FULL PAPER

Dalton
www.rsc.org/dalton

Palladacyclic complexes bearing CNN-type ligands as catalysts in the Heck reaction

Chi-Tien Chen,* Yi-Sen Chan, Yi-Ren Tzeng and Ming-Tsz Chen
Department of Chemistry, National Chung-Hsing University, Taichung 402, Taiwan, Republic of China. E-mail: ctchen@mail.nchu.edu.tw

Received 31st March 2004, Accepted 9th July 2004
First published as an Advance Article on the web 3rd August 2004

Preparations of novel unsymmetrical, tridentate nitrogen ligand precursors, PhN=C(CMe_2)(NPh)C=N$(CH_2)_2NMe_2$ (**1**) and PhN=C(CMe_2)(NPh)C=N(CH_2)Py (**2**), are described. Treatment of **1** with 1 molar equiv. (COD)$PdCl_2$ in the presence of NEt_3 or with 1 molar equiv. $Pd(OAc)_2$ affords orthometallated palladium(II) complexes, [PhN=C(CMe_2)-(N-η^1-Ph)C=N$(CH_2)_2NMe_2$]PdX (X = Cl (**3**); X = OAc (**4**)), respectively. Compound **3** can be yielded *via* the reaction of **4** with an excess of LiCl in methanol. Treatment of **2** with 1 molar equiv. of (COD)$PdCl_2$, $Pd(OAc)_2$ or $Pd(TFA)_2$ affords orthometallated palladium(II) complexes, [PhN=C(CMe_2)(N-η^1-Ph)C=NCH_2Py]PdX (X = Cl (**5**); X = OAc (**6**); X = TFA (**7**)), respectively. The crystal and molecular structures are reported for compounds **2**, **3**, **5** and **6**. The application of these novel palladacyclic complexes to the Heck reaction with aryl halide substrates was examined.

Introduction

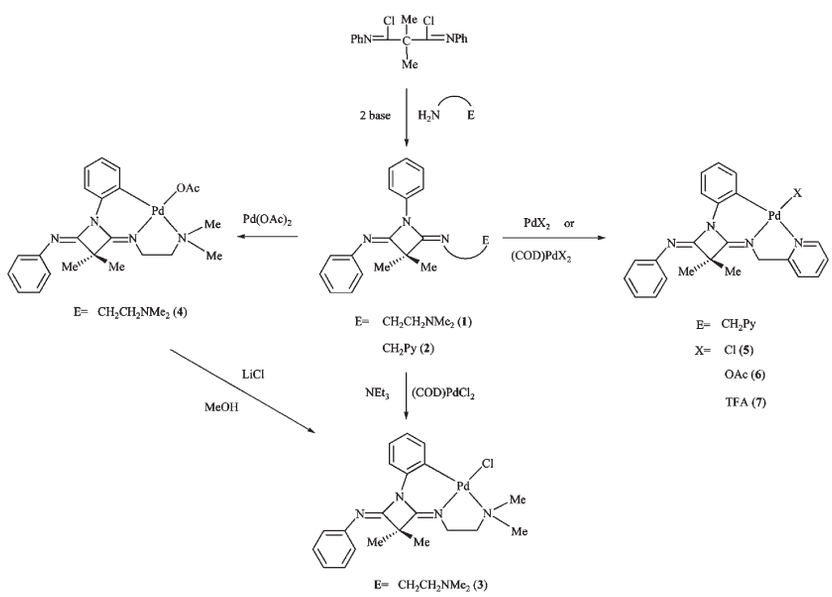
Transition metal-catalysed coupling reactions are the most powerful and versatile methods in organic chemistry and have been extensively studied since they are popular for the formation of various coupling products.[1] Palladium complexes seem to be active and suitable in preparing the target compounds due to their easy preparation and commercial availability. Catalysts can be either prepared *in situ* from commercially available palladium compounds and additives, or from the isolated palladacycles.[2–16] Among these complexes, palladacycles bearing metallated carbon atoms and dative group(s) are among the most active catalyst precursors for the promotion of such reactions.

Some nitrogen-containing palladacycles capable of mediating C–C coupling reactions have been reported. These complexes usually form dinuclear species with bridged ligands or mononuclear species in the presence of neutral dative group.[6–17] Except for pincer complexes,[7,18] unusual mononuclear palladacycles bearing amine or/and imine tridentate ligands have been reported.[19–21] We report herein the synthesis and characterisation of novel palladacycles supported by unsymmetrical CNN-type ligands in mononuclear species. Their catalytic activities toward the Heck reaction are investigated.

Results and discussion

Syntheses and characterisation of ligand precursors and palladacycles

Ligand precursors **1** and **2** were prepared from the reaction of 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride with 1.1 equivalents of *N*,*N*-dimethylethyleneamine or 2-aminomethylpyridine in the presence of 2.5 equivalents of NEt_3. A summary of syntheses and proposed structures is shown in Scheme 1. The spectroscopic data of **1** and **2** indicate two phenyl rings in each compound having different environments. The X-ray structure of **2** features a diimine compound bearing a four-membered heterocycle. One phenyl ring attaches to the nitrogen atom on the heterocycle whereas the other one attaches to one nitrogen atom of the imine groups. The molecular structure is shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. The C(1)–N(1) (1.253(2) Å) and C(3)–N(3) (1.257(2) Å) bond lengths are consistent with significant double bond character and the bond angles around imino C and N atoms are indicative of sp^2 centres. A plausible mechanism for the formation of both ligand precursors is proposed in Scheme 2. The first step is the elimination of one equivalent of HCl by base, followed by the shift of a proton from the amine group to the nitrogen atom on the imine group. The cyclisation is then achieved



Scheme 1

DOI: 10.1039/b404798b

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

N(1)–C(1)	1.253(2)	N(3)–C(3)	1.257(2)
N(1)–C(6)	1.459(2)	N(2)–C(12)	1.4152(18)
N(3)–C(18)	1.428(2)	N(2)–C(3)	1.4018(19)
N(2)–C(1)	1.4139(19)	N(4)–C(7)	1.336(2)
N(4)–C(11)	1.338(2)	C(1)–C(2)	1.541(2)
C(2)–C(3)	1.534(2)	C(12)–C(17)	1.385(2)
C(16)–C(17)	1.372(2)		
C(1)–N(1)–C(6)	117.80(14)	C(3)–N(3)–C(18)	118.70(13)
C(3)–N(2)–C(1)	93.39(11)	C(3)–N(2)–C(12)	134.20(13)
C(1)–N(2)–C(12)	132.18(13)	N(1)–C(1)–N(2)	128.37(14)
N(1)–C(1)–C(2)	140.47(15)	N(2)–C(1)–C(2)	91.14(11)
N(3)–C(3)–N(2)	128.76(14)	N(3)–C(3)–C(2)	139.36(14)
N(2)–C(3)–C(2)	91.87(12)	C(3)–C(2)–C(1)	83.56(11)
N(1)–C(6)–C(7)	112.27(14)		

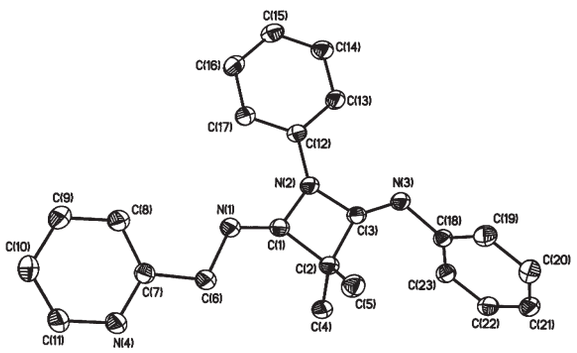
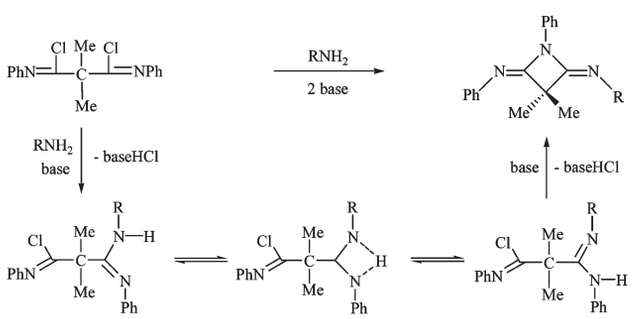


Fig. 1 Molecular structure of compound **2**. Hydrogen atoms on the carbon atoms are omitted for clarity.



Scheme 2 Plausible mechanism for preparing the ligand precursors.

by removal of the other equivalent of HCl with another equivalent of base to form the target compound.

Treatment of **1** with 1 molar equivalent of $(COD)PdCl_2$ in the presence of NEt_3 at room temperature yields complex **3** as a pale-yellow solid. One more tertiary carbon was found in the region of the phenyl ring based on the $^{13}C\{^1H\}$ NMR spectrum which indicates a metallated carbon atom being created during the reaction. Complex **3** can be synthesized by the reaction of **4** with an excess of lithium chloride in methanol at room temperature.[20] Suitable crystals of **3** for structural determination were obtained from CH_2Cl_2–hexane solution. The molecular structure is shown in Fig. 2 and selected bond lengths and angles are listed in Table 2. The bond angles (from 81.86(9) to 94.39(8)°) around the Pd metal centres indicate a complex having a slightly distorted square planar geometry, in which the palladium metal centre is coordinated with one imine nitrogen atom, one amine nitrogen atom, one metallated carbon atom, and one chloride atom. The small N(1)–Pd–N(2) angle (81.86(9)°) results from the relatively small bite size of the pendant group. The bond length of Pd–$C_{metallated}$ (2.025(3) Å) is within those (1.954(3)–2.104(4) Å) found in palladacycles with metallated carbon.[15,16,20–27] Similarly, the bond length of Pd–$N_{C=N}$ (2.002(2) Å) is within those (1.960(6)–2.122(3) Å) found in palladacycles[15,16,20–22,25] and those (2.0183(10)–2.077(12) Å) found in palladium imino complexes.[28–32] The bond length of Pd–N_{amine} (2.195(3) Å) is close to those (2.059(3)–2.196(4) Å) found in palladacycles.[14–16,21,23,24,26,27] The bond length of Pd–Cl (2.3181(8) Å) is within those (2.153(8)–2.4583(5) Å) found in palladacycles[14–16,21,22,25–27] and those (2.2703(16)–2.301(4) Å) found in palladium imino complexes.[29–32] Disorder is found for the carbon atoms C7 and C7′ on the pendant group. Treatment of **1** with 1 molar equivalent of $Pd(OAc)_2$ at room temperature affords complex **4** as a white solid. The spectroscopic and elemental analysis data are consistent with a structure similar to **3** with a difference of coordinating OAc instead of Cl.

Table 2 Selected bond lengths (Å) and angles (°) for **3**

Pd–N(1)	2.002(2)	Pd–N(2)	2.195(3)
Pd–C(15)	2.025(3)	Pd–Cl	2.3181(8)
N(1)–Pd–C(15)	93.20(104)	N(1)–Pd–N(2)	81.86(9)
C(15)–Pd–Cl	94.39(8)	N(2)–Pd–Cl	90.81(7)
C(15)–Pd–N(2)	174.43(9)	N(1)–Pd–Cl	170.20(7)

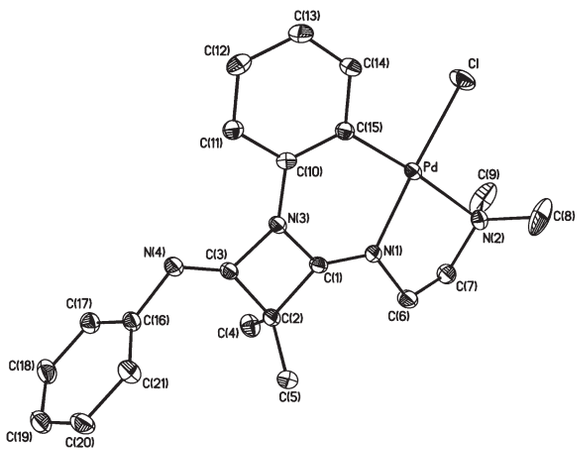


Fig. 2 Molecular structure of complex **3**. Hydrogen atoms on the carbon atoms omitted for clarity.

Reactions of **2** with 1 molar equiv. of $(COD)PdCl_2$, $Pd(OAc)_2$ or $Pd(TFA)_2$ afford orthometallated palladium(II) complexes, $[PhN{=}C(CMe_2)(N\text{-}\eta^1\text{-}Ph)C{=}NCH_2Py]PdX$ (X = Cl (**5**); X = OAc (**6**); X = TFA (**7**)), respectively. Similar to compound **3**, an additional tertiary carbon corresponding to metallated carbon was found in the $^{13}C\{^1H\}$ NMR spectrum of each complex. Suitable crystals of **5** and **6** for structural determination were obtained from CH_2Cl_2–hexane solution. The molecular structures of **5** and **6** are shown in Figs. 3 and 4, and selected bond lengths and angles are listed in Tables 3 and 4. Basically, compound **5** is quite similar to compound **3** with a different pendant group CH_2Py instead of $CH_2CH_2NMe_2$ for **3**. The palladium metal centre is coordinated with a similar mode as in **3** except for one nitrogen atom from pyridine instead of one amine nitrogen atom. Compound **6** is quite similar to compound **5** but with coordinated OAc instead of Cl for **5**. Bond lengths and bond angles are similar to those discussed above. The bond lengths of Pd–N_{Py} (2.1244(17) Å for **5** and 2.101(2) Å for **6**) are slightly longer than those (2.009(3)–2.037(2) Å) found in the literature.[30–34] The bond length of Pd–O_{OAc} (2.0558(18) Å) in **6** is comparable to those (2.027(9)–2.090(1) Å) found in the literature.[26–28]

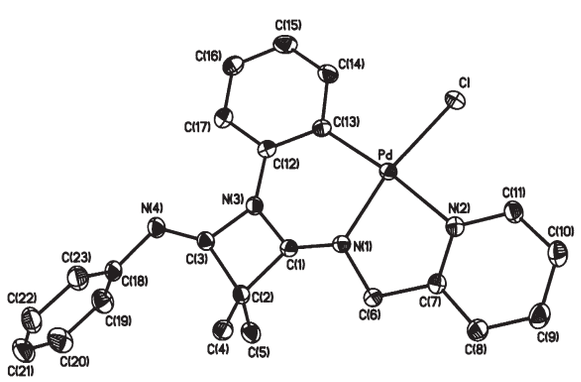


Fig. 3 Molecular structure of complex **5**. Hydrogen atoms on the carbon atoms are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for **5**

Pd–N(1)	1.9975(16)	Pd–N(2)	2.1244(17)
Pd–C(13)	2.019(2)	Pd–Cl	2.3334(6)
N(1)–Pd–C(13)	93.77(8)	N(1)–Pd–N(2)	79.89(7)
C(13)–Pd–Cl	94.95(6)	N(2)–Pd–Cl	91.68(5)
C(13)–Pd–N(2)	172.94(7)	N(1)–Pd–Cl	169.45(5)

Table 4 Selected bond lengths (Å) and angles (°) for **6**

Pd(1)–N(3)	1.988(2)	Pd(1)–N(4)	2.101(2)
Pd(1)–C(17)	1.995(3)	Pd(1)–O(1)	2.0558(18)
N(3)–Pd(1)–C(17)	94.51(10)	N(3)–Pd(1)–N(4)	80.06(9)
C(17)–Pd(1)–O(1)	90.69(9)	N(4)–Pd(1)–O(1)	94.70(8)
C(17)–Pd(1)–N(4)	174.25(8)	N(3)–Pd(1)–O(1)	174.69(7)

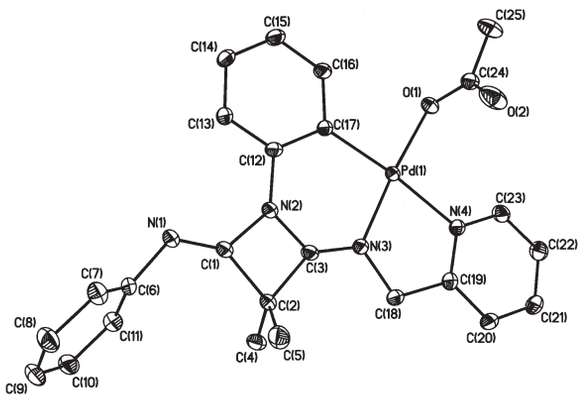
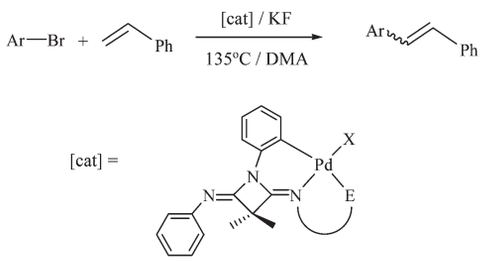


Fig. 4 Molecular structure of complex **6**. Hydrogen atoms on the carbon atoms are omitted for clarity.

Catalytic studies

The molecular structures of the palladacycles discussed above exhibit similar structural features to the nitrogen-based catalysts used for the carbon–carbon coupling reactions. Those results encouraged us to examine the activity of those complexes toward the Heck reaction (Scheme 3).



Scheme 3 Application of the palladacycles in the Heck reaction.

In order to investigate the catalytic activity, optimised conditions using the coupling of 4-bromoacetophenone with styrene catalysed by **5** were conducted. Selected results are listed in Table 5. The rate of the Heck reaction is solvent-dependent with *N*,*N*-dimethylacetamide (DMA) being the choice after several trials with THF, toluene and DMA (entries 3–11). For the choice of a base, we surveyed K_3PO_4, Cs_2CO_3 and KF (entries 5, 8 and 11). Finally, we found that use of 1 mol% **5** and 1.5 equiv. KF in DMA at 135 °C leads to the best conversion within 3 h (entry 11). Excellent conversion is observed with the same catalyst amount using 4-bromobenzaldehyde under the optimised conditions (entry 12). The same conditions were applied to examine the catalytic activity of **3**, **4**, **6** and **7**. The catalytic activities of **3** and **4**, however, showed lower conversions. The poor activities exhibited by **3** and **4** indicate that the pendant group with N_{py} is better than that with N_{amine} in this system. Excellent conversions are observed within 2 h for **6** and 1.5 h for **7** (entries 13 and 15). Enhancements in activity are also observed using 4-bromobenzaldehyde instead of 4-bromoacetophenone in both cases (entries 14 and 16). When the catalytic activities are compared, it can be seen that they fall in the order of **7** > **6** > **5**. This could result from the leaving nature of the anionic co-ligand, X. Due to the better activity and solubility of **7**, lower catalyst concentrations were investigated with **7** using catalyst/substrate ratios from 10^{-3} to 10^{-5} (entries 17–20). The reaction gave degrees of conversion to 98% within 24 h using a catalyst/substrate ratio of 10^{-5}. Compared with some $C_{metallated}$–N_{py} palladacycles,[11] $C_{metallated}$–N_{amine} palladacycles,[6,17] $C_{metallated}$–N_{imine} palladacycles,[6] $C_{metallated}$–N_{imine}–N_{imine} palladacycles,[20] diimino palladium complexes,[28] and dipyridyl palladium complexes,[35,36] the new CNN-type palladacycles show comparable catalytic activities toward the Heck coupling reaction. In some cases they exhibit even higher activities than for the others.

In summary, novel palladacycles, phosphine-free imine complexes, have been prepared and demonstrated catalytic activities toward the Heck C–C coupling reaction. Their catalytic activities are determined not only by the coordination ability of the pendant groups but also by the leaving nature of the anionic co-ligands. Under optimised conditions, complex **7** shows comparable activity to those of existing nitrogen-based palladacycle systems. Preliminary studies on fine-tuning of ligands and further application of metal complexes to the catalytic reactions are currently being undertaken.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Gemini-200 (200 MHz), Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by a Elementar Vario ELIV instrument.

Aniline (Acros), dimethylmalonyl dichloride (TCI), PCl_5 (RDH), 2-aminomethylpyridine (Acros), $Pd(OAc)_2$, $Pd(TFA)_2$ and $(COD)PdCl_2$ (Strem) were used as supplied. NEt_3 and *N*,*N*-dimethylethyleneamine were dried over CaH_2 and distilled before use.

Preparations

2,2-Dimethyl-*N*,*N*′-diphenylmalonamide. To a solution of aniline (2.6 ml, 29 mmol) in 60 ml diethyl ether, a dilute solution of dimethylmalonyl dichloride (0.9 ml, 7 mmol) in 65 ml diethyl ether was added at 0 °C. The reaction mixture was allowed to warm to room temperature. After 4 h of stirring, the white suspension was filtered. The residue was washed with 60 ml of water followed by 20 ml diethyl ether to afford a white solid. Yield, 1.89 g, 96%. ^{1}H NMR (400 MHz): δ 1.70 (s, CH_3, 6H), 7.14 (m, *p*-Ph, 2H), 7.34 (m, *m*-Ph, 4H), 7.54 (m, *o*-Ph, 4H), 8.48 (s, N*H*, 2H). ^{13}C{^{1}H} NMR (150 MHz): δ 24.2 (s, C(CH_3)$_2$), 50.8 (s, *tert*-*C*(CH_3)$_2$), 120.3, 124.8, 129.0 (*o*, *m*, *p*-C_6H_5), 137.3 (s, C_{ipso}–C_6H_5), 171.5 (s, *C*=O). Anal. Calc. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.59; H, 6.27; N, 9.82%.

2,2-Dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride. A mixture of 2,2-dimethyl-*N*,*N*′-diphenylmalonamide (5.82 g, 20.6 mmol) and PCl_5 (9.0 g, 43.3 mmol) in 100 ml toluene was stirred and refluxed for 3 h. The mixture was filtered when hot, and the volatiles were removed under reduced pressure to afford a yellow solid. Yield, 6.48 g, 99%. ^{1}H NMR (400 MHz): δ 1.81 (s, CH_3, 6H), 6.92 (m, *o*-Ph, 4H), 7.19 (m, *p*-Ph, 2H), 7.38 (m, *m*-Ph, 4H). ^{13}C{^{1}H} NMR (150 MHz): δ 25.3 (s, C(CH_3)$_2$), 59.7 (s, *tert*-*C*(CH_3)$_2$), 119.8, 125.1, 128.9 (*o*, *m*, *p*-C_6H_5), 146.8, 148.5 (C_{ipso}–C_6H_5 and *C*=N). Anal. Calc. For $C_{17}H_{16}N_2Cl_2$: C, 63.96; H, 5.05; N, 8.78. Found: C, 63.91; H, 4.78; N, 8.33%.

PhN=C(CMe$_2$)(NPh)C=N(CH$_2$)$_2$NMe$_2$ (1). To a flask containing 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride (1.7 g, 5.3 mmol) and NEt_3 (1.4 g, 13.3 mmol) in 20 ml $CHCl_3$, was added a dilute solution of *N*,*N*-dimethylethyleneamine (0.5 g, 5.9 mmol)

Table 5 Heck coupling reaction catalysed by new palladium complexes[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] (mol%)	*T*/°C	*t*/h	Conversion[b] (%)	Yield[c] (%)
1	**3**	4-Bromoacetophenone	KF	DMA	1	135	3	82	75
2	**4**	4-Bromoacetophenone	KF	DMA	1	135	3	52	
3	**5**	4-Bromoacetophenone	Cs_2CO_3	THF	1	70	3	4	—
4	**5**	4-Bromoacetophenone	Cs_2CO_3	Toluene	1	110	3	18	—
5	**5**	4-Bromoacetophenone	Cs_2CO_3	DMA	1	135	3	65	53
6	**5**	4-Bromoacetophenone	K_3PO_4	THF	1	70	3	14	—
7	**5**	4-Bromoacetophenone	K_3PO_4	Toluene	1	110	3	7	—
8	**5**	4-Bromoacetophenone	K_3PO_4	DMA	1	135	3	93	82
9	**5**	4-Bromoacetophenone	KF	THF	1	70	3	3	—
10	**5**	4-Bromoacetophenone	KF	Toluene	1	110	3	6	—
11	**5**	4-Bromoacetophenone	KF	DMA	1	135	3	99	89
12	**5**	4-Bromobenzaldehyde	KF	DMA	1	135	3	96	87
13	**6**	4-Bromoacetophenone	KF	DMA	1	135	2	95	87
14	**6**	4-Bromobenzaldehyde	KF	DMA	1	135	2	93	84
15	**7**	4-Bromoacetophenone	KF	DMA	1	135	1.5	99	91
16	**7**	4-Bromobenzaldehyde	KF	DMA	1	135	1.5	98	88
17	**7**	4-Bromoacetophenone	KF	DMA	0.1	135	5	97	87
18	**7**	4-Bromoacetophenone	KF	DMA	0.01	135	8	99	90
19	**7**	4-Bromoacetophenone	KF	DMA	0.005	135	20	97	90
20	**7**	4-Bromoacetophenone	KF	DMA	0.001	135	24	98	88

[a] Reaction conditions: 1 mmol aryl halide, 1.3 mmol styrene, 1.5 mmol base, 2 ml solvent. [b] Determined by ^{1}H NMR. [c] isolated yield. (average of two experiments).

in 10 ml $CHCl_3$. After 24 h of stirring, the volatiles were pumped off, and the residue was extracted with 30 ml hot hexane to afford a pale-yellow solid. Yield, 0.88 g, 50%. ^{1}H NMR (400 MHz): δ 1.46 (s, C(CH_3)$_2$, 6H), 2.32 (s, N(CH_3)$_2$, 6H), 2.59 (m, CH_2, 2H), 3.54 (m, CH_2, 2H), 6.93 (d, *o*-Ph, 2H, $^3J_{HH}$ = 7.6 Hz), 7.07 (t, *p*-Ph, 1H, $^3J_{HH}$ = 7.2 Hz), 7.13 (t, *p*-Ph, 1H, $^3J_{HH}$ = 7.2 Hz), 7.29 (t, *m*-Ph, 2H, $^3J_{HH}$ = 7.6 Hz), 7.37 (t, *m*-Ph, 2H, $^3J_{HH}$ = 8.0 Hz), 8.27 (d, *o*-Ph, 2H, $^3J_{HH}$ = 8.0 Hz). ^{13}C{^{1}H} NMR (150 MHz): δ 21.5 (s, C(CH_3)$_2$), 45.9 (s, N(CH_3)$_2$), 47.1 (s, (CH_2)$_2$), 57.9 (s, *tert*-C(CH$_3$)$_2$), 61.0 (s, (CH_2)$_2$), 119.2, 121.4, 123.2, 124.2, 128.54, 128.56 (*o*, *m*, *p*-C_6H_5), 137.2, 146.8, 158.0, 158.1 (two C_{ipso}–C_6H_5 and two C=N). Anal. Calc. for $C_{21}H_{26}N_4$: C, 75.41; H, 7.84; N, 16.75. Found: C, 75.28; H, 7.43; N, 16.44%.

PhN=C(CMe$_2$)(NPh)C=N(CH$_2$)Py (2). To a flask containing 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride (0.64 g, 2 mmol) and NEt_3 (0.51 g, 5.0 mmol) in 20 ml $CHCl_3$, was added a dilute solution of 2-aminomethylpyridine (0.23 g, 2.2 mmol) in 10 ml $CHCl_3$. After 20 h of stirring, the volatiles were pumped off, and the residue was extracted with 30 ml hot hexane to afford a pale-yellow solid. Yield, 0.37 g, 52%. ^{1}H NMR (600 MHz): δ 1.47 (s, C(CH_3)$_2$, 6H), 4.81 (s, CH_2, 2H), 6.94 (d, o-Ph, 2H, $^3J_{HH}$ = 7.2 Hz), 7.08 (t, *p*-Ph or 3- or 4-Py, 1H, $^3J_{HH}$ = 7.2 Hz), 7.17 and 7.18 (two overlapping t, *p*-Ph or 3- or 4-Py, 2H, $^3J_{HH}$ = 7.2 Hz), 7.29 (t, *m*-Ph, 2H, $^3J_{HH}$ = 7.2 Hz), 7.41 (t, *m*-Ph, 2H, $^3J_{HH}$ = 8.4 Hz), 7.59 (d, Py, 1H, $^3J_{HH}$ = 7.8 Hz), 7.72 (m, *p*-Ph or 3- or 4-Py, 1H), 8.39 (d, *o*-Ph, 2H, $^3J_{HH}$ = 7.8 Hz), 8.53 (m, Py, 1H). ^{13}C{^{1}H} NMR (150 MHz): δ 21.5 (s, C(CH_3)$_2$), 53.8 (s, CH_2), 58.1 (s, *tert*-C(CH$_3$)$_2$), 119.3, 121.1, 121.4, 121.8, 123.4, 124.5, 128.7, 136.8, 148.9 (CH–C_6H_5 and CH–Py), 137.4, 146.7, 158.0, 159.6, 160.2 (two C_{ipso}–C_6H_5, one C_{ipso}–Py and two C=N). Anal. Calc. for $C_{23}H_{22}N_4$: C, 77.94; H, 6.26; N, 15.81. Found: C, 77.63; H, 6.52; N, 15.60%.

[PhN=C(CMe$_2$)(N-η^1-C$_6$H$_4$)C=N(CH$_2$)$_2$NMe$_2$]PdCl (3). ***Method 1.*** To a flask containing (COD)$PdCl_2$ (0.35 g, 1.20 mmol) in 20 ml CH_2Cl_2, a solution of **1** (0.41 g, 0.56 mmol) and NEt_3 (0.2 ml, 1.4 mmol) in 10 ml CH_2Cl_2 was added at room temperature. After 48 h of stirring, the dark-green solution was washed twice with 20 ml water. The volatiles were removed from the organic layer and the residue was washed twice with 20 ml hexane to afford a pale-yellow solid. Yield, 0.17 g, 30%.

Method 2. To a flask containing LiCl (0.033 g, 0.77 mmol), a solution of **4** (0.076 g, 0.15 mmol) in 20 ml MeOH was added at room temperature. After 30 min of stirring, the suspension was filtered to afford a pale-yellow solid. The crude product was purified from CH_2Cl_2–hexane solution to afford a crystalline solid. Yield, 0.064 g, 88%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.49 (s, C(CH_3)$_2$, 6H), 2.64 (t, CH_2, 2H, $^3J_{HH}$ = 5.4 Hz), 2.75 (s, N(CH_3)$_2$, 6H), 3.71 (t, CH_2, 2H, $^3J_{HH}$ = 6.0 Hz), 6.95 (d, 2H, $^3J_{HH}$ = 7.8 Hz), 6.98 (t, 1H, $^3J_{HH}$ = 6.6 Hz), 7.12 (t, 1H, $^3J_{HH}$ = 7.2 Hz), 7.13 (t, 1H, $^3J_{HH}$ = 7.2 Hz), 7.33 (t, 2H, $^3J_{HH}$ = 7.2 Hz), 8.08 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 8.44 (d, 1H, $^3J_{HH}$ = 8.4 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 20.9 (s, C(CH_3)$_2$), 48.4 (s, N(CH_3)$_2$), 48.9 (s, CH_2), 56.8 (s, *tert*-C(CH$_3$)$_2$), 62.2 (s, CH_2), 116.9, 120.8, 124.1, 124.7, 125.1, 129.0, 141.2 (seven CH–C_6H_5), 125.9, 131.0, 145.6, 153.5, 157.8 (one η^1-Ph, two C_{ipso}–C_6H_5 and two C=N). Anal. Calc. for $C_{21}H_{25}ClN_4Pd$: C, 53.06; H, 5.30; N, 11.79. Found: C, 53.08; H, 5.17; N, 11.79%.

[PhN=C(CMe$_2$)(N-η^1-C$_6$H$_4$)C=N(CH$_2$)$_2$NMe$_2$]Pd(OAc) (4). To a flask containing $Pd(OAc)_2$ (0.17 g, 0.75 mmol) and **1** (0.31 g, 0.93 mmol), 20 ml THF was added at room temperature. After 16 h of stirring, the yellow suspension was filtered to afford a white solid. Yield, 0.24 g, 64%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.46 (s, C(CH_3)$_2$, 6H), 2.19 (s, OC(O)CH_3, 3H), 2.68 (t, CH_2, 2H, $^3J_{HH}$ = 6 Hz), 2.72 (s, N(CH_3)$_2$, 6H), 3.69 (t, CH_2, 2H, $^3J_{HH}$ = 6 Hz), 6.93 (m, 2H), 6.99 (m, 1H), 7.11 (m, 1H), 7.12 (m, 1H), 7.33 (m, 2H), 7.50 (m, 1H), 8.05 (d, 1H, $^3J_{HH}$ = 7.2 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 20.8 (s, C(CH_3)$_2$), 24.8 (s, O–C(=O)–CH_3) 48.3 (s, N(CH_3)$_2$), 48.8 (s, CH_2), 56.7 (s, *tert*-C(CH$_3$)$_2$), 61.6 (s, CH_2), 116.6, 120.9, 124.1, 124.5, 124.9, 128.9, 136.0 (seven CH–C_6H_5), 126.5, 131.1, 145.7, 153.6, 157.8 (one η^1-Ph, two C_{ipso}–C_6H_5 and two C=N), 177.6 (s, O–C(=O)–CH$_3$). Anal. Calc. for $C_{23}H_{28}O_2N_4Pd$: C, 55.37; H, 5.66; N, 11.23. Found: C, 55.55; H, 6.57; N, 11.03%.

[PhN=C(CMe$_2$)(N-η^1-C$_6$H$_4$)C=NCH$_2$Py]PdCl (5). To a flask containing (COD)$PdCl_2$ (0.37 g, 1.30 mmol) in 20 ml CH_2Cl_2, a solution of **2** (0.46 g, 1.30 mmol) in 10 ml CH_2Cl_2 was added at room temperature. After 24 h of stirring, the yellow suspension was filtered. The residue was washed with 20 ml toluene to afford a yellow solid. Yield, 0.46 g, 71%. Suitable crystals of **5** for structural determination were recrystallized from CH_2Cl_2–hexane solution. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 1.56 (s, C(CH_3)$_2$, 6H), 5.23 (s, CH_2, 2H), 6.95 (m, 1H), 6.99 (m, 2H), 7.14 (m, 1H), 7.16 (m, 1H), 7.37 (m, 2H), 7.40 (m, 2H), 7.85 (m, 1H), 8.14 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 8.42 (m, 1H), 9.32 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2): δ 20.7 (s, C(CH_3)$_2$), 57.3 (s, *tert*-C(CH$_3$)$_2$), 58.0 (s, CH_2), 117.0, 120.3, 120.9, 123.6, 124.27, 124.29, 124.9, 129.2, 138.5, 141.4, 149.8 (CH–C_6H_5 and CH–Py), 127.9, 131.0, 145.8, 154.0, 158.3, 158.8 (one η^1-Ph, two C_{ipso}–C_6H_5, one C_{ipso}–Py and two C=N). Anal. Calc. for $C_{23}H_{21}ClN_4Pd$: C, 55.77; H, 4.27; N, 11.31. Found: C, 55.09; H, 4.89; N, 11.41%.

Table 6 Summary of crystal data for compounds **2**, **3**, **5** and **6**

	2	**3**	**5**	**6**
Formula	$C_{23}H_{22}N_4$	$C_{21}H_{25}ClN_4Pd$	$C_{23}H_{21}ClN_4Pd$	$C_{25}H_{24}O_2N_4Pd$
M	354.45	475.30	495.29	518.88
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Rhombohedral	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
a/Å	8.7023(9)	9.9515(8)	35.2349(14)	8.1039(5)
b/Å	9.7380(11)	10.8850(9)	35.2349(14)	12.5455(7)
c/Å	13.0560(14)	11.1266(9)	8.6726(5)	13.1672(8)
α/°	71.287(2)	99.068(2)	90	112.4890(10)
β/°	84.039(2)	115.3140(10)	90	101.6740(10)
γ/°	68.003(2)	98.306(2)	120	104.6700(10)
V/Å^3	971.47(18)	1045.17(15)	9324.5(8)	1127.52(12)
Z	2	2	18	2
D_c/Mg m^{-3}	1.212	1.510	1.588	1.528
μ(Mo-Kα)/mm^{-1}	0.073	1.028	1.041	0.852
Reflections collected	5484	5792	17452	6308
No. of parameters	244	265	262	289
$R1$[a]	0.0533	0.0325	0.0238	0.0300
$wR2$[a]	0.1646	0.1025	0.0838	0.0987
GoF[b]	1.298	0.965	0.781	0.931

[a] $R1 = [\sum(|F_o| - |F_c|)/\sum|F_o|]$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 0.10$. [b] GoF = $[\sum w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

[PhN=C(CMe$_2$)(N-η^1-C$_6$H$_4$)C=NCH$_2$Py]Pd(OAc) (6). To a flask containing Pd(OAc)$_2$ (0.224 g, 1.0 mmol) and **2** (0.354 g, 1.0 mmol), 20 ml THF was added at room temperature. After 28 h of stirring, the yellow suspension was filtered. The residue was washed with 20 ml toluene to afford a white solid. Yield, 0.22 g, 41%. ^{1}H NMR (600 MHz): δ 1.50 (s, C(CH_3)$_2$, 6H), 2.28 (s, OC(=O)CH_3, 3H), 5.16 (s, CH_2, 2H), 6.93 (d, 2H, $^3J_{HH}$ = 7.2 Hz), 7.01 (m, 1H), 7.12 (m, 2H), 7.32 (m, 4H), 7.65 (m, 1H), 7.77 (m, 1H), 8.09 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 8.44 (d, 1H, $^3J_{HH}$ = 5.4 Hz). ^{13}C{^{1}H} NMR (150 MHz): δ 20.6 (s, C(*C*H$_3$)$_2$), 24.9 (s, O–C(=O)–*C*H$_3$), 56.9 (s, *tert*-*C*(CH$_3$)$_2$), 57.5 (s, *C*H$_2$), 116.6, 120.1, 120.8, 123.6, 124.2, 124.5, 125.0, 129.0, 135.9, 138.1, 148.6 (*C*H–*C*$_6$H$_5$ and *C*H–Py), 128.6, 130.6, 145.6, 153.5, 157.6, 158.6 (one η^1-Ph, two *C*$_{ipso}$–*C*$_6$H$_5$, one *C*$_{ipso}$–Py and two *C*=N), 177.7 (s, O–*C*(=O)–CH$_3$). Anal. Calc. for C$_{25}$H$_{24}$N$_4$O$_2$Pd: C, 57.87; H, 4.66; N, 10.80. Found: C, 57.23; H, 5.21; N, 10.85%.

[PhN=C(CMe$_2$)(N-η^1-C$_6$H$_4$)C=NCH$_2$Py]Pd(TFA) (7). To a flask containing Pd(TFA)$_2$ (0.332 g, 1.0 mmol) and **2** (0.354 g, 1.0 mmol), 20 ml THF was added at room temperature. After 16 h of stirring, the pale-gray suspension was filtered. The residue was washed with 20 ml toluene to afford pale-gray solid. Yield, 0.30 g, 52%. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.54 (s, C(CH_3)$_2$, 6H), 5.18 (s, CH_2, 2H), 6.95 (d, 2H, $^3J_{HH}$ = 7.8 Hz), 6.98 (t, 1H, $^3J_{HH}$ = 7.2 Hz), 7.13 (t, 1H, $^3J_{HH}$ = 7.8 Hz), 7.16 (t, 1H, $^3J_{HH}$ = 7.2 Hz), 7.29 ~ 7.38 (overlap, 5H), 7.79 (m, 1H), 8.05 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 8.17 (d, 1H, $^3J_{HH}$ = 5.4 Hz). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): δ 20.6 (s, C(*C*H$_3$)$_2$), 57.0 (s, *tert*-*C*(CH$_3$)$_2$), 57.9 (s, *C*H$_2$), 116.9, 120.4, 120.7, 123.7, 124.3, 124.6, 125.3, 129.1, 134.6, 138.4, 147.6 (*C*H–*C*$_6$H$_5$ and *C*H–Py), 127.2, 129.9, 145.3, 153.2, 157.5, 158.9 (one η^1-Ph, two *C*$_{ipso}$–*C*$_6$H$_5$, one *C*$_{ipso}$–Py and two *C*=N), 162.2 (q, O–C(=O)–*C*F$_3$). Anal. Calc. for C$_{25}$H$_{21}$F$_3$N$_4$O$_2$Pd: C, 52.41; H, 3.69; N, 9.78. Found: C, 51.77; H, 3.52; N, 9.64%.

Heck reaction. A prescribed amount of catalyst, base (1.5 equiv.) and aryl halide (1 equiv.) were placed in a Schlenk tube under nitrogen. Solvent (2 ml) and styrene (1.3 equiv.) were added by syringe, and the reaction mixture was heated to the prescribed temperature for the prescribed time.

Crystal structure data

Crystals were grown from concentrated hexane solution (**2**) or CH$_2$Cl$_2$–hexane solution (**3**, **5** or **6**), and isolated by filtration. Suitable crystals of **2**, **3**, **5** or **6** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 6.

CCDC reference numbers 216807 (**2**) and 216808 (**5**).

See http://www.rsc.org/suppdata/dt/b4/b404798b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We would like to thank the National Science Council of the Republic of China for financial support.

References

1 J. Hassan, M. Sévignon, C. Gozzi, E. Schulz and M. Lemaire, *Chem. Rev.*, 2002, **102**, 1359.
2 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
3 A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.
4 W. A. Herrmann, V. P. W. Böhm and C.-P. Reisinger, *J. Organomet. Chem.*, 1999, **576**, 23.
5 I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009.
6 J. Dupont, M. Pfeffer and J. Spencer, *Eur. J. Inorg. Chem.*, 2001, 1917.
7 M. Albrecht and G. van Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750.
8 A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 4176.
9 R. B. Bedford, *Chem. Commun.*, 2003, 1787.
10 M. L. Clarke, D. J. Cole-Hamilton and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2001, 2721.
11 I. P. Beletskaya, A. N. Kashin, N. B. Karlstedt, A. V. Mitin, A. V. Cheprakov and G. M. Kazankov, *J. Organomet. Chem.*, 2001, **622**, 89.
12 A. Schnyder, A. F. Indolese, M. Studer and H.-U. Blaser, *Angew. Chem., Int. Ed.*, 2002, **41**, 3668.
13 O. Navarro, R. A. Kelly, III and S. P. Nolan, *J. Am. Chem. Soc.*, 2003, **125**, 16194.
14 M. L. Zanini, M. R. Meneghetti, G. Ebeling, P. R. Livotto, F. Rominger and J. Dupont, *Inorg. Chim. Acta*, 2003, **350**, 527.
15 R. B. Bedford, C. S. J. Cazin, S. J. Coles, T. Gelbrich, P. N. Horton, M. B. Hursthouse and M. E. Light, *Organometallics*, 2003, **22**, 987.
16 R. B. Bedford, C. S. J. Cazin, S. J. Coles, T. Gelbrich, M. B. Hursthouse and V. J. M. Scordia, *Dalton Trans.*, 2003, 3350.
17 C. S. Consorti, M. L. Zanini, S. Leal, G. Ebeling and J. Dupont, *Org. Lett*, 2003, **5**, 983.
18 C. Seward, W.-L. Jia, R. Y. Wang and S. Wang, *Inorg. Chem.*, 2004, **43**, 978.

19 J. M. Vila, M. Gayoso, M. T. Pereira, M. L. Torres, J. J. Fernández, A. Fernández and J. M. Ortigueira, *J. Organomet. Chem.*, 1997, **532**, 171.
20 J. Bravo, C. Cativiela, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 2002, **650**, 157.
21 C. López, A. Pawełczyk, X. Solans and M. Font-Bardía, *Inorg. Chem. Commun.*, 2003, **6**, 451.
22 G. Zhao, Q.-G. Wang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1998, 1241.
23 G. He, K. F. Mok and P.-H. Leung, *Organometallics*, 1999, **18**, 4027.
24 P.-H. Leung, K.-H. Ng, Y. Lin, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1999, 2435.
25 M. López-Torres, P. Juanatey, J. J. Fernández, A. Fernández, A. Suárez, R. Mosteiro, J. M. Ortigueira and J. M. Villa, *Organometallics*, 2002, **21**, 3628.
26 Y. Li, S. Selvaratnam, J. J. Vittal and P.-H. Leung, *Inorg. Chem.*, 2003, **42**, 3229.
27 P. Štěpnička and I. Císařová, *Organometallics*, 2003, **22**, 1728.
28 G. A. Grasa, R. Singh, E. D. Stevens and S. P. Nolan, *J. Organomet. Chem.*, 2003, **687**, 269.
29 Z. Weng, L. L. Koh and T. S. A. Hor, *J. Organomet. Chem.*, 2004, **689**, 18.
30 T. V. Laine, M. Klinga and M. Leskelä, *Eur. J. Inorg. Chem.*, 1999, 959.
31 T. V. Laine, U. Piironen, K. Lappalainen, M. Klinga, E. Aitola and M. Leskelä, *J. Organomet. Chem.*, 2000, **606**, 112.
32 R. Chen, J. Bacsa and S. F. Mapolie, *Polyhedron*, 2003, **22**, 2855.
33 J. L. Serrano, L. García, J. Pérez, E. Pérez, J. Vives, G. Sánchez, G. López, E. Molins and A. G. Orpen, *Polyhedron*, 2002, **21**, 1589.
34 B. J. O'Keefe and P. J. Steel, *Organometallics*, 2003, **22**, 1281.
35 T. Kawano, T. Shinomaru and I. Ueda, *Org. Lett.*, 2002, **4**, 2545.
36 C. Nájera, J. Gil-Moltó, S. Karlström and L. R. Falvello, *Org. Lett.*, 2003, **5**, 1451.