Unsymmetrical pincer CNN palladium complex of 7-ferrocenylmethyl-3-methyl-3,7-diazabicyclo[3.3.1]nonane

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The new unsymmetrical ferrocenyI containing bispidine derivative 7 was synthesized as a ligand pre-
cursor in five steps starting from N-Boc-4-oxopiperidine. The corresponding palladium CNN pincer
complex 8 was prepared by direct cyclopalladation of the ligand 7 with Li2PdCl4 in MeOH. The molecular
structure of the obtained palladacycle was determined by multinuclear NMR (1H, 13C, 15N) and confirmed
by X-ray diffraction analysis. The pincer complex 8 demonstrated high catalytic activity in some cross-
coupling reactions of aryl halides with phenylboronic acid, norbornene and ethyl acrylate.

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1. Introduction

Since the synthesis of the first cyclopalladium complex of
ferrocene derivative dimethylaminomethylferrocene [1], the
chemistry of this class of compounds was developed actively, and
today the collection of known ferrocene CN palladium complexes
includes hundreds of structures. They were obtained from the
ferrocenyl aromatic N-heterocycles, or from ferrocenylalkyl de-
rivatives, having in a-position C = N bond (imines, oximes, etc.) in
which the nitrogen atom is sp2 hybridized. Stable dimeric cyclo-
palladates could be isolated usually when the substituents on the
nitrogen atoms were two methyl [1,2] or ethyl [3] groups. The at-
ttempts to obtain cyclopalladium complexes of the ferroceny-
lalkylamines with other N-substituents were reported to be
unsuccessful [4] except for a few examples, in which complexes
were isolated as monomers and palladacycle was supported by Pd
coordination with second intra- or intermolecular heteroatomic
ligand [5,6].

Cyclopalladate complexes with intramolecular coordination of
Pd with two heteroatoms, known as the pincer complexes, became
the point of active studies due to their high stability, possibility of
structural modification and exhibited catalytic activity. In the ma-
majority of known non-symmetrical ferrocene CNN pincer complexes
at least one N atom is sp2 hybridized (Fig. 1, A–D).

As far as we know Kang et al. [5] reported the first non-
symmetrical pincer compound of this series in which both N
atoms are sp3 (Fig. 1, E). Thus it can be expected that by using the
ligand with an appropriate structure including the ferroceny-
lalkylmethyl group and two amino groups it is possible to obtain a
stable pincer Pd complex with two N(sp3) atoms. The structure of
3,7-diazabicyclo[3.3.1]nonane (bispidine) (Fig. 2, 1), with its chair-
chair preferential conformation, appeared to be the appropriate
base.

It is known that symmetrical 3,7-dialkylbispidines as well as
their synthetic precursors 9-bispidinones when reacted with
transition metal salts, in particular, palladium and platinum, form
the NN coordination complexes [7]. In the case of two N-allyl
groups, along with NN coordinated Pt compounds the cyclo-
platinum complex obtained by substituting the vinyl proton of the
allyl group was isolated [7c]. Very recently we demonstrated [8],
that in the course of interaction of 3-benzyl-7-methylbispidine
with palladium salts the novel and very stable unsymmetrical
CNN pincer complex was formed [Fig. 2, 2], while the NN
coordination complex was found only as minor compound. It seems that
the replacement of the benzyl group for ferrocenylmethyl one
would allow to obtain the stable cyclopalladate with two nitrogen atoms in sp³ hybridization.

Synthesis and study of the catalytic properties in the cross-coupling reactions of unsymmetrical CNN pincer palladium complexes is the subject of many investigations. All of them refer to those compounds in which the palladium atom is attached to an aromatic ring [9]. Ferrocene complexes of similar structure are represented much less [10], and their catalytic properties in the cross-coupling reactions were studied, to our knowledge, only in respect of one of them [11].

In this paper we report on the synthesis of the new unsymmetrical ferrocenyl containing CNN pincer ligand based on the bispidine frame and its corresponding palladium complex. The obtained Pd complex was examined as a catalyst in the cross-coupling reactions of aryl halides with phenylboronic acid, norbornene and ethyl acrylate.

2. Result and discussion

2.1. Synthesis and characterization

The unsymmetrical CNN pincer ligand 7 was prepared in five steps as shown in Scheme 1.

First, according to the previously published methods [12], N-benzyl-N-Boc-bispinedine 3 was obtained by a double Mannich reaction from N-Boc-4-oxopiperidine, benzylamine, and paraformaldehyde (74% yield). The Huang–Minlon variation of Wolff–Kishner reduction of the carbonyl functionality in 3 afforded a 66% yield of bispinedine 4. The N-benzyl protecting group was cleaved from N-benzyl-N-Boc-bispinedine 4 using palladium on activated charcoal (5%) as a catalyst and ammonium formate as a hydrogen source. N-Boc-bispinedine 5 was isolated in a yield of 85%. N-Boc-N-ferrocenylmethylbispinedine 6 was synthesized by the reductive amination of ferrocenecarboxaldehyde with 5 and sodium tri-acetoxyborohydride in THF in a yield of 83%. All N-Boc-protected bispines 3-6 were easily purified by column chromatography on SiO₂ or Al₂O₃ (for ferrocene compound 6). Finally, lithium aluminum hydride reduction of 6 generated in almost quantitative yield N-methyl-N-ferrocenylmethylbispinedine 7 (96%), that did not require any purification. Bispinedine 7 was isolated as the orange oil that is quite stable in the solid state and less stable in solution.

The direct cyclopalladation of N-methyl-N-ferrocenylmethylbispinedine 7 was carried out in a three different ways, but the only one pincer palladium complex 8 was isolated in all cases. The attempts to isolate other Pd complexes, CN cyclopalladium or NN coordination, from the reaction mixture failed. The most efficiently was found to proceed the reaction of 7 and Li₂PdCl₄ in the presence of stoichiometric amounts of sodium monohydrate in methanol at room temperature. This reaction afforded a 67% yield of complex 8. The interaction of 7 with PdCl₂(CH₂CN)₂ in CH₂Cl₂ at room temperature resulted in the isolation of the compound 8 in a yield of 23%. Only 14% yield of the palladium complex 8 was achieved in the reaction of ligand 7 with Na₂PdCl₄ and sodium acetate monohydrate in methanol at room temperature. The unsymmetrical pincer palladium complex 8 was isolated as an orange crystalline compound, air and moisture stable both in the solid state and in solution. It is insoluble in most of the common solvents (benzene, toluene, ethyl acetate, ether, acetone etc.), slightly soluble in chloroform and moderately in dichloromethane.

The structures of the two new ferrocene bispinedine derivatives 6 and 7 and complex 8 were determined using NMR (¹H, ¹³C and ¹⁵N), IR, EI-MS spectroscopy data and were confirmed by elemental analyses and X-ray diffraction analysis (for complex 8). The assignment of the signals in NMR spectra has been performed by the use of 2D COSY, HMOC, HMB(C)(¹H,¹⁵N) and HMBC(¹H,¹⁵N) techniques. The numbering of atoms used for NMR assignment is shown in Scheme 1.

Thus, the IR data of compounds 6-8 demonstrated the presence of the group of bands relating to the vibrations of ferrocene framework, the disappearance of the band 1690 cm⁻¹ corresponding to the carbonyl group while going from N-Boc-N-ferrocenylmethylbispinedine 6 to N-methyl-N-ferrocenylmethylbispinedine 7, the appearance of intense bands 345 and 285 cm⁻¹ relating to the vibrations of Pd-Cl bonds in the IR spectra of palladium complex 8.

The ¹H NMR spectrum of complex 8 is consistent with orthometalation of ferrocene ring. A decrease of the overall intensity of cyclopentadienyl protons in the ¹H NMR spectrum of the complex 8 corresponds to the presence of 1,2-disubstituted ferrocene ring and confirms the occurrence of metalation. The above result is in a good agreement with the elemental analysis data. In the ¹³C NMR spectrum of complex 8 the resonance of the new quaternary aromatic carbon (C15-Pd) appeared at 92.67 ppm, which is consistent with previously published data for the other ferrocene cyclopalladated complexes [13]. The resonance of another aromatic quaternary carbon (C11-C), which appeared in the ligand 7 at 82.76 ppm, in the complex 8 obviously shifted downfield and observed at 94.69 ppm, as it was noted for the pincer complex 2 [8]. The comparison of the ¹H NMR spectrum of the ligand 7 with that of the corresponding complex 8 indicates the downfield shift of
most alkyl protons upon complex formation. It should be noted, that all signals in the proton spectrum of compound 7 are quite broadened, probably due to the partial oxidation of the ferrocenyl moiety during the registration of the NMR spectrum. Each proton of bispide frame as well as the protons of CH₂ at the position 10 displayed separate signals in the ¹H NMR spectrum of compound 8. The methylene protons at the position 9 must be magnetically nonequivalent both in the complex 8 and in the ligand 7, owing to the nitrogen atoms in positions 3 and 7 have different substituents (CH₂Fc and CH₃). A difference in the shielding of those protons in the complex 8 (0.09 ppm) is considerably more than in the ligand 7 (0.02 ppm). Due to the fact that the FeCp fragment is located in a plane perpendicular to the coordination plane of the Pd atom, the CH protons at the positions 1 and 5 are magnetically nonequivalent. The CH₂ protons pairs at the positions 2, 4, 6, 8, and 10 become diastereotopic probably due to the influence of the magnetic anisotropy of the above fragment. This influence is also evident in the fact, that in each pair of the diastereotopic methylene protons of NCH₂-groups the proton, which is in a lower field, is noticeably broadened. The CH₂ protons of benzyl group in the position 10 formed the AB system, upper field component of which is appreciably more broadened in comparison with the downfield one probably due to more close proximity one of these protons to the FeCp fragment. From the above data it follows that 8 represents an unsymmetrical pincer CNN palladium complex wherein the palladium atom is coordinated with two nitrogen atoms. This is confirmed by the chemical shifts of ¹⁵N nuclei obtained from spectra HMBC (¹H, ¹⁵N). In going from the ligand 7 to the complex 8 the shielding of both nitrogen atoms at the position 3 and at the position 7, increases (Δδ = 5.6 and 16.3 ppm correspondingly) that consistent with the literature data for the ¹⁵N chemical shifts of sp²-hybridized nitrogen atoms coordinated to a palladium atom [14].

The molecular structure of complex 8 was confirmed by the X-ray analysis. A single crystal of 8 was grown by slow evaporation of CH₂Cl₂ solution. According to XRD complex 8 crystallizes in the racemic space group P-1 (Fig. 3). The palladium atom is characterized by square-planar environment that is coincide with the mirror plane of bispide ligand. The latter is characterized by chair-chair conformation. The conformation of the 5-membered Pd(1), N(3), C(11), C(15), C(10) cycle is flattened envelope with the deviation of C(10) atom by 0.103(6)Å. The cyclopentadienyl rings are in eclipsed conformation. The coordination with palladium does not perturb C-C bonds in cyclopentadienyl ring (bonds are 1.419(6)-1.431(6) for C₅H₅ vs. 1.414(6)-1.430(6) for C₅H₅Fe one), while cause some elongation of Fe(1)–C(15) bond up to 2.069(4) Å in comparison with the rest ones (2.026(4)-2.050(4) Å). All intra- and intermolecular contacts in 8 correspond to the normal Van-der-Waals C···H, C···Cl and C···C interactions.

Scheme 1. Synthesis of the ligand 7 and unsymmetrical CNN pincer palladium complex 8.

Fig. 3. The general view of 8 in crystal in representation of non-hydrogen atoms by probability ellipsoids of atomic displacements (p = 50%). Selected bond lengths (Å): Pd(1)–C(14) 1.944(4), Pd(1)–N(3) 2.097(4), Pd(1)–N(7) 2.175(4), Pd(1)–Cl(1) 2.3074(10), N(3)–C(4) 1.497(5), N(3)–C(10) 1.525(6), N(7)–C(17) 1.471(6), N(7)–C(8) 1.491(6); bond angles (°) C(15)-Pd(1)-N(3) 84.34(16), C(15)-Pd(1)-N(7) 171.69(16), N(3)-Pd(1)-N(7) 87.43(14), N(3)-Pd(1)-Cl(1) 90.94(13), N(3)-Pd(1)-Cl(1) 175.07(10), N(7)-Pd(1)-Cl(1) 173.41(11), C(2)-N(3)-C(4) 109.9(3), C(2)-N(3)-C(10) 107(3), C(4)-N(3)-C(10) 110.2(3), C(2)-N(3)-Pd(1) 109.0(3), C(4)-N(3)-Pd(1) 108.7(3), C(10)-N(3)-Pd(1) 111.1(3), C(17)-N(7)-C(6) 108.6(4), C(17)-N(7)-C(8) 108.5(4), C(6)-N(7)-C(8) 111.3(4), C(17)-N(7)-Pd(1) 113.4(3), C(6)-N(7)-Pd(1) 108.4(3), C(8)-N(7)-Pd(1) 106.7(3).
2.2. Catalytic studies

In this paper we present the study results of the catalytic activity of the new pincer complex 8 in several cross-coupling Suzuki reactions (Table 1). All the experiments were carried out under the conditions adopted previously in our investigations for the other unsymmetrical pincer CNN palladium complex with ferrocenyl ligand C (Fig. 1) [11a]. This allowed us to make a correct comparison between catalytic data for complexes 8 and C, obtained both in the previous and in the present works.

The Suzuki cross-coupling reactions were conducted with the phenylboronic acid and three aryl bromides in MeOH/H2O for 5 h with K2CO3 as a base. When the reactions were carried out at 55 °C all aryl bromides demonstrated equally high yields of the products (Table 1, entries 1–3). Comparative results were shown in the reactions of these aryl bromides in the same conditions with the complex C [11a]. However, the complex 8 proved to be an active catalyst in the Suzuki reaction also at ambient temperature and afforded 74–90% yields of corresponding biphenyls (Table 1, entries 4–6) in contrast to the complex C, which was not effective at room temperature even when the reactions were carried for 24 h [11a].

According to the presented results the better catalytic activity in the Suzuki reactions was demonstrated by bipyridine-containing complex 8 with Pd coordinated with two N(sp3) atoms. Less active appeared to be bipyridine-containing complex C with Pd coordinated with two N(sp3). It was previously shown that both Pd-N(sp2) bonds in the complex C are equally stable [15]. But in the other ferrocenyl CNN pincer complexes with Pd coordinated to N(amime) and N(imine) the bond Pd-N(sp3) is more resistant that the Pd-N(sp2) one [10a,b]. From this point of view the complex C must be more stable than 8. It can be assumed that the higher stability of the complex C possibly would lead to the slower generation of the true catalytic active Pd(0) particles and to the lower activity of the complex C as it was mentioned before concerning the other palladium palladacycles [9a].

In addition to the Suzuki reaction, the complex 8 showed catalytic activity in other cross-coupling reactions (Table 2). The yields of the products were excellent in the reactions of the Heck hydroarylation of 2-norbornene (entries 1–2) and only moderate in the Heck reaction (entries 3–4).

In all cross-coupling experiments the formation of small amounts of black palladium nanoparticles was observed, which is typical for the processes involving phosphine-free cyclopalladated catalytic systems [16].

Table 1
The results of catalytic cross-coupling Suzuki reaction.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>T (°C)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>55</td>
<td>9a-c</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>MeO</td>
<td>55</td>
<td>9b</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>Me(C-O)</td>
<td>55</td>
<td>9c</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>Me</td>
<td>21</td>
<td>9a</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>MeO</td>
<td>21</td>
<td>9b</td>
<td>77</td>
</tr>
<tr>
<td>6</td>
<td>Me(C-O)</td>
<td>21</td>
<td>9c</td>
<td>90</td>
</tr>
</tbody>
</table>

a Reaction conditions: aryl bromide (1 mmol), PhB(OH)2 (1.5 mmol), K2CO3 (2.0 mmol), cat. 8 (0.5 mol %), MeOH (8 ml), H2O (4 ml), 5 h.

Table 2
The results of catalytic cross-coupling Heck hydroarylation of 2-norbornenea and Heck reaction.b

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Hal</th>
<th>Partner reagent</th>
<th>Cat 8 (mol%)</th>
<th>T (°C)</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>I</td>
<td>2-Norbornene</td>
<td>0.1</td>
<td>65</td>
<td>10a</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>MeO</td>
<td>I</td>
<td>2-Norbornene</td>
<td>0.1</td>
<td>65</td>
<td>10b</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>Br</td>
<td>Ethylacrylate</td>
<td>0.5</td>
<td>140</td>
<td>11a</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>MeO</td>
<td>Br</td>
<td>Ethylacrylate</td>
<td>0.5</td>
<td>140</td>
<td>11b</td>
<td>75</td>
</tr>
</tbody>
</table>

a Reaction conditions: aryl iodide (1 mmol), 2-norbornene (3.4 mmol), HCO2H (3 mmol), Et3N (1.8 mmol), DMSO (5 ml), 5 h.

b Reaction conditions: aryl bromide (1 mmol), ethyl acrylate (1.5 mmol), K2CO3 (2 mmol), DMF (5 ml), 5 h.

3. Conclusion

In summary, we have synthesized the new unsymmetrical ferrocenyl containing ligand based on the bispidine frame. The corresponding palladium CNN pincer complex 8, wherein the palladium is coordinated with two N(sp3) atoms, was prepared by direct cyclopalladation of the ligand precursor and appeared to be the efficient catalyst in some cross-coupling reactions of aryl halides with phenylboronic acid, norbornene and ethyl acrylate. Catalytic activity of palladacycle 8 in the Suzuki reactions appeared to be higher than that of the complex C where Pd is coordinated with two N(sp2) atoms.

4. Experimental

4.1. General

The NMR experiments were carried out using a Bruker Avance™ 600 spectrometer operating at 600.22 MHz for 1H and 150.93 MHz for 13C, Bruker Avance™ 500 (500.13 and 125.77 MHz), Bruker Avance™ 400 (400.13 and 100.61 MHz). The spectrometers were equipped with inverse gradient probe-head. 1H chemical shift data are given in units δ relative TMS calibrated with residual protonic solvent (CHCl3 at 7.26 ppm and CD2Cl2 at 5.33 ppm). The multiplicities of a signal is indicated as follows: s, singlet; d, doublet; m, multiplet; dd, doublet of doublets. 13C chemical shifts are given relative TMS calibrated to the solvent, CDC13 at 77.26 ppm and CD2Cl2 at 54.24 ppm. 1H and 13C chemical shifts were measured and assigned by 2D experiments. 2D inverse proton detected heteronuclear shift correlation spectra, gs-HMQC (1H-13C) and gs-HMBC (1H-13C) were obtained using standard pulse sequence from the Bruker library. 2D gradient selected 1H-13N HMBC experiment was recorded on a 600 MHz Bruker spectrometer (1H: 600.22 MHz; 13N:60.83 MHz) using a 5 mm broadband probe with 2-gradient; the spectral widths of 1H and 15N dimensions were 6 and 30 kHz, respectively; 16 scans were acquired for each t1 increment with total 128 increments; 100 ms was used for the evolution time of J1H,15N couplings (5 Hz). The data was processed with zero-filling on F1 and F2 dimension. The 13N chemical shifts have been measured relative to neat CH3NO2.

El mass spectra were taken on a FINNIGAN POLARIS Q spectrometer at 70 eV and the temperature of the ion chamber 250 C.
spectra were recorded on a FT-IR Tensor 37 spectrometer (Bruker) in KBr pellets, thin film or nujol. The assignment of absorption bands in the IR spectra was made according to ref. [17]. Ferrocene-carboxaldehyde [18] and PhB(OH)₂ [19] were obtained according to the literature procedures. All other chemicals and solvents were used as purchased. All prepared in cross-coupling reactions products had been reported previously and were characterized by comparison with their reported ¹H NMR spectra.

4.2. 3-Benzyl-7-((tert-butoxycarbonyl)-3,7-diazabicyclo[3.3.1]non-9-one, 3

To a boiling suspension of paraformaldehyde (6 g, 0.2 mol) in MeOH (80 ml) was added dropwise a solution of N-Boc-4-oxopiperidine (10 g, 0.05 mol), benzylamine (5.45 ml, 0.05 mol) and acetic acid (2.86 ml, 0.05 mol) in 80 ml of MeOH. The mixture was refluxed with stirring for 6 h, diluted with water, extracted with CH₂Cl₂, washed with NaHCO₃ water solution, brine, dried over Na₂SO₄ and evaporated. The residue was purified by SiO₂ column chromatography with AcOEt/petroleum ether (1/4) to afford 3 (12.1 g, 74%) as a colorless oil. IR (thin film, cm⁻¹): 1733 (C=O), 1694 (OC=O); 737, 700 (C₅H₅), El-MS, m/z (RI %): 330 [M⁺] (5), 273 [M⁺-Bu'] (73), 229 [M⁺-C₅H₅] (16), 1H NMR (400 MHz, CDCl₃) δ 3.74–7.24 (m, 5H, Ph), 4.59 (d, J = 13.3 Hz, 1H, CH₂NBoc), 4.43 (d, J = 13.3 Hz, 1H, CH₂NBoc), 3.54 (d, J = 13.2 Hz, 1H, CH₂Ph), 3.48 (d, J = 13.2 Hz, 1H, CH₂Ph), 3.42–3.32 (m, 4H, CH₂NBoc, CH₂N(Boc)N), 2.77–2.61 (m, 2H, CH₂N[Boc]N), 2.44 (s, 1H, CH), 2.41 (br s, 1H, CH), 1.55 (s, 9H, CMe₃). ¹³C NMR (101 MHz, CDCl₃) δ 213.58 (C=O), 154.75 (C=O, Boc), 137.43 (ipso-Ph), 128.75 (o-Ph), 128.32 (m-Ph), 127.24 (p-Ph), 80.04 (CMe₃), 61.82 (CH₂Ph), 59.03 and 58.67 (CH₂N(Boc)), 50.45 and 49.75 (CH₂NBoc), 47.55 (CH), 28.58 (CMe₃).

4.3. 3-Benzyl-7-((tert-butoxycarbonyl)-3,7-diazabicyclo[3.3.1]nonane, 4

To a stirring at 70 °C solution of 3 (12.1 g, 0.037 mol), hydrazine monohydrate (9 ml, 0.184 mol) and diglyme (60 ml) was added KOH (14.5 g, 0.259 mol). The mixture was stirred at 150 °C 6 h, cooled to 80 °C, diluted with water (150 ml) and stirred for 30 min. The resulting mixture was extracted with petroleum ether (3 × 150 ml). The combined organic layers were washed with water, brine, dried over Na₂SO₄ and evaporated. The residue was purified by SiO₂ column chromatography with AcOEt/petroleum ether (1/9) to afford 4 (7.7 g, 66%) as a colorless oil. IR (thin film, cm⁻¹): 1689 (OC=O), 736, 699 (C₅H₅), El-MS, m/z (RI %): 37 [M⁺-H] (21), 259 [M⁺-t-Bu'] (100), 215 [M⁺-Boc⁺] (39). ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.22 (m, 5H, Ph), 4.19 (d, J = 13.0 Hz, 1H, CH₂NBoc), 4.02 (d, J = 13.1 Hz, 1H, CH₂NBoc), 3.47 (d, J = 13.6 Hz, 1H, CH₂Ph), 3.32 (d, J = 13.6 Hz, 1H, CH₂Ph), 3.20–2.97 (m, 3H, CH₂NBoc, CH₂NBn), 2.91 (d, J = 10.8 Hz, 1H, CH₂NBn), 2.25 (d, J = 10.8 Hz, 1H, CH₂NBn), 2.18 (d, J = 10.8 Hz, 1H, CH₂Bn), 1.90 (br s, 1H, CH), 1.81 (br s, 1H, CH), 1.68 and 1.62 (2H, AB system, J = 12.2 Hz, 2H, CH₂, 1.55 (s, 9H, CMe₃). ¹³C NMR (101 MHz, CDCl₃) δ 155.08 (C=O), 139.03 (ipso-Ph), 128.59 (o-Ph), 128.07 (m-Ph), 126.63 (p-Ph), 78.73 (CMe₃), 63.51 (CH₃Ph), 59.03 and 58.74 (CH₂NBn), 48.42 and 47.59 (CH₂NBoc), 31.18 (CH₃), 29.00 (CH), 28.73 (CMe₃).

4.4. 3-(tert-Butoxycarbonyl)-3,7-diazabicyclo[3.3.1]nonane, 5

A mixture of 4 (20 g, 0.063 mol), ammonium formate (16 g, 0.254 mol) and 5% Pd/C (contains 50% H₂, 4 g) in MeOH (350 ml) was refluxed with stirring for 1 h, cooled and filtered through celite. The solution was evaporated to the volume of 100 ml and 10 N NaOH (100 ml) was added. The mixture was refluxed with stirring for 1 h, extracted with CHCl₃, washed with brine, dried over Na₂SO₄ and evaporated. The residue was purified by SiO₂ column chromatography with CHCl₃/MeOH (9/1) to afford 5 (12.2 g, 85%) as a colorless oil. IR (thin film, cm⁻¹): 1691 (OC=O), El-MS, m/z (RI %): 227 [M⁺+H] (68), 169 [M⁺-Bu'] (72), 126 [M⁺-Boc⁺] (48). ¹H NMR (600 MHz, CDCl₃) δ 4.14–4.05 (m 2H, CH₂NBoc), 3.19–3.02 (m, 4H, CH₂NBoc, CH₂NHB), 2.97 (d, J = 13.1 Hz, 2H, CH₂NHB), 1.89 and 1.77 (d, AB system, J = 12.6 Hz, 2H, CH₂), 1.72–1.55 (m, 3H, 2CH₃-NH), 1.47 (s, 9H, CMe₃). ¹³C NMR (151 MHz, CDCl₃) δ 155.43 (C=O, Boc), 79.61 (CMe₃), 51.82 (CH₂NHB), 49.46 and 48.42 (CH₂NBoc), 31.57 (CH₂), 28.51 (CMe₃), 28.28 (CH).
4.7. (7-Methyl-3,7-diazabicyclo[3.3.1]nonan-3-ylmethyl)ferrocenyl-[C,N,N]-palladium chloride, 8

Method A: To a solution of Na2PdCl4 (0.458 g, 1.56 mmol) and sodium acetate monohydrate (0.212 g, 1.56 mmol) in MeOH (30 ml) and H2O (10 ml) was added a solution of 7 (0.526 g, 1.56 mmol) in 10 ml of MeOH. The mixture was stirred for 6 h at room temperature, filtered through celite and evaporated. The crude was mixed with water and extracted with chloroform. The organic layers were dried over Na2SO4, filtered, evaporated and purified by SiO2 column chromatography (CHCl3, then CHCl3/MeOH = 10:1) to afford 8 (0.112 g, 14%).

Method B: To a suspension of PdCl2 (0.157 g, 1.60 mmol) and sodium acetate monohydrate (0.072 g, 1.90 mmol) in MeOH (15 ml) was added a solution of 7 (0.205 g, 0.60 mmol) in 15 ml of CH2Cl2. The mixture was stirred for 6 h at room temperature, evaporated and purified by SiO2 column chromatography (CHCl3, then CHCl3/MeOH = 10:1) to afford 8 (0.072 g, 23%).

Method C: A mixture of PdCl2 (0.284 g, 1.60 mmol) and lithium chloride (0.081 g, 1.90 mmol) in MeOH (15 ml) was stirred for 5 h and cooled. To the obtained solution was added a solution of 7 (0.539 g, 1.60 mmol) and sodium acetate monohydrate (0.516 g, 67%) as an orange crystals. Decomposes without melting at 110 °C. The remaining material was filtered through celite and evaporated. The crude was mixed with water and extracted with chloroform. The organic layers were dried over Na2SO4, filtered, evaporated and purified by SiO2 column chromatography (CHCl3, then CHCl3/MeOH = 10:1) to afford 8 (0.516 g, 67%) as an orange crystals. Decomposes without melting at about 180 °C. Anal. C, 47.31; H, 5.27; N, 5.84; Cl, 7.58%. Calc. for C20H25ClFeN2Pd: C, 47.53; H, 5.46; N, 5.83; Cl, 7.38%. IR (KBr, ν/cm−1): 1100, 994, 813, 480 (FcH); IR (nujol, ν/cm−1): 343.4 (N3).

4.8. General procedure for the Suzuki reaction

To the solution of phenylboronic acid (1 mmol) in MeOH (8 ml) and H2O (4 ml) was added consistently K2CO3 (2 mmol), aryl bromide (1 mmol) and palladium complex 8 (0.5 mol %). The mixture was stirred at ambient temperature or heated at 55 °C for 5 h. Then it was diluted with water and extracted with CHCl3. The combined organic phase was dried over Na2SO4, evaporated and purified by chromatography on SiO2 (petroleum ether/CH3Cl).

4.9. General procedure for the Heck hydroarylation of 2-norbornene

A mixture of aryl iodide (1 mmol), 2-norbornene (3.4 mmol), HCO2H (3 mmol), Et3N (3.8 mmol), palladium complex 8 (0.1 mol %), and DMSO (5 ml) was stirred at 65 °C for 5 h. After the reaction mixture was cooled to ambient temperature, it was diluted with water and extracted with petroleum ether. The combined organic layers were dried over Na2SO4, evaporated and purified by chromatography on SiO2 (petroleum ether).

4.10. General procedure for the Heck coupling reaction

A mixture of aryl bromide (1 mmol), ethyl acrylate (1.5 mmol), K2CO3 (2 mmol), palladium complex 8 (0.5 mol %) and DMF (5 ml) was stirred at 140 °C for 5 h. After the reaction mixture was cooled to ambient temperature, it was diluted with water and extracted with AcOEt. The combined organic layers were dried over Na2SO4, evaporated and purified by chromatography on SiO2 (petroleum ether/AcOEt).

4.11. X-ray crystallography

X-ray diffraction data for 8 were collected on a Bruker APEX II diffractometer (X(MoKα) = 0.71072 Å, 2θ < 56.5°, Φ and ω scans with 0.5° scan step and 10 s per frame exposure). Red crystals of C20H25ClFeN2Pd at 120(2) K are triclinic, space group P-1, a = 8.7118(10), b = 10.6395(12), c = 11.0454(17), α = 116.370(2), β = 79.606(3), γ = 76.765(2)°, V = 871.24(19) Å3, Z = 2, dcalc = 1.826 g cm−3. The indexing revealed that the structure was twinned. Frames were integrated by a narrow-frame algorithm using SAINT software package [20], both twin domains were included in the integration. Semi-empirical absorption correction was applied with TWINABS [21] program using intensity data for equivalent reflections. Intensities of 4356 independent reflections (Rint = 0.0719) out of 7356 collected were used in structure solution and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F2 in the anisotropic-isotropic approximation. The positions of hydrogen atoms were calculated. Hydrogen atoms were refined in riding model with Uiso(H) equal to 1.5 Ueq(C) and 1.2 Ueq(C) of the connected methyl and other carbon atoms. The refinement converged to R1 = 0.0422 (calculated for 3828 observed reflections with I > 2σ(I)), wR2 = 0.0973 and GOF = 1.042. The refinement was performed with SHELXL software package [22]. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center, CCDC number 1538852.

References
