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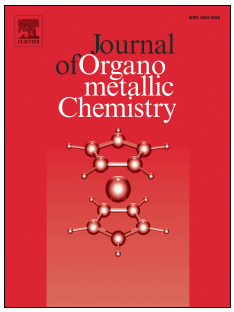

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PII: S0022-328X(17)30404-7

DOI: 10.1016/j.jorganchem.2017.06.009

Reference: JOM 19996

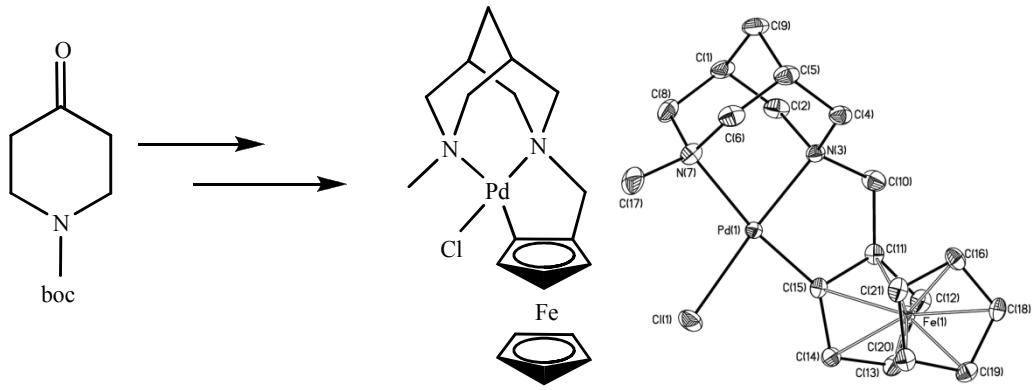
To appear in: *Journal of Organometallic Chemistry*

Received Date: 5 April 2017

Revised Date: 9 June 2017

Accepted Date: 9 June 2017

Please cite this article as: L.A. Bulygina, N.D. Kagramanov, N.S. Khrushcheva, K.A. Lyssenko, A.S. Peregudov, V.I. Sokolov, Unsymmetrical pincer CNN palladium complex of 7-ferrocenylmethyl-3-methyl-3,7-diazabicyclo[3.3.1]nonane, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.06.009.



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

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Abstract

The new unsymmetrical ferrocenyl containing bispidine derivative **7** was synthesized as a ligand precursor 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 Li_2PdCl_4 in MeOH. The molecular structure of the obtained palladacycle was determined by multinuclear NMR (^{1}H, ^{13}C, ^{15}N) 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.

Keywords: Ferrocene; Bispidine; Unsymmetrical CNN pincer palladium(II) complex; Catalytic activity; C-C Cross-coupling reactions

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 derivatives, having in α-position C = N bond (imines, oximes, etc.) in which the nitrogen atom is sp^2 hybridized. Stable dimeric cyclopalladates could be isolated usually when the substituents on the nitrogen atoms were two methyl [1, 2] or ethyl [3] groups. The attempts to obtain cyclopalladium complexes of the ferrocenylalkylamines 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 majority of known non-symmetrical ferrocene CNN pincer complexes at least one N atom is sp^2 hybridized (Fig. 1, **A**-**D**).

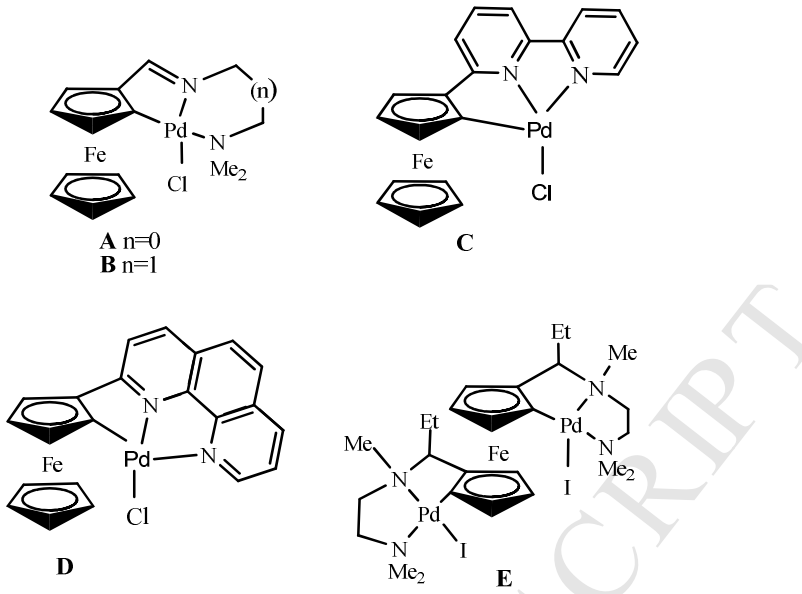


Fig.1. Examples of known ferrocenyl unsymmetrical CNN pincer palladium complexes.

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 sp^3 (Fig.1, **E**). Thus it can be expected that by using the ligand with an appropriate structure including the ferrocenylmethyl group and two amino groups it is possible to obtain a stable pincer Pd complex with two N(sp^3) 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.

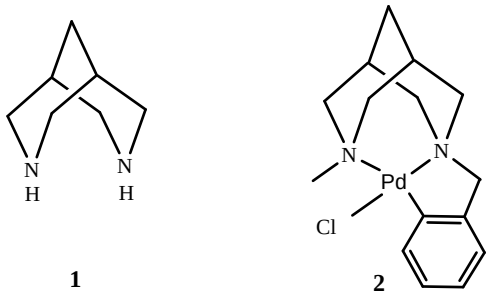


Fig.2. 3,7-diazabicyclo[3.3.1]nonane **1** and unsymmetrical CNN pincer palladium complex **2.**

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 cycloplatinum 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 sp^3 hybridization.

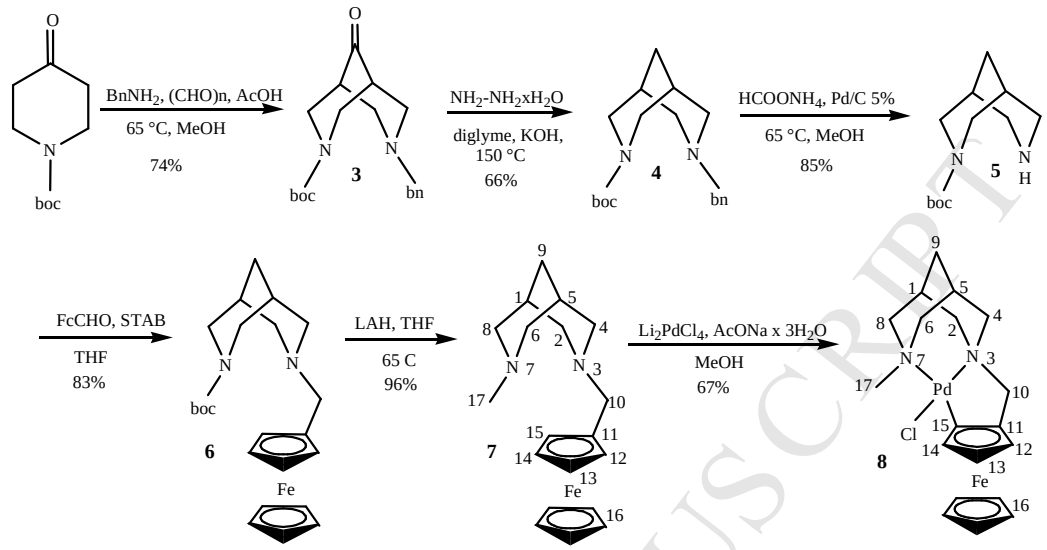
Synthesis and study of the catalytic properties in the cross-coupling reactions of unsymmetrical CNN pincer palladium complexes is the subject of many investigations. All of them refer to those compounds in which the palladium atom is attached to an aromatic ring [9]. Ferrocene complexes of similar structure 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.



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

First, according to the previously published methods [12], N-benzyl-N-Boc-bispidinone **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 bispidine **4**. The N-benzyl protecting group was cleaved from N-benzyl-N-Boc-bispidine **4** using palladium on activated charcoal (5%) as a catalyst and ammonium formate as a hydrogen source. N-Boc-bispidine **5** was isolated in a yield of 85%. N-Boc-N-ferrocenylmethylbispidine **6** was synthesized by the reductive amination of ferrocenecarboxaldehyde with **5** and sodium triacetoxyborohydride in THF in a yield of 83%. All N-Boc-protected bispidines **3-6** were easily purified by column chromatography on SiO_2 or Al_2O_3 (for ferrocene compound **6**). Finally, lithium aluminum hydride reduction of **6** generated in almost quantitative yield N-methyl-N-ferrcenylmethylbispidine **7**

(96%), that did not require any purification. Bispidine **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-ferrocenylmethylbispidine **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 Li_2PdCl_4 in the presence of stoichiometric amounts of sodium acetate monohydrate in methanol at room temperature. This reaction afforded a 67% yield of complex **8**. The interaction of **7** with $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 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 Na_2PdCl_4 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 bispidine derivatives **6** and **7** and complex **8** were determined using NMR (^1H, ^{13}C and ^{15}N), 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, HMQC, HMBC(^1H,^{13}C) и HMBC(^1H,^{15}N) 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-ferrocenylmethylbispidine **6** to N-methyl-N-ferrocenylmethylbispidine **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 ^{1}H NMR spectrum of complex **8** is consistent with *ortho*-metallation of ferrocene ring. A decrease of the overall intensity of cyclopentadienyl protons in the ^{1}H 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 ^{13}C 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 ^{1}H 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 bispidine frame as well as the protons of CH_2 at the position 10 displayed separate signals in the ^{1}H NMR spectrum of **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 (CH_2Fc and CH_3). 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 CH_2 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 NCH_2-groups the proton, which is in a lower field, is noticeably broadened. The CH_2 protons of benzyl group in the position 10 formed the AB system, upfield 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 a unsymmetrical pincer CNN palladium complex wherein the palladium atom is coordinated with two nitrogen atoms. This is confirmed by the chemical shifts of ^{15}N nuclei obtained from spectra HMBC (^{1}H, ^{15}N). In going from the ligand **7** to the complex **8** the shielding of the both nitrogen atoms at the position 3 and at the position 7, increases ($\Delta\delta$ = 5.6 and 16.3 ppm correspondingly) that consistent with the literature data for the ^{15}N chemical shifts of sp^3-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 CH_2Cl_2 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 bispidine 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 C_5H_4 vs. 1.414(6)-1.430(6) for C_5H_3CPd 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, H…Cl and C…C interactions.

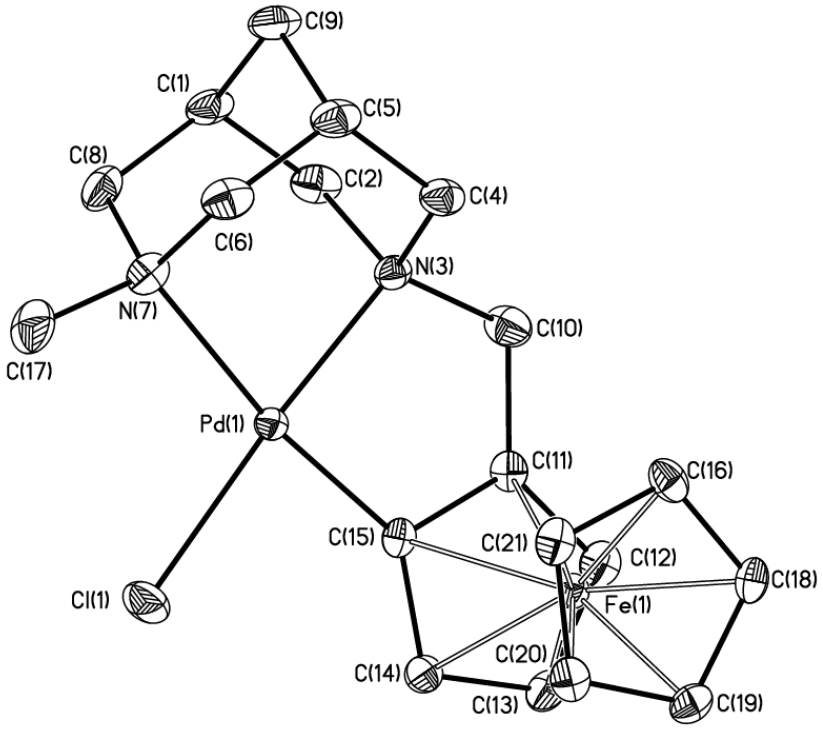


Fig.3. The general view of **8** in crystal in representation of non-hydrogen atoms by probability ellipsoids of atomic displacements (p=50%). Selected bond lengths (Å): Pd(1)-C(15) 1.944(4), Pd(1)-N(3) 2.097(4), Pd(1)-N(7) 2.175(4), Pd(1)-Cl(1) 2.3074(10), N(3)-C(4) 1.497(5), N(3)-C(10) 1.525(6), N(7)-C(17)

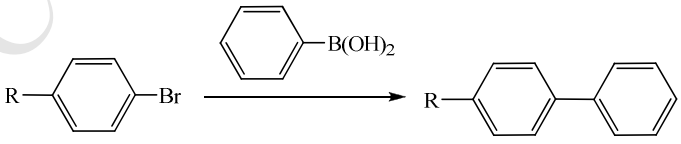
1.471(6), N(7)-C(8) 1.491(6); bond angles (°) C(15)-Pd(1)-N(3) 84.34(16), C(15)-Pd(1)-N(7) 171.69(16), N(3)-Pd(1)-N(7) 87.43(14), C(15)-Pd(1)-Cl(1) 90.94(13), N(3)-Pd(1)-Cl(1) 175.07(10), N(7)-Pd(1)-Cl(1) 97.31(11), C(2)-N(3)-C(4) 109.9(3), C(2)-N(3)-C(10) 107.9(3), C(4)-N(3)-C(10) 110.2(3), C(2)-N(3)-Pd(1) 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.

Table 1

The results of catalytic cross-coupling Suzuki reaction [a].



9 a-c

Entry	R	T (°C)	Product	Yield[b] (%)
1	Me	55	**9a**	98
2	MeO	55	**9b**	89

3	Me(C=O)	55	**9c**	99
4	Me	21	**9a**	74
5	MeO	21	**9b**	77
6	Me(C=O)	21	**9c**	90

[a] *Reaction conditions:* aryl bromide (1 mmol), $PhB(OH)_2$ (1.5 mmol), K_2CO_3 (2.0 mmol), cat. **8** (0.5 mol %), MeOH (8 mL), H_2O (4 ml), 5 h.

[b] Isolated yields after column chromatography.

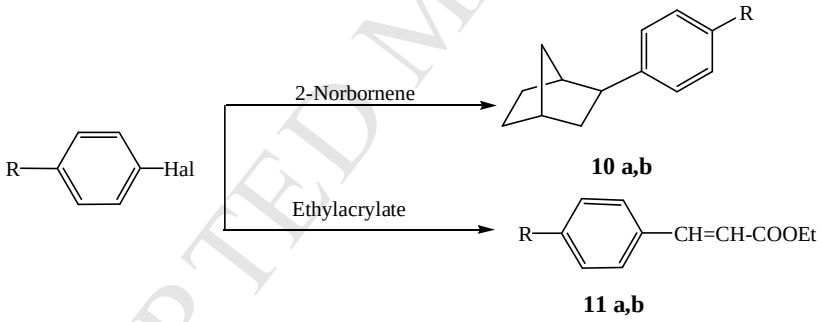
The Suzuki cross-coupling reactions were conducted with the phenylboronic acid and three aryl bromides in $MeOH/H_2O$ for 5 h with K_2CO_3 as a base. When the reactions were carried out at 55° C all aryl bromides demonstrated equally high yields of the products (Table 1, entries 1-3). Comparative results 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 bispidine-containing complex **8** with Pd coordinated with two N(sp^3) atoms. Less active appeared to be bipyridine-containing complex **C** with Pd coordinated with two N(sp^2). It was previously shown that both Pd-N (sp^2) bonds in the complex **C** are equally stable [15]. But in the other ferrocenyl CNN pincer complexes with Pd coordinated to N(amine) and N(imine) the bond Pd-N(sp^2) is more resistant that the Pd-N(sp^3) one [10 a, 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 pincer palladium complexes [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)

Table 2

The results of catalytic cross-coupling Heck hydroarylation of 2-norbornene [a] and Heck reaction [b].



Entry	R	Hal	Partner reagent	Cat **8** (mol%)	T (°C)	Product	Yield[c] (%)
1	H	I	2-Norbornene	0.1	65	**10a**	97
2	MeO	I	2-Norbornene	0.1	65	**10b**	95
3	Me	Br	Ethylacrylate	0.5	140	**11a**	48
4	MeO	Br	Ethylacrylate	0.5	140	**11b**	75

[a] *Reaction conditions:* aryl iodide (1 mmol), 2-norbornene (3.4 mmol), HCO_2H (3 mmol), Et_3N (3.8 mmol), DMSO (5 ml), 5 h.

[b] *Reaction conditions:* aryl bromide (1 mmol), ethyl acrylate (1.5 mmol), K_2CO_3 (2 mmol), DMF (5 ml), 5 h.

[c] Isolated yields after column chromatography.

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].

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(sp^3) 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(sp^2) atoms.

4. Experimental

General

The NMR experiments were carried out using a Bruker Avance^{TM} 600 spectrometer operating at 600.22 MHz for ^{1}H and 150.93 MHz for ^{13}C, Bruker Avance^{TM} 500 (500.13 and 125,77 MHz), Bruker Avance^{TM} 400 (400.13 and 100.61 MHz). The spectrometers were equipped with inverse gradient probe-head. ^{1}H chemical shift data are given in units δ relative TMS calibrated with residual protonic solvent ($CHCl_3$ at 7.26 ppm and CD_2Cl_2 at 5.33 ppm). The multiplicity of a signal is indicated as follows:br, broad; s, singlet; d, doublet; m,

multiplet; dd, doublet of doublets. ^{13}C chemical shifts are given relative TMS calibrated to the solvent, $CDCl_3$ at 77.26 ppm and CD_2Cl_2 at 54.24 ppm . ^{1}H and ^{13}C chemical shifts were measured and assigned by 2D experiments. 2D inverse proton detected heteronuclear shift correlation spectra, gs-HMQC (^{1}H-^{13}C) and gs-HMBC (^{1}H-^{13}C) were obtained using standard pulse sequence from the Bruker library. 2D gradient selected ^{1}H-^{15}N HMBC experiment was recorded on a 600 MHz Bruker spectrometer (^{1}H: 600.22 MHz; ^{15}N:60.83 MHz) using a 5 mm broadband probe with z-gradient; the spectral widths of ^{1}H and ^{15}N 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 J_{NH} couplings (5Hz). The data was processed with zero-filling on F1 and F2 dimension. The ^{15}N chemical shifts have been measured relative to neat CH_3NO_2.

EI mass spectra were taken on a FINNIGAN POLARIS Q spectrometer at 70 eV and the temperature of the ion chamber 250 C. IR 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]. Ferrocenecarboxaldehyde [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 ^{1}H NMR spectra.

3-Benzyl-7-(tert-butyloxycarbonyl)-3,7-diazabicyclo[3.3.1]nonan-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 CH_2Cl_2, washed with $NaHCO_3$ water solution, brine, dried over Na_2SO_4 and evaporated. The residue was purified by SiO_2 column chromatography with AcOEt/petroleum ether (1/4) to afford **3** (12.1 g, 74 %) as a colorless oil. IR (thin film, ν , cm $^{-1}$): 1733 (C=O), 1694 (OC=O), 737, 700 (C_6H_5). EI-MS, m/z (RI, %): 330 $[M]^+$ (5), 273 $[M\text{-}t\text{-}Bu]^+$ (73), 229 $[M\text{-}Boc]^+$ (16). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5H, Ph), 4.59 (d, *J* = 13.3 Hz, 1H, CH_2NBoc), 4.43 (d, *J* = 13.3 Hz, 1H, CH_2NBoc), 3.54 (d, *J* = 13.2 Hz, 1H, CH_2Ph), 3.48 (d, *J* = 13.2 Hz, 1H, CH_2Ph), 3.42-3.12 (m, 4H, CH_2NBoc, CH_2NBn), 2.77 - 2.61 (m, 2H, CH_2NBn), 2.44 (s, 1H, CH), 2.41 (br s, 1H, CH), 1.55 (s, 9H, CMe_3). ^{13}C NMR (101 MHz, $CDCl_3$) 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 ($\underline{C}Me_3$), 61.82 (CH_2Ph), 59.03 and 58.67 (CH_2NBn), 50.45 and 49.75 (CH_2NBoc), 47.55 (CH), 28.58 ($C\underline{Me_3}$).

3-Benzyl-7-(tert-butyloxycarbonyl)-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 (3x150 ml). The combined organic layers were washed with water, brine, dried over Na_2SO_4 and evaporated. The residue was purified by SiO_2 column chromatography with AcOEt/petroleum ether (1/9) to afford **4** (7.7 g, 66 %) as a colorless oil. IR (thin film, ν , cm $^{-1}$): 1689 (OC=O), 736, 699 (C_6H_5). EI-MS, m/z (RI, %): 317 $[M+H]^+$ (21), 259 $[M\text{-}t\text{-}Bu]^+$ (100), 215 $[M\text{-}Boc]^+$ (39). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (m, 5H, Ph), 4.19 (d, *J* = 13.0 Hz, 1H, CH_2NBoc), 4.02 (d, *J* = 13.1 Hz, 1H, CH_2NBoc), 3.47 (d, *J* = 13.6 Hz, 1H, CH_2Ph), 3.32 (d, *J* = 13.6 Hz, 1H, CH_2Ph), 3.20 – 2.97 (m, 3H, CH_2NBoc, CH_2NBn), 2.91 (d, *J* = 10.8 Hz, 1H, CH_2NBn), 2.25 (d, *J* = 10.8 Hz, 1H, CH_2Bn), 2.18 (d, *J* = 10.8 Hz, 1H, CH_2Bn), 1.90 (br s, 1H, CH), 1.81(br s, 1H, CH), 1.68 and 1.62 (d, AB system, *J* = 12.2 Hz, 2H, CH_2), 1.55 (s, 9H, CMe_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.08 (C=O), 139.03 (*ipso*-Ph), 128.59 (o-Ph), 128.07 (m-Ph), 126.63 (p-Ph), 78.73 ($\underline{C}Me_3$), 63.51 (CH_2Ph), 59.03 and 58.74 (CH_2NBn), 48.42 and 47.59 (CH_2NBoc), 31.18 (CH_2), 29.00 (CH), 28.73 ($C\underline{Me}_3$).

3-(tert-Butyloxycarbonyl)-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% H_2O, 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 $CHCl_3$, washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by SiO_2 column chromatography with $CHCl_3$/MeOH (9/1) to afford **5** (12.2 g, 85 %) as a colorless oil. IR (thin film,ν, cm $^{-1}$): 1691 (OC=O). EI-MS, m/z (RI, %): 227 $[M+H]^+$ (68), 169 $[M\text{-}t\text{-}Bu]^+$ (72), 126 $[M\text{-}Boc+H]^+$ (48). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.14 – 4.05 (m 2H, CH_2NBoc), 3.19 – 3.02 (m, 4H, CH_2NBoc, CH_2NH), 2.97 (d, *J* = 13.1 Hz, 2H, CH_2NH), 1.89 and 1.77 (d, AB system, *J* = 12.6 Hz, 2H, CH_2), 1.72-1.55 (m, 3H, 2CH+NH), 1.47 (s, 9H, CMe_3). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.43 (C=O, Boc), 79.61 ($\underline{C}Me_3$), 51.82 (CH_2NH), 49.46 and 48.42 (CH_2NBoc), 31.57 (CH_2), 28.51 ($C\underline{Me}_3$), 28.28 (CH).

3-(tert-Butyloxycarbonyl)-7-ferrocenylmethyl-3,7-diazabicyclo[3.3.1]nonane ***6.***

To a solution of **5** (1 g, 4.4 mmol) in THF (50 ml) was added ferrocenecarboxaldehyde (1.13 g, 5.3 mmol) and by portions sodium triacetoxyborohydride (3.50 g, 16.5 mmol). The mixture was stirred for 2 h at room temperature, diluted with water, basified with sodium hydroxide solution to pH 10, extracted with ether, washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by Al_2O_3 column chromatography with AcOEt/petroleum ether (1/9) to afford **6** (1.57 g, 83 %) as an orange powder. M.p. 112° C. Anal.: C, 64.95; H, 7.69; N, 6.57%. Calc. for $C_{23}H_{32}FeN_2O_2$: C, 65.10; H, 7.60; N, 6.60%. IR (KBr, ν , cm $^{-1}$): 1690 (OC=O), 1105, 998, 819, 487 (FcH). EI-MS, m/z (RI, %): 424 $[M]^+$ (53), 368 $[M\text{-t-Bu+H}]^+$ (14), 324 $[M\text{-Boc+H}]^+$ (28). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.18 – 4.11 (m, 1H, CH_2NBoc + 2H, C_5H_4), 4.11 – 4.06 (s, 5H, C_5H_5 + m, 2H, C_5H_4), 3.98 (d, *J* = 13.0 Hz, 1H, CH_2NBoc), 3.34 (d, *J* = 13.3 Hz, 1H, CH_2Fc), 3.26 (d, *J* = 13.3 Hz, 1H, CH_2Fc), 3.06 (dd, *J* = 13.1, 3.7 Hz, 1H, CH_2NBoc), 2.99 (dd, *J* = 13.1, 3.8 Hz, 1H, CH_2NBoc), 2.89 (d, *J* = 10.7 Hz, 1H, $\underline{CH_2}NCH_2Fc$), 2.81 (d, *J* = 10.7 Hz, 1H, $\underline{CH_2}NCH_2Fc$), 2.22 (d, *J* = 11.0 Hz, 2H, $\underline{CH_2}NCH_2Fc$), 2.18 (d, *J* = 11.0 Hz, 2H, $\underline{CH_2}NCH_2Fc$), 1.79 (br s, 1H, CH), 1.73 (br s, 1H, CH), 1.61 (d, *J* = 12.2 Hz, 1H, CH_2), 1.55 – 1.47 (m, 1H, CH_2 + s, 9H, CMe_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.21 (C=O), 83.03 (*ipso*-C_5H_4), 78.48 ($\underline{C}Me_3$), 70.06 (C_5H_4), 68.42 (C_5H_5), 67.49 (C_5H_4), 58.40 (CH_2Fc), 57.77 and 57.55 ($\underline{C}H_2NCH_2Fc$), 48.76 and 47.69 (CH_2NBoc), 31.27 (CH_2), 29.12 (CH), 29.02 (CH), 28.76 ($C\underline{Me}_3$)

3--ferrocenylmethyl-7-methyl-3,7-diazabicyclo[3.3.1]nonane, ***7****.*

To a gently boiling under Ar atmosphere suspension of lithium aluminium hydride (0.30 g, 7.9 mmol) in THF (40 ml) was slowly added a solution of **6**

(0.80 g, 1.9 mmol) in 5 ml of THF. The mixture was refluxed with stirring for 3 h. After being cooled, the reaction was quenched successively with water (0.3 ml), 40% water solution of NaOH (0.3 ml) and water (0.9 ml), stirred for 30 min, filtered and evaporated. The crude was dissolved in $CHCl_3$/MeOH (9/1), passed through thin layer of Al_2O_3 and evaporated to afford **7** (0.62 g, 96%) as an orange oil. Anal.: C, 67.37; H, 7.84; Fe, 16.50; N, 8.34%. Calc. for $C_{19}H_{26}FeN_2$: C, 67.46; H, 7.75; Fe, 16.51; N, 8.28%. IR (thin film, ν , cm^{-1}): 1105, 1002, 817, 484 (FcH). EI-MS, m/z (RI, %): 338 $[M]^+$ (59). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 4.18 (br s, 2H, C_5H_4, H13 and 14), 4.13 (br s, 2H, C_5H_4, H12 and15), 4.12 (br s, 5H, C_5H_5), 3.39 (br s, 2H, CH_2Fc), 2.80 (br d, *J* = 9.5 Hz, 2H $\underline{CH_2}NCH_2Fc$), 2.78 (br d, *J* = 9.7 Hz, 2H, $\underline{CH_2}NCH_3$), 2.32 (dd, *J* = 11.0, 3.5 Hz, 2H, $\underline{CH_2}NCH_3$), 2.20 (dd, *J* = 10.8, 3.0 Hz, 2H, $\underline{CH_2}NCH_2Fc$), 2.15 (br s, 3H, CH_3), 1.85 (br s, 2H, 2CH), 1.38 and 1.40 (d, AB-system, *J* = 12.0 Hz, 2H, CH_2). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 82.76 (*ipso*-C_5H_4), 70.45 (C_5H_4, C13 and 14), 68.43 (C_5H_5), 67.68 (C_5H_4, C12 and 15), 60.01 ($\underline{C}H_2NCH_2Fc$), 58.27 (CH_2Fc), 56.94 (CH_2NBoc), 46.37 (CH_3), 30.66 (CH_2), 29.91 (CH). ^{15}N NMR (^{1}60.80 MHz, CD_2Cl_2,) δ -346.8 (N7), -337.8 (N3).

(7-methyl-3,7-diazabicyclo[3.3.1]nonan-3-ylmethyl)ferrocenyl]-(C,N,N)-palladium chloride, ***8***.

Method A: To a solution of Na_2PdCl_4 (0.458 g, 1.56 mmol) and sodium acetate monohydrate (0.212 g, 1.56 mmol) in MeOH (30 ml) and H_2O (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 Na_2SO_4, filtered, evaporated and purified by SiO_2 column chromatography ($CHCl_3$, then $CHCl_3$/MeOH = 10:1) to afford **8** (0.112 g, 14%).

Method B: To a suspension of $PdCl_2(CH_3CN)_2$ (0.157 g, 0.60 mmol) in CH_2Cl_2 (15 ml) was added a solution of **7** (0.205 g, 0.60 mmol) in 15 ml of CH_2Cl_2. The mixture was stirred for 6 h at room temperature, evaporated and purified by SiO_2 column chromatography ($CHCl_3$, then $CHCl_3$/MeOH = 10:1) to afford **8** (0.072 g, 23%).

Method C: A mixture of $PdCl_2$ (0.284 g, 1.60 mmol) and lithium chloride (0.081 g, 1.90 mmol) in MeOH (15 ml) was refluxed with stirring for 3 h and cooled. To the obtained solution was added a solution of **7 (**0.539 g, 1.60 mmol) and sodium acetate monohydrate (0.217 g, 1.60 mmol) in 5 ml of MeOH. The mixture was stirred for 5 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 Na_2SO_4, filtered and evaporated. The solid residue was washed with acetone and dried 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 $C_{19}H_{25}ClFeN_2Pd$: 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 $^{-1}$): 345, 285 (Pd-Cl). EI-MS, m/z (RI, %): 478 $[M]^+$ (23), 338 $[M\text{-}PdCl+H]^+$ (15). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 4.40 (br d, *J* = 12.2 Hz, 1H, $\underline{CH_2}NCH_2Fc$), 4.31 (br s, 1H, C_5H_3, H13), 4.22 (s, 5H, C_5H_5), 4.04 (br s, 1H, C_5H_3), 4.03 (br s, 1H, C_5H_3), 3.77 (d, *J* = 12.0 Hz, 1H, $\underline{CH_2}NCH_2Fc$), 3.67 (d, *J* = 12.0 Hz, 1H, $\underline{CH_2}NCH_3$), 3.62 (d, *J* = 15.2 Hz, 1H, CH_2Fc), 3.55 (br d, *J* = 15.0 Hz, 1H, CH_2Fc), 3.46 (d, *J* = 12.0 Hz, 1H, $\underline{CH_2}NCH_3$), 3.00 (dd, *J* = 12.0, 2.9 Hz, 1H, $\underline{CH_2}NCH_2Fc$), 2.93 (dd, *J* = 12.0, 3.00 Hz, 1H, $\underline{CH_2}NCH_2Fc$), 2.57 (s, 3H, CH_3), 2.50 (dd, *J* = 12.2, 3.2 Hz, 1H,

$\underline{CH_2}NCH_3$), 2.40 (dd, *J* = 12.3, 3.1 Hz, 1H, $\underline{CH_2}NCH_3$), 2.26 (m, 1H, CH), 2.16 (m, 1H, CH), 1.81 (dm, *J* = 12.9 Hz, 1H, CH_2), 1.72 (d, *J* = 12.9 Hz, 1H, CH_2). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 94.69 (*ipso*-C_5H_3, C-C), 92.67 (*ipso*-C_5H_3, C-Pd), 70.39 (C_5H_3, C13), 69.18 (CH_2Fc), 69.13 (C_5H_5), 65.37 (C_5H_3), 65.31 ($\underline{CH_2}NCH_2Fc$), 64.90 ($\underline{CH_2}NCH_2Fc$), 61.15 ($\underline{CH_2}NCH_3$), 61.00 ($\underline{CH_2}NCH_3$), 60.09 (C_5H_3), 52.04 (CH_3), 31.40 (CH_2), 30.59 (CH), 30.36 (CH). ^{15}N NMR (^{1}60.80 MHz, CD_2Cl_2,) δ -363.1 (N7), -343.4 (N3).

General procedure for the Suzuki reaction

To the solution of phenylboronic acid (1.5 mmol) in MeOH (8 ml) and H_2O (4 ml) was added consistently K_2CO_3 (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 $CHCl_3$. The combined organic phase was dried over Na_2SO_4, evaporated and purified by chromatography on SiO_2 (petroleum ether/$CHCl_3$).

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

A mixture of aryl iodide (1 mmol), 2-norbornene (3.4 mmol), HCO_2H (3 mmol), Et_3N (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 Na_2SO_4, evaporated and purified by chromatography on SiO_2 (petroleum ether).

General procedure for the Heck coupling reaction.

A mixture of aryl bromide (1 mmol), ethyl acrylate (1.5 mmol), K_2CO_3 (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 Na_2SO_4, evaporated and purified by chromatography on SiO_2 (petroleum ether/AcOEt).

X-ray crystallography.

X-ray diffraction data for **8** were collected on a Bruker APEX II diffractometer (λ(MoKα) = 0.71072Å, 2θ < 56.5°, φ and ω scans with 0.5° scan step and 10 s per frame exposure). Red crystals of $C_{19}H_{25}ClFeN_2Pd$ at 120(2) K are triclinic, space group P-1, a = 8.7118(10), b = 10.6395(12), c = 11.0454(17)Å, α =61.307(2), β = 79.606(3), γ=76.765(2)°, V = 871.24(19) $Å^3$, 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 F^2 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 SHELX software package [22]. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center, CCDC number 1538852.

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- The ferrocene CNN pincer palladium complex with two N(sp^3) atoms was synthesized
- The molecular structure was confirmed by X-ray diffraction analysis in single crystal
- The complex demonstrates high activity as (pre)catalyst in the Suzuki reaction