explored for the Heck reaction of bromobenzene with styrene to ascertain the optimum conditions for producing 1,2-diphenylethene. Besides the palladium complex pre-catalyst, in principle, the catalytic behavior can also be significantly affected by the inorganic base and organic solvent used. The trial conditions were fixed at a slight excess (1.2 equivalent) of styrene and 1.1 equivalent of inorganic base to bromobenzene with a catalytic amount of **C1** ($[Pd]/[bromobenzene] = 4 \times 10^{-5}$); the conversion of bromobenzene was monitored and results are tabulated in Table 2. According to our previous experience,⁴⁸ the *N,N'*-dimethylacetamide (DMA) is a preferred solvent and this was utilized in the presence of different inorganic bases (entries 1-6, Table 2). As shown by entries 1 to 3 with the base as Na₂CO₃, it is necessary to activate the catalytic system by elevating the reaction temperature; trace amounts of bromobenzene were converted over 12 h at 120 °C (entry 1) and more than 99 % of bromobenzene was converted over 12 h at 150 °C (entry 3) without observing any remaining bromobenzene. Indeed, even 80 % of bromobenzene was converted within 6 h at 150 °C (entry 2). With such observations, it is arguable whether the palladium complex remains the same at 150 °C; the palladium complex (**C1**) in *N,N'*-dimethylacetamide (DMA) solution was refluxed for 12 h at 150 °C and was recovered in 95 % yield after being re-crystallization, confirming the unchanged nature of the palladium complex under the reaction conditions employed. No better result was observed for the catalytic system when other bases such as NaOAc (entry 4), K₂CO₃ (entry 5) and NaOH (entry 6) were employed. In addition, the solvent DMA was the most effective solvent in comparison to others including *N,N'*-dimethylformamide (DMF) (entry 7), tetrahydrofuran (THF) (entry 8), CH₃CN (entry 8) and toluene (entry 10).

Table 2. Optimization of bromobenzene and styrene using complex **C1**^a.



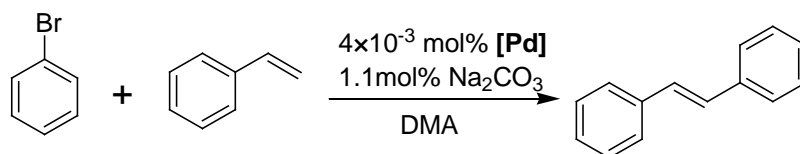
Entry	Base	Solvent	Temp.(°C)	Time(h)	Conversion (%) ^b	TOF(h ⁻¹) ^c
1	Na ₂ CO ₃	DMA	120	12	trace	-
2	Na ₂ CO ₃	DMA	150	6	80	1700
3	Na ₂ CO ₃	DMA	150	12	≥ 99	2100
4	NaOAc	DMA	150	12	51	1100
5	K ₂ CO ₃	DMA	150	12	75	1600
6	KOH	DMA	150	12	trace	-
7	Na ₂ CO ₃	DMF	150	12	90	1900
8	Na ₂ CO ₃	THF	60	12	trace	-
9	Na ₂ CO ₃	CH ₃ CN	80	12	trace	-
10	Na ₂ CO ₃	Toluene	110	12	trace	-

^a Reaction conditions: 2.0 mmol bromobenzene, 2.4 mmol styrene, 2.2 mmol base, 4.0 mL solvent.

^b Determined by GC.

^c TOF: mol bromobenzene/mol Pd h.

The optimized conditions observed for complex **C1**, 1.2 equivalent of styrene and 1.1 equivalent of Na₂CO₃ to bromobenzene with the [Pd]/[bromobenzene] as 4×10^{-5} at 150 °C for 12 h in DMA, were then employed for all palladium complexes in the Heck coupling reaction (Table 3); quantitative conversion was achieved (entry 1-4). Thus, these ligands can be said to provide suitable coordination about the palladium center to efficiently promote the Heck reaction. Even on reducing the loading of complex **C1** to half, the conversion of bromobenzene achieved was still as high as 89 % (entry 5) over 12 h and 98 % over 24 h. Moreover, when the substances and Na₂CO₃ were mixed in DMA, and then the due amounts of PdCl₂(CH₃CN)₂ and ligand **L1** were added to the solution, the conversion of bromobenzene observed was 81 % (entry 6) over 12 h. In addition, a small amount of suspended particles were also observed, possibly due to a side reaction of PdCl₂(CH₃CN)₂ and Na₂CO₃. Such studies are an indication of the stability of α -diiminopalladium (II) dichlorides (eg. **C1**) in the presence of Na₂CO₃ in the DMA solution.

Table 3. Heck reaction of bromobenzene and styrene by **C1-C4**^a.

Entry	Cat.	Mol % Pd	Conversion(%) ^b	TOF(h ⁻¹) ^c
1	C1	0.004	≥ 99	2100
2	C2	0.004	≥ 99	2100
3	C3	0.004	≥ 99	2100
4	C4	0.004	≥ 99	2100
5	C1	0.002	89	3700
6	PdCl ₂ + L1	0.004	81	1700

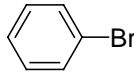
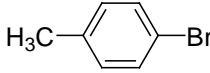
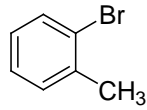
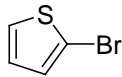
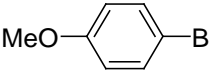
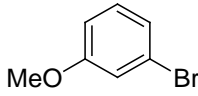
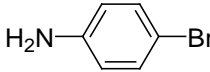
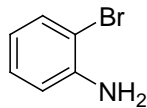
^a Reaction conditions: 2.0 mmol bromobenzene, 2.4 mmol styrene, 2.2 mmol Na₂CO₃, 4.0 mL DMA, 150 °C, 12 h.

^b Determined by GC.

^c TOF: mol bromobenzene/mol Pd h.

Given its catalytic efficacy in the Heck reaction, the complex **C1** was studied further in the coupling of a number of aryl halides and olefins. The results are summarized in Table 4. In the Heck reaction, the effect of varying the aryl bromides were investigated using an olefin as the substrate under the optimized reaction conditions (entries 1-8). From the Table 4, it could be observed that the coupling reactions achieved good activities. However, the aryl bromides showed relative lower activities than did bromobenzene, which is consistent with previous literature observations⁵² reflecting the bulk of the substituents. In addition, the position of substituents also influenced the results due to electronic effects, such as entry 2-8 in Table 4. Moreover, the lower activities observed for 2-bromothiophene, 2-bromobenzenamine and 4-bromoaniline (entries 4, 7 and 8, in Table 4) were tentatively attributed to the potential coordination between the functional groups (amine and sulfur atom) and the palladium species. All products were isolated and confirmed by ¹H and ¹³C NMR spectroscopy and by comparison with literature data.⁵³⁻⁵⁵

Table 4. Heck reaction of aryl bromides and styrene using complex **C1**.^a

Entry	ArBr	Conversion (%) ^b	TOF(h ⁻¹) ^c
1		99	2100
2		86	1800
3		75	1600
4		58	1200
5		70	1500
6		73	1500
7		57	1200
8		47	1000

^a Reaction conditions: 2.0 mmol ArBr, 2.4 mmol styrene, 2.2 mmol Na₂CO₃, 4.0 mL DMA, 150 °C, 12 h.

^b Determined by GC.

^c TOF: mol ArBr/mol Pd h.

3. Conclusion

A series of palladium complexes have been synthesized and characterized, including by single-crystal X-ray analysis; the palladium atom is coordinated by their two nitrogen atoms and two chloride atoms. All showed catalytic activity for Heck coupling between aryl bromide and olefins, exhibiting high thermal stability.

4. Experimental section

4.1. General considerations and materials

All manipulations of moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. All organic compounds used as ligands were prepared according to our previous procedure.⁴⁹ Melting points were determined using a digital electrothermal apparatus without calibration. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; δ values are given in ppm and J values in Hz. The IR spectra were obtained on a PerkinElmer FT-IR 2000 spectrophotometer by using the KBr disc in the range of 4000-400 cm^{-1} . Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Conversions were determined by CP-3800 GC.

4.2. Synthesis of palladium complexes (C1-C4)

The complexes (C1-C4) were prepared by the reaction of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with the corresponding ligands (L1-L4) in dichloromethane according to the literature method.^{48,56} Herein, only the synthesis of palladium complex C1 is described: the ligand 4,5-bis(2,6-dimethylphenylimino) pyrenylidene (L1) (0.34 mmol, 0.15 g) and $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (0.34 mmol, 0.09 g) were added to a flame-dried Schlenk flask tube, then 10 ml dichloromethane was subsequently added with rapid stirring at room temperature for 12 h. The solvent was removed *in-vacuo* and the residual solid was washed with Et_2O several times. Finally, C1 was isolated as a red powder (0.10 g, 52.7 %). Mp: > 250 °C. FT-IR (KBr, cm^{-1}): 3055, 2920, 2852, 1728, 1621, 1579, 1356, 1306, 1262, 1707, 836, 762, 705. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.13 (d, $J = 8.0$, 2H), 7.84 (s, 2H), 7.45 (d, $J = 8.0$, 2H), 7.33-7.27 (m, 6H), 7.25-7.23 (m, 2H), 2.36(s, 12H). ^{13}C NMR (400 MHz, CDCl_3 , TMS): δ 166.8, 147.4, 136.5, 132.6, 130.4, 129.5, 128.9, 128.4, 128.2, 128.1, 127.1, 124.8, 18.7. Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{N}_2\text{Pd}$: C, 62.40; H, 4.26; N, 4.55. Found: C, 62.15; H, 4.43; N, 4.22.

4.2.1. Complex C2

Using the same procedure as for the synthesis of C1, the red powder C2 was produced in 17.2 % yield. Mp: > 250 °C. FT-IR (KBr, cm^{-1}): 3058, 2964, 2869, 2361, 1623, 1583, 1460, 1356, 1302, 1223, 833, 754, 705. ^1H NMR (400 MHz, CDCl_3 , TMS):

δ 8.13 (d, $J = 8.00$, 2H), 7.86 (s, 2H), 7.47-7.43 (m, 4H), 7.37-7.30 (m, 6H), 3.12-3.07 (m, 4H), 2.59-2.54 (m, 4H), 1.28 (t, $J = 7.6$, 12H). ^{13}C NMR (400 MHz, CDCl_3 , TMS): δ 166.9, 146.6, 136.1, 133.1, 132.5, 131.1, 128.7, 128.2, 128.0, 127.3, 126.9, 125.1, 24.8, 13.1. Anal. Calcd for $\text{C}_{36}\text{H}_{34}\text{Cl}_2\text{N}_2\text{Pd}$: C, 64.34; H, 5.10; N, 4.17. Found: C, 64.18; H, 5.28; N, 4.04.

4.2.2. Complex **C3**

Using the same procedure as for the synthesis of **C1**, the red powder **C3** was produced in 54.3 % yield. Mp: > 250 °C. FT-IR (KBr, cm^{-1}): 3056, 2963, 2902, 2371, 1971, 1624, 1617, 1575, 1472, 1302, 1033, 838, 709. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.14 (d, $J = 6.8$, 2H), 7.86 (s, 2H), 7.54 (d, $J = 7.2$, 2H), 7.08 (s, 4H), 2.33 (s, 6H), 2.23 (s, 12H). ^{13}C NMR (400 MHz, CDCl_3 , TMS): δ 167.1, 145.4, 138.1, 136.0, 132.5, 130.4, 130.3, 128.2, 128.1, 127.8, 127.2, 125.0, 21.5, 18.7. Anal. Calcd for $\text{C}_{34}\text{H}_{30}\text{Cl}_2\text{N}_2\text{Pd}$: C, 63.42; H, 4.70; N, 4.35. Found: C, 63.35; H, 4.77; N, 4.13.

4.2.1. Complex **C4**

Using the same procedure as for the synthesis of **C1**, the red powder **C4** was produced in 45.1 % yield. Mp: > 250 °C. FT-IR (KBr, cm^{-1}): 3058, 2962, 2870, 2361, 2336, 1622, 1600, 1507, 1452, 1359, 1304, 835, 705. ^1H NMR (400 MHz, CDCl_3 , TMS): δ 8.13 (d, $J = 8.00$, 2H), 7.85 (s, 2H), 7.50 (d, $J = 8.4$, 2H), 7.34 (t, $J = 7.6$, 2H), 7.13 (s, 4H), 3.06-2.99 (m, 4H), 2.56-2.50 (m, 4H), 2.46 (s, 6H), 1.24 (t, $J = 7.6$, 12H). ^{13}C NMR (400MHz, CDCl_3 , TMS): δ 167.2, 144.4, 138.2, 135.8, 132.8, 132.5, 131.1, 128.1, 127.9, 127.7, 127.9, 125.2, 24.8, 21.9, 13.2. Anal. Calcd for $\text{C}_{38}\text{H}_{38}\text{Cl}_2\text{N}_2\text{Pd}$: C, 65.20; H, 5.47; N, 4.00. Found: C, 64.96; H, 5.63; N, 3.74.

4.3. Heck reaction

General procedure for the Heck reaction of bromobenzene with styrene in the presence of palladium complex, as a typical procedure, the example uses **C1** as in entry 3 of Table 2. A 50 ml oven-dried Schlenk flask was charged under nitrogen with 2.0 mmol bromobenzene (210 μl , 313 mg), 2.4 mmol styrene (280 μl , 254 mg), anhydrous 2.2 mmol Na_2CO_3 (233 mg) and 4.0 ml DMA. A 100 μl solution of 4 mmol complex **C1** in 5 ml DMA was added via syringe to the above solution, and then the reactor was sealed and placed in a 150 °C oil bath, and the mixture was stirred for 12 h. After

cooling to room temperature, the mixture was diluted with EtOAc and water. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using petroleum ether.

4.4. X-ray crystallographic studies

Single crystals of complexes **C1** and **C3** suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into dichloromethane solutions at room temperature. X-ray studies were carried out on a Rigaku Saturn724 + CCD with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K; cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.⁵⁷ Details of the X-ray structure determinations and refinements are provided in Table 5.

Table 5. Crystal data and structure refinements for **C1** and **C3**

	C1	C3
empirical formula	C ₃₂ H ₂₆ Cl ₂ N ₂ Pd	C ₃₄ H ₃₀ Cl ₂ N ₂ Pd
cryst color	black	black
Fw	615.85	643.90
T (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
cryst syst	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/c
a (Å)	13.232(3)	10.874(2)
b (Å)	11.569(2)	12.136(2)
c (Å)	19.224(4)	22.022(4)
α (deg)	90	90
β (deg)	92.42(3)	91.48(3)
γ (deg)	90	90
V (Å ³)	2940.4(10)	2905.4(10)
Z	4	4
D _{calcd} (mgm ⁻³)	1.391	1.472
μ (mm ⁻¹)	0.835	0.849
$F(000)$	1248	1312
cryst size (mm)	0.46 x 0.25 x 0.11	0.26 x 0.16 x 0.15
θ range (deg)	1.83 - 27.49	1.92 - 27.50
limiting indices	-17 \leq h \leq 16 -15 \leq k \leq 14	-12 \leq h \leq 14 -15 \leq k \leq 15

	$-24 \leq l \leq 24$	$-28 \leq l \leq 25$
no. of rflns collected	21007	20161
no. unique rflns [R(int)]	6689(0.0450)	6633(0.0566)
completeness to θ (%)	99.2 ($\theta = 27.49$)	99.3 ($\theta = 27.50$)
goodness of fit on F^2	1.052	1.056
final R indices [$I > 2\sigma(I)$]	R1 = 0.0546 wR2 = 0.1556	R1 = 0.0608 wR2 = 0.1867
R indices (all data)	R1 = 0.0606 wR2 = 0.1693	R1 = 0.0706 wR2 = 0.2047
largest diff peak and hole ($e \text{ \AA}^{-3}$)	0.852 and -0.703	0.828 and -0.932

References

- [1] Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.
- [2] Mizoroki, T. Mori, K. Ozaki, A. *Bull. Chem. Soc., Jpn* **1971**, *44*, 581.
- [3] Whitcombe, N. J. Hii, K. K. Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449.
- [4] Beletskaya, I. P. Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.
- [5] Crisp, G. T. *Chem. Soc. Rev.* **1998**, *27*, 427.
- [6] Cabri, W. Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2.
- [7] Dieck, H. A. Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133.
- [8] Dieck, H. A. Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.
- [9] Sonogashira, K. Tohda, Y. Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.
- [10] Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46.
- [11] Miyaura, N. Yamada, K. Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3340.
- [12] Miyaura, N. Suzuki, A. *J. Chem. Soc. Chem. Commun.* **1979**, 866.
- [13] Xi, C. Wu, Y. Yan, X. *J. Organomet. Chem.* **2008**, *693*, 3842.
- [14] Liu, Y. Wu, Y. Xi, C. *Appl. Organomet. Chem.* **2009**, *23*, 329.
- [15] Knowles, J. Whiting, P. A. *Org. Biomol. Chem.* **2007**, *5*, 31.
- [16] Zhang, S. Shi, L. Ding, Y. *J. Am. Chem. Soc.* **2011**, *133*, 20218.
- [17] Shibasaki, M. Vogl, E. M. Ohshima, T. *Adv. Synth. Catal.* **2004**, *346*, 1533.
- [18] Spencer, A. *J. Organomet. Chem.* **1983**, *258*, 101.
- [19] Herrmann, W. A. Brossmer, C. Ófele, K. Reisinger, C. T. Priermeier, T. Beller, M. Fischer, H. *Angew. Chem., Int. Edn Engl.* **1995**, *34*, 1844.
- [20] Zapf, A. Beller, M. *Chem. Eur. J.* **2001**, *13*, 2908.
- [21] Berthiol, F. Doucet, H. Santelli, M. *Tetrahedron Lett.* **2003**, *44*, 1221.
- [22] Littke, A. F. Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10;
- [23] Littke, A. F. Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989.
- [24] Ehrentraut, A. Zapf, A. Beller, M. *Synlett* **2000**, *11*, 1589.
- [25] Shaughnessy, K. H. Kim, P. Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 2677.
- [26] Grasa, G. A. Singh, R. Stevens, E. D. Nolan, S. P. *J. Organomet. Chem.* **2003**, *687*, 269.

- [27] Cabri, W. Candiani, I. Bedeschi, A. Santi, R. *J. Org. Chem.* **1993**, *58*, 7421.
- [28] Buchmeiser, M. R. Wurst, K. *J. Am. Chem. Soc.* **1999**, *121*, 11101.
- [29] Silberg, J. Schareina, T. Kempe, R. Wurst, K. Buchmeiser, M. R. *J. Organomet. Chem.* **2001**, *622*, 6.
- [30] Buchmeiser, M. R. Schareina, T. Kempe, R. Wurst, K. *J. Organomet. Chem.* **2001**, *634*, 39.
- [31] Kawano, T. Shinomaru, T. Ueda, I. *Org. Lett.* **2002**, *4*, 2545.
- [32] Nájera, C. Gil-Moltó, J. Karlström, S. Falvello, L. R. *Org. Lett.* **2003**, *5*, 1451.
- [33] Mino, T. Shirae, Y. Sasai, Y. Sakamoto, M. Fujita, T. *J. Org. Chem.* **2006**, *71*, 6834.
- [34] L.K. Johnson, C.M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **117** (1995) 6414;
- [35] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* **118** (1996) 11664;
- [36] D.P. Gates, S.A. Svejda, E. Onate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, *Macromolecules* **33** (2000) 2320.
- [37] Chen, R. Mapolie, S. F. *J. Mol. Catal. A: Chem.* **2003**, *193*, 33.
- [38] Zhang, W. Sun, W.-H. Wu, B. Zhang, S. Ma, H. Li, Y. Chen, J. Hao, P. *J. Organomet. Chem.* **2006**, *691*, 4759.
- [39] Pelagatti, P. Carcelli, M. Costa, M. Lanelli, S. Pelizzi, C. Rogolino, D. *J. Mol. Chem. A: Chem.* **2005**, *226*, 107.
- [40] Clark, J. H. Macquarrie, D. J. Mubofu, E. B. *Green Chem.* **2000**, *2*, 53.
- [41] Yu, J. Liu, H. Zhang, W. Hao, X. Sun, W.-H. *Chem. Comm.* **2011**, *47*, 3257.
- [42] Zhao, W. Song, S. Yang, W. Liu, H. Hao, X. C. Redshaw, Sun, W.-H. *Polymer* **2012**, *53*, 130.
- [43] Yu, J. Huang, W. Wang, L. Redshaw, C. Sun, W.-H. *Dalton Trans.* **2011**, *40*, 10209.
- [44] Lai, J. Zhao, W. Yang, W. Redshaw, C. Liang, T. Liu, Y. Sun, W.-H. *Polym. Chem.* **2012**, *3*, 787.
- [45] Hou, X. Cai, Z. Chen, X. Wang, L. Redshaw, C. Sun, W.-H. *Dalton Trans.* **2012**, *41*, 1617.
- [46] Liu, H. Zhao, W. Hao, X. Redshaw, C. Huang, W. Sun, W.-H. *Organometallics*

2011, 30, 2418.

[47] Liu, H. Zhao, W. Yu, J. Yang, W. Hao, X. Redshaw, C. Chen, L. Sun, W.-H. *Catal. Sci. Tech.* **2012**, 2, 415.

[48] Ban, Q. Zhang, J. Liang, T. Redshaw, C. Sun, W.-H. *J. Organomet. Chem.* **2012**, 713, 151.

[49] Song, K. Yang, W. Li, B. Liu, Q. Redshaw, C. Li, Y. Sun, W.-H. *Dalton Trans.*
DOI: 10.1039/b000000x

[50] Lavery, A. Nelson, S. M. *J. Chem. Soc. Dalton Trans.* **1984**, 4, 615.

[51] Chen, R. Bacsa, J. Mapolie, S. F. *Polyhedron* **2003**, 22, 2855.

[52] Yao, Q.W. Kinney, E. P. Zheng, C. *Org. Lett.* **2004**, 6, 2997.

[53] Wang, Z. Ding, Q. He, X. Wu, J. *Org. Biomol. Chem.* **2009**, 7, 863.

[54] Sawant, D. Wagh, Y. Bhatte, K. Panda, A. Bhanage, B. *Tetrahedron Lett.* **2011**, 52, 2390.

[55] Kantam, M. L. Reddy, P. V. Srinivas, P. Bhargava, S. *Tetrahedron Lett.* **2011**, 52, 4490.

[56] Overman, L. E. Ricca, D. J. Tran, V. D. *J. Am. Chem. Soc.* **1993**, 115, 2042.

[57] G.M. Sheldrick, SHELXTL-97, Program for the Refinement of Crystal structures, University of Göttingen, Germany, 1997.