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Highly active ferrocenylamine-derived palladacycles for carbon–carbon cross-coupling reactions

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Abstract

{[(*N*-Methyl-*N*-*p*-R-benzyl)amino]benzyl}ferrocenes **4a–c** (R = H(a), OCH_3(b), CH_3(c)) were synthesized by *N*-methylation of the corresponding *sec*-amines **3a–c**with the reagent CH_3I-*t*-BuOK. Treatment of **4a–c** with Na_2PdCl_4 in the presence of NaOAc produced a pair of palladacycles σ-Pd[(η^5-C_5H_5)Fe(η^5- $C_5H_3CH(C_6H_5)N(CH_3)CH_2$-$C_6H_4$-R)]Cl($PPh_3$) **5a–c** (R = same as before) consisting of R_NR_P and S_NS_P configurations. The structure of **5a** was determined by single crystal X-ray analysis. High catalytic activities of **5a–c** for the Suzuki coupling of aryl chlorides with phenylboronic acid and the Heck reaction of bromobenzene with styrene were observed.

Keywords: Ferrocene; Amine; Palladacycles; Crystal; Carbon–carbon cross-coupling

1. Introduction

Functionalized biaryls are a class of important intermediates in the synthesis of natural products possessing biological activities [1]. These biaryls can be obtained by Suzuki coupling of functionalized aryl halides and phenylboronic acid, catalyzed by palladium–phosphine complexes such as $Pd(PPh_3)_4$, $Pd(PPh_2)Cl_2$, $Pd(OAc)_2/PPh_3$, etc. [2] or by the recently emerged N-heterocyclic carbene (NHC)–palladium complexes [3]. However, cyclopalladated complexes (also called palladacycles) as alternative catalysts have also been proven to be efficient in such couplings [4,5]. In addition, these palladacycles have been already used successfully in the Heck reaction, which gives a variety of olefins [4,6]. Previous researches on Suzuki coupling catalyzed by palladacycles containing nitrogen-donor atoms focused mainly on imines [5a,5b,5c,5d,5e,5f,5l], oximes [5g,5h], etc., and most of the palladacycles were found to be active to the C_{aryl}–Br or C_{aryl}–I bond, although several examples were also reported to be efficient to the C_{aryl}–Cl bond [5a,5c,5d,5h,5l]. To our best knowledge, research on the Suzuki coupling catalyzed by amine-derived palladacycles, particularly for activation of the C_{aryl}–Cl bond, are still scarce [5a,5i]. Thus it is essential to exploit the new type of amine-derived palladacycles to activate aryl chlorides, because of the low costs and easily purchased substrates. Several years ago we initiated a program, the synthesis of cyclometallated ferrocenylamines and their applications in carbon–carbon bond formation. It was observed that cyclopalladation or platination of {[(*N*-methyl-*N*-benzyl or phenyl)amino]methyl} ferrocenes always produced a pair of racemic metallocycles consisting of R_NR_P and S_NS_P configurations [7]. Most importantly, when a variety of phenyls are attached directly to the nitrogen in the ferrocenylamines, the corresponding palladacycles are thermally unstable and thus cannot be used as catalysts in carbon–carbon cross-coupling [7a]. In order to evaluate the catalytic efficiency of amine-derived palladacycles in this coupling, in this paper, we will present herein the synthesis of three palladacycles derived from {[(*N*-methyl-*N*-benzyl)amino]benzyl} ferrocenes and their catalysis in the Suzuki coupling of aryl chlorides with

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phenylboronic acid. In addition, the Heck reaction of bromobenzene with styrene catalyzed by these palladacycles, as mentioned above, will also be discussed.

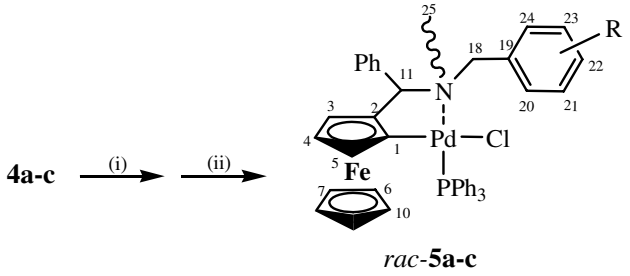
2. Results and discussion

2.1. Synthesis of ferrocenylamines 4a–c and their cyclopalladated complexes 5a–c

The preparation of *tert*-ferrocenylamines **4a–c** is shown in Scheme 1. Condensation of benzoylferrocene and 4 equiv. of benzylamine catalyzed by titanium tetrachloride [8] in toluene produced the dark-red ferrocenylketimines **2a–c** in good yields. Reduction of **2a–c** with $LiAlH_4$-$AlCl_3$ [9] in THF gave *sec*-amines **3a–c**, respectively in moderate yields. An attempt at the synthesis of **4a–c** from **3a–c** by our earlier used protocol, i.e. using aqueous HCHO, $NaCNBH_3$ in HOAc, [10] was unsuccessful due to the easier debenzylation of the former reactant [9,11] under such reaction conditions. Thus, CH_3I was chosen as the methylation reagent and *t*-BuOK as the base to synthesize **4a–c** from **3a–c** (Scheme 1). **4a–c** were finally obtained as orange solids in yields of 50–65%.

The synthesis of palladacycles **5a–c** is outlined in Scheme 2. Treatment of **4a–c** with 1 equiv. of Na_2PdCl_4–PPh_3 in methanol produced red-brown solids **5a–c** in 70–80% yields after purification by column chromatography (see Section 4). Similar to our earlier obtained palladacycles [7a,7b,7c], **5a–c** are very stable in air and easily soluble in CH_2Cl_2, $CHCl_3$, ethyl acetate, acetone and benzene, but are insoluble in ethanol and hexane.

Compounds **2–5** were characterized by elemental analysis, IR and ^1H NMR. Elemental analyses of **2–5** are in good agreement with their proposed formula. The IR and ^1H NMR spectra of **2–4** are very similar to those observed in imines, *sec*-amines and *tert*-amines derived from the starting materials formylferrocene and benzylamines [7b,7c]. The IR spectra of **5a–c** show two medium absorption bands at $\nu \sim 1100$ and 1000 cm^{-1}, implying that each of these palladacycles contains a free cyclopentadienyl (Cp) ring [12]. The ^1H NMR spectra of **5a–c**clearly demonstrate that the chemical shifts of N–CH_3 are located downfield ($\delta \sim 2.80$ ppm) compared to those of the free *tert*-amines **4a–c** ($\delta \sim 1.99$ ppm). This change can be rationalized by N–Pd coordination, which decreases the electron density



Scheme 2. (i) Na_2PdCl_4/NaOAc/CH_3OH. (ii) PPh_3/CH_3OH. R = H (a), 4-OCH_3 (b), 4-CH_3 (c).

of the N atom and causes the δ-values of N–CH_3 to shift downfield. In addition, the satellites of H20–H24 in the phenyl ring all exhibit their unique AA′XX′ splitting patterns (except **5a**), indicating that palladacycles **5a–c** are formed *via* the activation of the $C_{Ferrocenyl}$–H bond rather than the C_{phenyl}–H bond [13].

Since the nitrogen atom in **4a–c** connects directly to three different groups and a rapid N-inversion [14] exists, after the coordination of the nitrogen atom with palladium, the forms of the N–Pd coordinated intermediates (Fig. 1) can be simplified as two kinds, i.e., one has a R_N configuration, and another has the opposite, regardless of the chirality of C11. Accordingly, the following activation of the C–H bond in the Cp ring will produce theoretically four isomeric palladacycles (two pairs of racemes, *i.e.*, R_NR_P and S_NS_P, S_NR_P and R_NS_P). Similar to our earlier observations [7], only one pair of raceme R_NR_P and S_NS_P was found to dominate in these reactions, the other pair of raceme R_NS_P and S_NR_P was observed in trace amounts and can be easily removed by

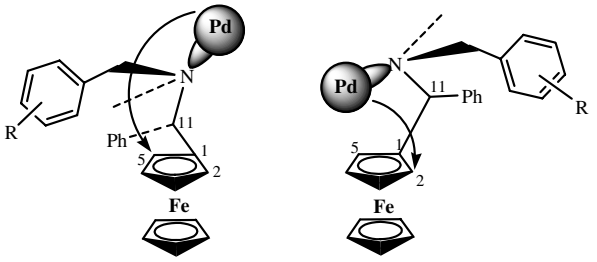
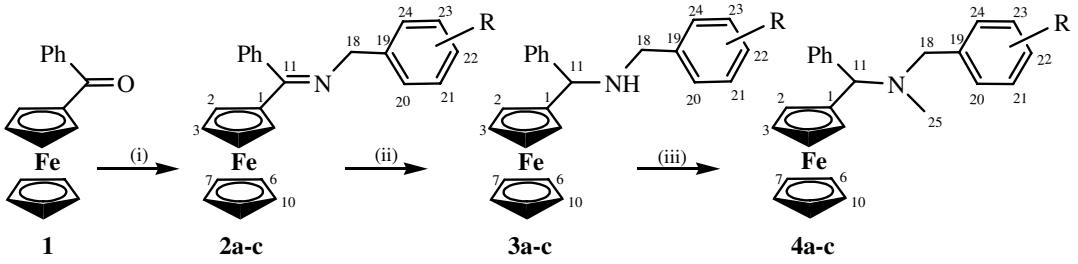


Fig. 1. The possible activation modes of C–H bonds in the Cp ring for N–Pd coordinated intermediates (left: R_N, right: S_N).



Scheme 1. (i) $RC_6H_4CH_2NH_2$/$TiCl_4$/toluene, reflux. R = H (a), 4-OCH_3 (b), 4-CH_3 (c). (ii) $LiAlH_4$/$AlCl_3$/THF. (iii) CH_3I/*t*-BuOK, THF.

chromatography. This stereoselective C–H bond activation is probably attributed to the preferred N–Pd orientations in the intermediates (Fig. 1), which allow the palladium atom to approach preferably to the C2–H or C5–H bond and then activate each of them. To some extent, the preferred N–Pd orientations in these intermediates are relevant to the geometries of the *tert*-ferrocenylamines [15]. In addition, zero optical rotations of **5a**–**c** measured at the given conditions ($\lambda = 5893$ Å, CH_2Cl_2, 293 K) also indicate that these palladacycles consist of racemes.

The structure of **5a** was determined by single crystal X-ray analysis (Fig. 2, S_NS_P). Crystallographic data for **5a** are given in Table 1, selected bond lengths and angles are listed in Table 2. X-ray diffraction studies demonstrates that **5a** consists of the discrete molecule {Pd[(η^5-C_5H_5)Fe(η^5-C_5H_3CHPhN(CH_3)$CH_2C_6H_5$)](PPh$_3$)Cl} separated by van der Waals contacts. The palladium atom is in a slightly distorted square-planar environment, bonded to Cl(1), P(1), N(1) and C(1). The deviation of each atom from the mean plane is Pd(1), −0.1015; Cl(1), −0.0489; P(1), 0.1071; N(1), 0.1149; C(1), −0.0716 Å, respectively. **5a** contains a bicycle, which is formed by the substituted Cp ring of the ferrocenyl fragment and a five-membered palladacycle with an envelope-like conformation. The N(1)–Pd(1) bond length of 2.224(3) Å is slightly longer than those observed in cyclopalladated [(*N*,*N*-dimethylamino)methyl]ferrocene (FcN, 2.170 Å) [16] and [({*N*-methyl-*N*-4-nitrobenzyl}-amino)methyl]ferrocene (BFcN, 2.195 Å) [7c]. In addition, the PPh$_3$ moiety in **5a** adopts a *trans*-configuration to N(1), with a N(1)–Pd(1)–P(1) bond angle of 167.53(7)°, which is slightly less than that in cyclopalladated BFcN (169.00(9)°). The Pd(1)–C(1) bond length of 2.002(3) Å is nearly the same as those observed in cyclopalladated FcN (1.983(1) Å) and BFcN (1.988(4) Å). The average C–C bond length (1.418 Å) in the ferrocenyl moiety is very close to the reported values of other ferrocene derivatives [17]. The Fe–C (Cp ring) bond lengths range from 2.036 to 2.082 Å. The eclipsed two Cp rings are planar and nearly parallel (interplanar angle of 2.2°).

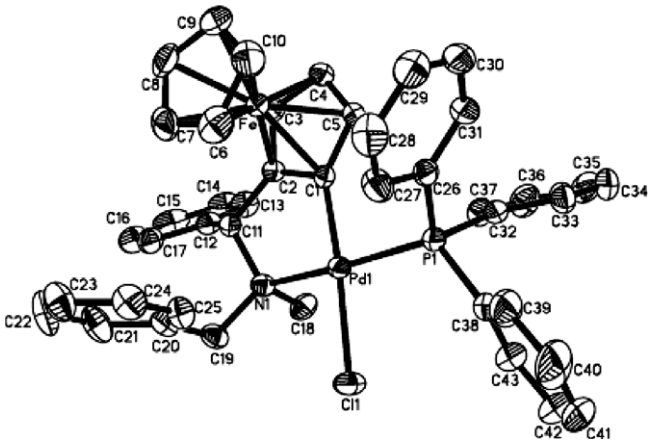


Fig. 2. X-ray crystal structure of **5a** (H atoms are all omitted for clarity).

Table 1
Crystallographic data for **5a**

Compound	**5a**
Empirical formula	$C_{43}H_{39}ClFeNPPd$
Formula weight	798.42
Crystal dimensions (mm)	$0.28 \times 0.22 \times 0.20$
Crystal system, space group	monoclinic, $P2(1)/n$
a (Å)	10.716(8)
b (Å)	17.638(1)
c (Å)	19.259(2)
α (°)	90
β (°)	94.153(1)
γ (°)	90
V (Å^3)	3631(5)
Z	4
ρ_{calc} (g cm^{-3})	1.461
μ (mm^{-1})	1.044
θ Range for data collection	$2.23 \leqslant \theta \leqslant 24.08°$
Limiting indices	$-10 \leqslant h \leqslant 12$, $-20 \leqslant k \leqslant 20$, $-21 \leqslant l \leqslant 22$
Reflections collected/unique [R_{int}]	19259/6383 [0.0375]
Data/restraints/parameters	6383/0/434
Final R_1, wR_2	0.0323, 0.0768
Largest difference in peak and hole (e Å^{-3})	0.542 and −0.345

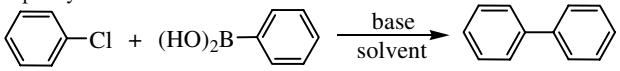
Table 2
Selected bond lengths and angles for **5a**

Bond lengths (Å)			
Pd(1)–P(1)	2.2401(1)	C(1)–C(2)	1.431(4)
Pd(1)–Cl(1)	2.3920(2)	N(1)–C(11)	1.524(4)
C(2)–C(11)	1.520(4)	N(1)–C(19)	1.499(4)
Bond angles (°)			
C(1)–Pd(1)–N(1)	82.18(1)	C(18)–N(1)–C(19)	107.5(2)
N(1)–Pd(1)–Cl(1)	91.24(7)	C(1)–Pd(1)–P(1)	91.67(9)
C(11)–N(1)–Pd(1)	109.92(2)	C(1)–Pd(1)–Cl(1)	173.25(8)
C(19)–N(1)–C(11)	110.2(2)	P(1)–Pd(1)–Cl(1)	94.51(5)
C(18)–N(1)–C(11)	112.1(2)	C(2)–C(1)–Pd(1)	114.15(2)

2.2. Suzuki coupling

Before investigation of the Suzuki coupling for aryl chlorides, the coupling of bromobenzene and phenylboronic acid catalyzed by **5a**–**c** (under the conditions K_2CO_3, THF) was studied. The coupling results showed that 100% of biphenyl was obtained, indicating that palladacycles **5a**–**c** are excellent catalysts for activation of the C_{phenyl}–Br bond. To examine the catalytic efficiency of **5** for the coupling of aryl chlorides, a quick survey of solvents including dioxane, toluene, THF and DMF/H_2O was made (Table 3). Table 3 revealed that using K_2CO_3 as the base and 0.1 mol% of **5a** as the catalyst the coupling reaction in dioxane gave the best results (Entry 1, 89%, Table 3). We further investigated the effect of the bases, e.g., K_2CO_3, Cs_2CO_3, K_3PO_4 and *t*-BuOK in the same reaction (Table 3). It was found that K_2CO_3 was better than the others (Entries 4–7). Therefore, K_2CO_3 was ultimately chosen as the base for this system.

Table 3
Influence of solvents and bases on the Suzuki coupling of chlorobenzene with phenyl-boronic acid[a]



Entry	Solvent	Base	Yield (%)[b]
1	dioxane	K_2CO_3	89.1
2	toluene	K_2CO_3	45.9
3	THF	K_2CO_3	51.3
4	DMF/H_2O	K_2CO_3	36.2
5	dioxane	Cs_2CO_3	67.6
6	dioxane	K_3PO_4	15.0
7	dioxane	*t*-BuOK	26.7

[a] Reaction conditions: catalyst *rac*-**5a** (0.1 mol%), PhCl (1 mmol), $PhB(OH)_2$ (1.5 mmol), base (2 mmol), solvent (10 cm^3), reflux, 10 h.
[b] Determined by GC, based on PhCl, average of two runs.

Under the optimized conditions as mentioned above, the relative activities of **5a**–**c** for the Suzuki coupling of aryl chlorides and phenylboronic acid were studied (Table 4). When the reactions were carried out at 100 °C for 10 h, **5a**–**c** all exhibited good activity with the loading as low as 0.1 mol % (Entries 1–3). However, when 0.01% of **5a** was used, the coupling yield was lower (Entry 4, 22.3%). Under the optimized reaction conditions (K_2CO_3, dioxane, 100 °C, 10 h) phenylboronic acid could couple efficiently with the aryl chlorides ranging from electron-donating to electron-withdrawing groups (Entries 5–10). In particular, for 4-$CH_3C_6H_5Cl$ the coupling yield was up to 98.0% (Entry 6). Even for the bulky 2,4-dinitrophenyl chloride, its coupling with phenylboronic acid was also achieved and the resulting biaryl yield was moderate.

2.3. Heck reaction

We initially examined the Heck reaction of chlorobenzene with styrene catalyzed by **5a**–**c**. Unfortunately the product yields were much lower (yield < 3%), and these results were consistent with the another group's observations [6]. Later we paid attention to the reaction of bromobenzene with styrene, and the results are summarized in Table 5. It was found that using DMF as the solvent and K_2CO_3 as the base at 140 °C for 7 h, an excellent yield of product could be obtained when the loading of palladacycle **5b** was as low as 0.1 mol% (Entry 6). Similar to the Suzuki coupling, when 0.01% of catalyst was used, the coupling yield was lower (Entry 8, 39%).

3. Conclusions

tert-Ferrocenylamines were easily synthesized by *N*-methylation of the corresponding *sec*-amines with CH_3I. Treatment of these *tert*-amines with Na_2PdCl_4 afforded racemic palladacycles with a σ Pd–C_{sp^2}, Ferrocenyl bond. These palladacycles have been proven to be highly efficient catalysts for the Suzuki coupling of aryl chlorides with phenylboronic acid and the Heck reaction of bromobenzene with styrene under the given conditions.

4. Experimental

4.1. Materials and instruments

Benzoylferrocene, enzylamines, $TiCl_4$, $LiAlH_4$, $AlCl_3$, CH_3I, *t*-BuOK, NaOAc, PPh_3 were obtained commercially and were used without further purification. Na_2PdCl_4 was prepared in our laboratory. All of the solvents were purified with standard methods prior to use. Melting points were obtained on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were measured on a Carlo Erba 1106 Elemental analyzer. ^1H NMR spectra were obtained with Bruker AV-400 spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. IR spectra were recorded on a BIO-RAD 3000 spectrophotometer.

4.2. Preparation of ferrocenylketimines (*2*)

General procedure: **2a**–**c** were prepared according to the literature method [8].

4.2.1. $\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4C(C_6H_5)=NCH_2C_6H_5)\}$ (*2a*)

Yield: (80%); a dark-red liquid; *Anal.* Calc. for $C_{24}H_{21}FeN$: C, 76.00; H, 5.58; N, 3.69. Found, C, 76.08; H, 5.69; N, 3.90%. FT-IR (KBr): 3084(w), 3027(w), 2856(w), 1614(vs), 1494(s), 1453(m), 1343(m), 1289(s), 1181(m), 1106(s), 1026(s), 1003(s), 822(s),703(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.81 (bs, 2H, H2, H5), 4.08 (bs, 2H, H3, H4), 4.14 (s, 5H, η^5-C_5H_5), 4.50 (s, 2H, H18), 7.45–7.89 (m, 10H, Ph).

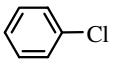
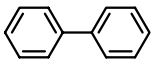
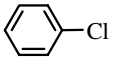
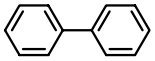
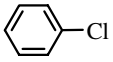
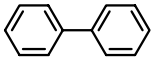
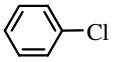
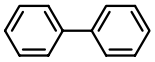
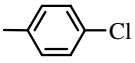
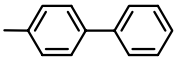
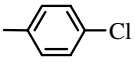
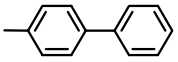
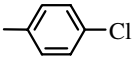
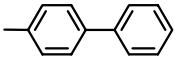
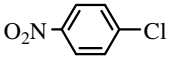
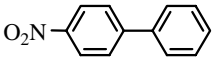
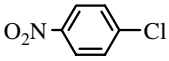
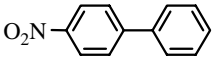
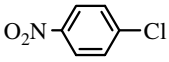
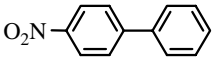
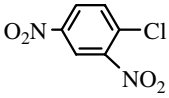
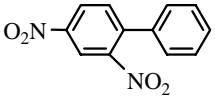
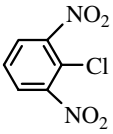
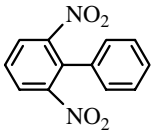
4.2.2. $\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4C(C_6H_5)=NCH_2C_6H_4\text{-}OCH_3\text{-}4)\}$ (*2b*)

Yield: (76%); a dark-red liquid; *Anal.* Calc. for $C_{25}H_{23}FeNO$: C, 73.36; H, 5.66; N, 3.42. Found, C, 73.25; H, 5.73; N, 3.19%. FT-IR (KBr): 3088(w), 3022(w), 2909(w), 1611(vs), 1511(vs), 1462(s), 1291(s), 1245(vs), 1173(m), 1101(s), 1035(s), 818(s), 702(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.82 (s, 3H, OCH_3), 3.87 (bs, 2H, H2, H5), 4.11 (bs, 2H, H3, H4), 4.17 (s, 5H, η^5-C_5H_5), 4.55 (s, 2H, H18), 6.99–7.50 (m, 4H, H20, H21, H23, H24), 7.25–7.38 (m, 5H, Ph).

4.2.3. $\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4C(C_6H_5)=NCH_2C_6H_4CH_3\text{-}4)\}$ (*2c*)

Yield: (85%); a dark-red liquid; *Anal.* Calc. for $C_{25}H_{23}FeN$: C, 76.35; H, 5.89; N, 3.56. Found: C, 76.21; H, 5.56; N, 3.81%. FT-IR (KBr): 3093(w), 3021(w), 2922(w), 1614(vs), 1515(s), 1480(s), 1290(vs), 1179(w), 1106(s), 1002(s), 820(vs), 703(vs) cm^{-1}. ^1H

Table 4
Palladacycles-catalyzed conversion of aryl chlorides to biaryls[a]

Entry	Aryl halide	Catalyst (mol%)	Product	Yield (%)[b]
1		*rac*-**5a**(0.1)		89.1
2		*rac*-**5b**(0.1)		86.5
3		*rac*-**5c**(0.1)		85.2
4		*rac*-**5a**(0.01)		22.3
5		*rac*-**5a**(0.1)		91.7
6		*rac*-**5b**(0.1)		98.0
7		*rac*-**5c**(0.1)		95.1
8		*rac*-**5a**(0.1)		72.4
9		*rac*-**5b**(0.1)		78.7
10		*rac*-**5c**(0.1)		80.6
11		*rac*-**5c**(0.1)		68.5
12		*rac*-**5b**(0.1)		45.3

[a] Reaction conditions: ArCl (1 mmol), $PhB(OH)_2$ (1.5 mmol), K_2CO_3 (2 mmol), dioxane (10 cm^3), 100 °C, 10 h.
[b] Determined by GC, based on aryl chloride used, average of two runs.

NMR ($CDCl_3$): δ 2.15 (s, 3H, CH_3), 3.85 (bs, 2H, H2, H5), 4.10 (bs, 2H, H3, H4), 4.16 (s, 5H, η^5-C_5H_5), 4.53 (s, 2H, H18), 7.13–7.25 (m, 4H, H20, H21, H23, H24), 7.43–7.55 (m, 5H, Ph).

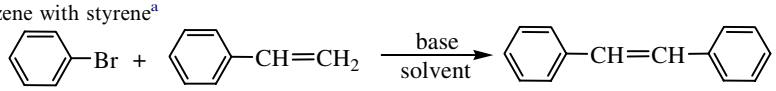
4.3. Preparation of sec-ferrocenylamines (*3*)

General procedure: **3a**–**c** were prepared with a modification of the 'Cais' method [8]. The difference was the reduction conditions. In our experiment, 3% mmol of $AlCl_3$ was used as the catalyst and THF as the solvent.

4.3.1. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH(C_6H_5)NHCH_2C_6H_5$)} (*3a*)

Yield: (77%); an orange solid; m.p. 68–70 °C. *Anal.* Calc. for $C_{24}H_{23}FeN$: C, 75.60; H, 6.08; N, 3.67. Found: C, 75.63; H, 6.25; N, 3.82%. FT-IR (KBr): 3328(s), 3084(m), 3022(m), 2948(m), 2857(m), 1598(m), 1493(vs),

Table 5
The Heck reaction of bromobenzene with styrene[a]



Entry	Solvent	Catalyst (mol%)	T (°C)	Base	Yield (%)[b]
1	1,4-dioxane	*rac*-**5b**(0.1)	80	K_2CO_3	3.0
2	1,4-dioxane	*rac*-**5b**(1)	100	K_2CO_3	5.0
3	toluene	*rac*-**5b**(1)	100	K_2CO_3	3.0
4	DMF	*rac*-**5b**(0.1)	100	K_2CO_3	22.0
5	DMF	*rac*-**5b**(1)	140	K_2CO_3	100
6	DMF	*rac*-**5b**(0.1)	140	K_2CO_3	100
7	DMF	*rac*-**5b**(0.1)	140	*t*-BuOK	87.0
8	DMF	*rac*-**5b**(0.01)	140	K_2CO_3	39.0
9	DMF	*rac*-**5a**(0.1)	140	K_2CO_3	96.0
10	DMF	*rac*-**5c**(0.1)	140	K_2CO_3	98.0

[a] All reactions were carried out with 1 mmol of PhBr, 1.5 mmol of styrene and 2 mmol of base in 10 cm^3 of solvent for 7 h.
[b] Determined by GC, based on PhBr, average of two runs.

1452(vs), 1283(m), 1197(m), 1105(vs), 1022(s), 996(s), 820(vs), 699(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.17 (s, 1H, NH), 3.58–3.80 (q, 2H, H18) 4.06 (s, 1H, H11), 4.04 (s, 5H, η^5-C_5H_5), 4.30 (bs, 2H, H2, H5), 4.48 (bs, 2H, H3, H4), 7.23–7.43 (m, 10H, Ph).

4.3.2. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH(C_6H_5)NHCH_2C_6H_4$-$OCH_3$-4)} (**3b**)

Yield: (72%); a yellow solid; m.p. 57–60 °C. *Anal*. Calc. for $C_{25}H_{25}FeNO$: C, 73.00; H, 6.13; N, 3.41. Found: C, 73.09; H, 6.31; N, 3.55%. FT-IR (KBr): 3324(m), 3083(m), 3022(m), 2954(s), 2827(m), 1610(vs), 1512(vs), 1452(s), 1300(m), 1247(vs), 1174(s), 1105(vs), 1036(s), 1001(s), 821(vs), 700(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.17 (s, 1H, NH), 3.51–3.74 (q, 2H, H18), 3.82 (s, 3H, OCH_3), 4.04 (s, 5H, η^5-C_5H_5), 4.05 (s, 1H, H11), 4.30 (bs, 2H, H2, H5), 4.46 (bs, 2H, H3, H4), 6.90–7.41 (m, 4H, H20, H21, H23, H24), 7.23–7.34 (m, 5H, Ph).

4.3.3. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH(C_6H_5)NHCH_2C_6H_4$-$CH_3$-4)} (**3c**)

Yield: (81%); a yellow solid; m.p. 93–94 °C. *Anal*. Calc. for $C_{25}H_{25}FeN$: C, 75.96; H, 6.37; N, 3.54. Found: C, 75.89; H, 6.15; N, 3.90%. FT-IR (KBr): 3324(m), 3073(m), 3013(m), 2924(m), 2821(m), 1597(m), 1508(vs), 1451(s), 1333(m), 1179(m), 1104(vs), 1021(s), 996(s), 817(vs), 699(vs) cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.17 (s, 1H, NH), 2.14 (s, 3H, CH_3), 3.54–3.76 (q, 2H, H18), 4.04 (s, 5H, η^5-C_5H_5), 4.05 (s, 1H, H11), 4.30 (bs, 2H, H2, H5), 4.47 (bs, 2H, H3, H4), 7.12–7.21 (m, 4H, H20, H21, H23, H24), 7.41–7.53 (m, 5H, Ph).

4.4. Synthesis of tert-ferrocenylamines (**4**)

General procedure: To a stirred solution of **3** (2 mmol) in 20 cm^3 of THF was added CH_3I (3 mmol) in 5 cm^3 THF and *t*-BuOK (3 mmol). The mixture was kept in the dark at room temperature and stirred for 48 h. TLC monitored the reaction progress until it was complete. The solvent was removed under reduced pressure and 30 cm^3 of water was then added. The mixture was extracted with diethyl ether (3×20 cm^3) and separated. The extracts were combined, dried over Na_2SO_4 and removed to give crude products which were purified by column chromatography (silica gel, ethyl acetate/hexane = 1:5, v/v) to afford **4a**–**c**.

4.4.1. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH(C_6H_5)N(CH_3)CH_2$-$C_6H_5$)} (**4a**)

Yield: (58%); an orange solid; m.p. 64–66 °C. *Anal*. Calc. for $C_{25}H_{25}FeN$: C, 75.96; H, 6.37; N, 3.54. Found: C, 75.88; H, 6.60; N, 3.81%. FT-IR (KBr): 3081(s), 3019(s), 2957(s), 2783(s), 1596(s), 1493(vs), 1452(vs), 1366(m), 1286(m), 1106(vs), 1002(vs), 818(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.95 (s, 3H, H25), 3.22–3.51 (q, 2H, H18), 3.79 (s, 5H, η^5-C_5H_5), 4.13 (s, 1H, H11), 4.11 (bs, 2H, H2, H5), 4.34 (bs, 2H, H3, H4), 7.19–7.52 (m, 10H, Ph).

4.4.2. {(η^5-C_5H_5)Fe(η^5-C_5H_4 $CH(C_6H_5)N(CH_3)CH_2$-$C_6H_4OCH_3$-4)} (**4b**)

Yield: (50%); an orange solid; m.p. 72–73 °C. *Anal*. Calc. for $C_{26}H_{27}FeNO$: C, 73.42; H, 6.40; N, 3.29. Found: C, 73.37; H, 6.58; N, 3.36%. FT-IR (KBr): 3088(m), 3024(m), 2953(s), 2831(m), 2775(m), 1605(vs), 1510(vs), 1452(vs), 1296(m), 1242(vs), 1106(vs), 1002(vs), 818(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.98 (s, 3H, H25), 3.23–3.51 (q, 2H, H18), 3.85 (s, 3H, OCH_3), 3.81 (s, 5H,η^5-C_5H_5), 4.14 (s, 1H, H11), 4.13 (bs, 2H, H2, H5), 4.36 (bs, 2H, H3, H4), 6.91–7.42 (m, 4H, H20, H21, H23, H24), 7.26–7.35 (m, 5H, Ph).

4.4.3. {(η^5-C_5H_5)Fe(η^5-$C_5H_4CH(C_6H_5)N(CH_3)CH_2$-$C_6H_4CH_3$-4)} (**4c**)

Yield: (65%); an orange solid; m.p. 70–72 °C. *Anal*. Calc. for $C_{26}H_{27}FeN$: C, 76.29; H, 6.65; N, 3.42. Found: C, 76.23; H, 6.43; N, 3.60%. FT-IR (KBr): 3091(m),

3023(m), 2956(s), 2776(m), 1600(m), 1513(vs), 1452(vs), 1286(m), 1106(vs), 1002(vs), 805(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.99 (s, 3H, H25), 2.35 (s, 3H, CH_3), 3.24–3.52 (q, 2H, H18), 3.83 (s, 5H, η^5-C_5H_5), 4.16 (s, 1H, H11), 4.15 (bs, 2H, H2, H5), 4.38 (bs, 2H, H3, H4), 7.13–7.22 (m, 4H, H20, H21, H23, H24), 7.44–7.55 (m, 5H, Ph).

4.5. Synthesis of cyclopalladated tert-ferrocenylamines (5)

General procedure: To a stirred solution of **4** (1 mmol), sodium acetate (82 mg, 1 mmol) in 30 cm^3 of methanol was added dropwise a solution of Na_2PdCl_4 (0.29 g, 1 mmol) in 15 cm^3 of methanol. The mixture was stirred for 4 h at room temperature under argon and TLC monitored the reaction's progress. Then PPh_3 (0.41 g, 1.5 mmol) was added and the mixture was stirred for another 30 min. The solvent was removed in vacuo, and the residues were purified by column chromatography (silica gel, ethyl acetate/hexane = 1:2, v/v) to give **5**.

4.5.1. [PdCl(PPh$_3$){(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH(C$_6$H$_5$)N-(CH$_3$)CH$_2$C$_6$H$_5$)}] (5a)

Yield: (72%); a red solid; m.p. > 193 °C (dec.). *Anal.* Calc. for $C_{43}H_{39}ClFeNPPd$: C, 64.68; H, 4.92; N, 1.75. Found: C, 64.60; H, 4.89; N, 1.82%. FT-IR (KBr): 3054(w), 2955(w), 2922(w), 1486(m), 1450(m), 1435(vs), 1095(s), 999(s), 823(m), 752(s), 701(vs) cm^{-1}. ^1H NMR($CDCl_3$): δ 2.88 (m, 2H, H18), 3.21 (s, 3H, H25), 4.84 (s, 1H, H11), 3.85 (s, 5H, η^5-C_5H_5), 3.76 (d, 1H, H5), 4.08 (m, 1H, H4), 4.16 (d, 1H, H3), 7.73–7.82 (m,10H, 2Ph), 7.35–7.54 (m, 15H, PPh_3).

4.5.2. [PdCl(PPh$_3$){(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH(C$_6$H$_5$)N-(CH$_3$)CH$_2$C$_6$H$_4$OCH$_3$-4)}] (5b)

Yield (80%); a red solid; m.p. > 189 °C (dec.). *Anal.* Calc. for $C_{44}H_{41}ClFeNOPPd$: C, 63.79; H, 4.99; N, 1.69. Found: C, 63.72; H, 4.81; N, 1.96%. FT-IR (KBr): 3045(w), 2954(w), 1512(vs), 1454(m), 1435(vs), 1246(s), 1178(s), 1100(s), 995(m), 816(s), 747(s), 702(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.79 (s, 3H, H25), 3.24 (m, 2H, H18), 3.43 (s, 3H, OCH_3), 3.73 (s, 5H, η^5-C_5H_5), 3.74 (m, 1H, H5), 3.80 (m, 1H, H4), 3.95 (d, 1H, H3), 4.96 (s, 1H, H11), 6.90–7.05 (m, 4H, H20, H21, H23, H24), 7.39–7.66 (m, 15H, PPh_3), 7.70–7.85 (m, 5H, Ph).

4.5.3. [PdCl(PPh$_3$){(η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_3$CH(C$_6$H$_5$)N-(CH$_3$)CH$_2$C$_6$H$_4$ CH$_3$-4)}] (5c)

Yield (70%); a red solid; m.p. > 172 °C (dec.). *Anal.* Calc. for $C_{44}H_{41}ClFeNPPd$: C, 65.04; H, 5.09; N, 1.72. Found: C, 65.12; H, 4.85; N, 1.65%. FT-IR (KBr): 3051(w), 2954(w), 2920(w), 1484(s), 1455(s), 1437(vs), 1185(m), 1103(s), 1002(m), 823(m), 751(s), 693(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.43 (s, 3H, CH_3), 2.79 (s, 3H, H25), 3.21 (m, 2H, H18), 3.50 (s, 5H, η^5-C_5H_5), 5.16 (s, 1H, H11), 3.73 (m, 1H, H5), 3.82 (d, 1H, H3), 4.10 (m, 1H, H4), 7.13–7.22 (m, 4H, H20, H21, H23, H24), 7.39–7.56 (m, 15H, PPh_3), 7.70–7.85 (m, 5H, Ph).

4.6. General procedure for the Suzuki coupling

Palladacycles **5** (0.1 mmol%), aryl chlorides (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), dioxane (10 cm^3) were added to a 25 cm^3 round-bottomed flask and the mixture was heated at 100 °C for 10 h. Upon cooling, the reaction mixture was poured into water and extracted with CH_2Cl_2, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and yields are based on aryl chlorides.

4.7. General procedure for the Heck reaction

Palladacycles **5** (0.1 mmol%), bromobenzene (1.0 mmol), styrene (1.5 mmol), K_2CO_3 (2 mmol), DMF (10 cm^3) were added to a 25 cm^3 round-bottomed flask and the mixture was heated at 140 °C for 7 h. Upon cooling, the reaction mixture was poured into water and extracted with CH_2Cl_2, concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and yields are based on bromobenzene.

4.8. X-ray crystallographic study of 5a

Crystals of **5a** were grown at room temperature by slow evaporation of a mixture of hexane and ethyl acetate over a period of one week. A single crystal of this complex was mounted on a Bruker SMART CCD diffractometer equipped with monochromated graphite Mo Kα (λ = 0.71073 Å) radiation at ambient temperature (T = 293 K) using the ω–2θ multi-scans technique for data collection. Semi-empirical absorption corrections were applied using the SABABS program [18]. The structure was solved by direct methods and refined by the full-matrix least-squares procedure on F^2 using the SHELX suite of programs [19]. The values of R_1 were given based on F_o with a typical threshold of $F^2 \geqslant 2\sigma(F^2)$. The weighted R-factors wR were based on F^2 with calc. $w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 0.0827P]$ where $P = (F_o^2 + 2F_c^2)/3$ for **5a**. Crystallographic data for **5a** are summarized in Table 1. Selected bond lengths and angles for **5a** are presented in Table 2.

5. Supplementary material

CCDC 603093 contains the supplementary crystallographic data for **5a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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