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Suzuki Aryl Coupling Catalysed by Palladium Bis(phosphane) Pincer Complexes Based on Ferrocene; X-ray Structure Determination of $\{PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}OTf$

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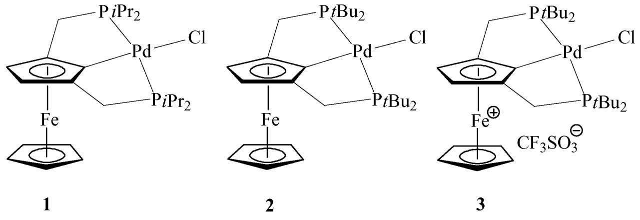
Keywords: Metallocenes / Homogeneous catalysis / Phase-transfer catalysis / Cross-coupling reactions / X-ray diffraction

Palladium P,C,P pincer complexes $PdCl[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**1**, R = *i*Pr; **2**, R = *t*Bu) and $\{PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}OTf$ (**3**) catalyse Suzuki aryl coupling under homogeneous conditions as well as in multiphase system (triphase system: organic/Aliquat 336/aqueous solvent); the X-ray structure of complex **3**, in which the iron atom is oxidised, has been determined and compared with that of its neutral precursor **2**.

Introduction

The chemistry of transition-metal complexes containing tridentate monoanionic aryl ligands, the so-called "pincer" ligands, has been extensively studied over the past decade, because of the high stability of these compounds and possibility to catalyse various organic transformations.[1] Recently, we have undertaken the study of a new generation of pincer complexes: dimetallic bis(phosphane) P,C,P pincer complexes based on metallocenes.[2,3] These pincer systems reveal interesting structural peculiarities, chemical reactivity and catalytic properties. Thus, dihydrido iridium pincer complexes based on ferrocene and ruthenocene, $IrH_2[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}M(C_5H_5)]$ (M = Fe, Ru), exhibit high catalytic activity in the transfer dehydrogenation of cyclooctane.[3] We wished to test the catalytic activity of metallocene-based pincer complexes in other reactions of organic substrates.

Here we report the preliminary catalytic investigation of ferrocene- and ferrocenium-based palladium pincer complexes $PdCl[\{2,5\text{-}(R_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**1**, R = *i*Pr; **2**, R = *t*Bu) and $\{PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}OTf$ (Tf = CF_3SO_2) (**3**), respectively, (Scheme 1), in the Suzuki cross-coupling reaction under traditional homogeneous conditions and in alternative reaction media, the multiphase (decane/water) system, in the presence of a liquid phase-transfer catalyst Aliquat 336 (tricaprylmethylammonium chloride, A336).



Scheme 1.

It is known that benzene-based palladium pincer complexes catalyse C–C bond formation reactions, such as the Heck olefin arylation,[1] and Suzuki[1,4] and Stille[5] cross-coupling reactions, and display excellent and good activity and TONs (turnover numbers). While many examples of pincer complexes as catalysts in the Heck reaction are reported in the literature, there are only a few examples for Suzuki coupling. Bis(phosphinite) P,C,P pincer complexes **4** and **5** were successfully applied by Bedford and coworkers[4a] as a highly efficient catalyst for the coupling of deactivated and sterically hindered aryl bromides with phenylboronic acid in toluene at 130 °C in the presence of K_2CO_3 (Scheme 2). It has recently been reported that related bis(phosphinite) iodopalladium pincer complexes **6**–**8**,[4b] as well as pincer-type biscarbene palladium complexes **9** and **10**,[4c] moderately catalyse the Suzuki coupling of 4-bromoacetophenone in the presence of 0.1–0.01 mol-% of the catalysts. The palladium S,C,S pincer complex **11** has

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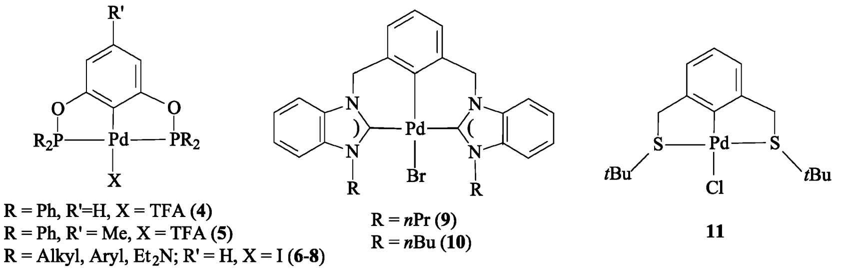


Scheme 2.

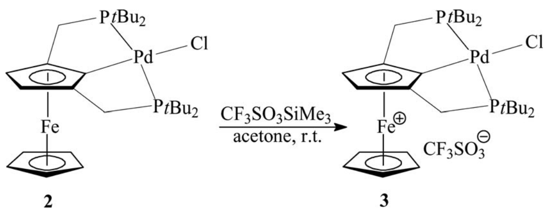
also been employed in Suzuki-type couplings; however, its application was limited since it was only active in the reaction of *p*-bromotoluene with phenylboronic acid with a 69% yield of the corresponding biphenyl.[4d]

The use of alternative, "green" reaction media, such as ionic liquids, water or multiphase solvent systems, in palladium-catalysed cross-coupling reactions has been widely investigated and applied.[6] Earle, Seddon and co-workers[7] performed the Heck reaction with a triphase system comprising an ionic liquid phase containing the Pd catalyst, a water layer to scavenge inorganic by-products and an organic phase that contained the reagents and products; separation of the product/by-product/catalyst could be achieved by taking advantage of this triple-phase system. These types of multiphase systems with quaternary ammonium salts are effective as media for the Heck reaction[8a] and can promote formation of Pd nanoparticles that remain immobilised in the onium catalyst-philic phase.[8b] The successful application of ionic liquids in the Suzuki coupling reaction under mild conditions has also been demonstrated.[9] The organometallic aqua complex $\{Pd(H_2O)[2,6\text{-}(tBu_2SCH_2)_2C_6H_3]\}_2(SO_4)$ prepared from **11** was employed as a catalyst in the pH-dependent cross-coupling reaction of water-soluble organic halides in aqueous media.[10] To the best of our knowledge, there has been no report on the application of palladium pincer complexes in C–C coupling reactions in multiphase catalytic systems.

Results and Discussion

Synthesis of $\{PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}OTf$ (3)

Chloridopalladium pincer complexes **1** and **2** based on ferrocene were synthesised previously[2] by cyclometallation of the corresponding diphosphanes with $PdCl_2(NCPh)_2$ and fully characterised by X-ray crystallography. When we attempted to replace the chlorine atom by an OTf group by treatment of an acetone solution of **2** with trimethylsilyl triflate, we unexpectedly obtained paramagnetic ferrocenium-based pincer complex **3** (Scheme 3), which was fully characterised by a single-crystal X-ray diffraction study. The ferrocenium-based pincer complex $\{PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}PF_6$ was obtained earlier by chemical oxidation of **2** with $[Cp_2Fe]PF_6$ and was characterised by ^{31}P- and ^{1}H NMR spectroscopy.[2] This cationic complex with the PF_6 counterion is less soluble in organic solvents than **3**, and this was the reason why we chose complex **3** for use in the Suzuki coupling reaction.



Scheme 3.

X-ray Crystal Structure of Complex 3

The solid structure of a ferrocenium-based pincer complex **3** determined by single-crystal X-ray crystallography is the first example of a ferrocene-based pincer system in which the iron atom is in the oxidised form. It was therefore interesting to compare this crystal structure with that of its neutral precursor. The molecular structure of **3** and relevant data are given in Figure 1. The palladium centre has a distorted square-planar geometry and is similar to that of complexes **1** and **2**.[2] However, there are marked differences between the structural parameters of **3** and those of the nonoxidised precursor **2**. The value of P(1)–Pd–P(2) angle in complex **3**, 161.18(4)°, is somewhat larger than the corresponding angle in **2**, 157.57(4)° [this angle for **1** is 160.39(6)°]. The C(1)–Pd–Cl angle in **3** [178.0(1)°] is similar to that in complex **1** [178.9(2)°] with the less bulky isopropyl groups at the P atoms than to that in precursor **2** [175.5(1)°], as is the case for the above-mentioned P(1)–Pd–P(2) angle. It should also be noted that the Pd–Cl bond [2.3741(9) Å] in complex **3** is appreciably shorter than that in **2** and **1** [2.403(1) and 2.400(2) Å, respectively]. Remarkably, the cyclopentadienyl rings in **3** are not parallel, and the tilting angle between the rings is 7.7°, whereas, in complex **2**, this angle is only 4.5°. In metallocene-based pincer complexes, the cyclopentadienyl rings may not be parallel, and the chelated metal atom may be lifted above the metallated ring plane because of the close contact between the nonmetallated cyclopentadienyl ring and the pseudoequatorial organyl groups at the phosphorus atoms.[3] This difference may be indicative of the weakening of the iron–cyclopentadienyl ring bond in the ferrocenium-based pincer complex **3** relative to that in the nonoxidised precursor **2**. Thus, the distances from the Fe atom to the centroid of the substituted and unsubstituted cyclopentadienyl rings in **3** are 1.697 and 1.718 Å, while the corresponding distances in **2** are 1.638 and 1.662 Å. The Pd atom in **3** is lifted above the metallated cyclopentadienyl ring plane by 0.118 Å, which is somewhat larger than that in **2** (0.069 Å).

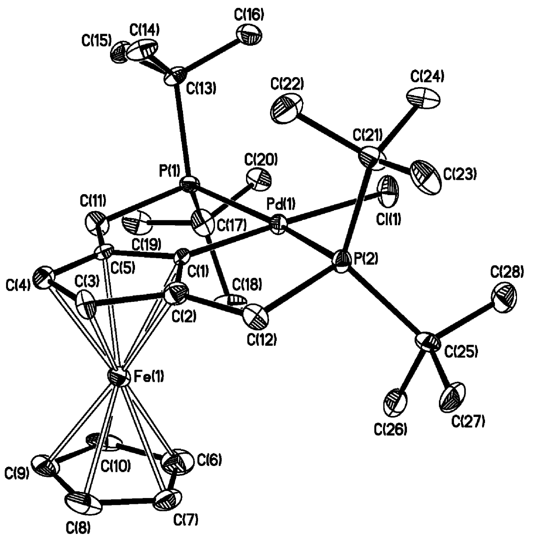


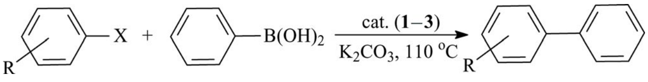
Figure 1. An ORTEP representation of the molecular structure of the cationic complex **3** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Pd(1)–C(1) 1.948(3), Pd(1)–P(1) 2.333(1), Pd(1)–P(2) 2.337(1), Pd(1)–Cl(1) 2.3741(9); P(1)–Pd(1)–P(2) 161.18(4), C(1)–Pd(1)–Cl(1) 178.0(1), C(1)–C(2)–C(12) 120.7(5), C(1)–C(5)–C(11) 119.1(5).

Catalytic Properties of Complexes 1–3

The catalytic activities of pincer complexes **1**–**3** were evaluated in the Suzuki coupling reaction of phenylboronic acid with electronically activated aryl bromide and chloride and electronically deactivated and sterically hindered aryl bromides at 110 °C in the presence of K_2CO_3 as a base. The results are summarised in Tables 1 (homogeneous conditions) and 2 (multiphase conditions).

As can be seen from these data (Table 1, Entries 1–7; Table 2, Entries 1–8), the cross-coupling reactions of phenylboronic acid with "easy-to-couple" substrate 4-bromoacetophenone proceeded efficiently under homogeneous conditions as well as in the triphase system. The reactions with complexes **1** and **3** were almost complete within 4.5 h (84% yield) under homogeneous conditions with a catalyst loading of 0.01 mol-%. In the multiphase system, quantitative yields of the product diaryl, which crystallises from the reaction media (decane phase) after cooling of the reaction mixture, were afforded. The reaction with complex **3** as a catalyst was performed in air (Table 2, Entry 8), and good activity was observed. Complex **2** is less efficient in this coupling reaction under homogeneous conditions (Table 1,

Table 1. Suzuki coupling of aryl halides with phenylboronic acid catalysed by palladium metallocene-based P,C,P pincer complexes under homogeneous conditions.[a]



Entry	Aryl halide	Catalyst [mol-%]	Time [h]	Yield [%][b]
1	4-bromoacetophenone	**1** (0.01)	2.5	60
2	4-bromoacetophenone	**1** (0.01)	4.5	84
3	4-bromoacetophenone	**1** (0.01)	9	91
4	4-bromoacetophenone	**1** (0.01)	12	94
5	4-bromoacetophenone	**2** (0.01)	15	66
6	4-bromoacetophenone	**3** (0.01)	4.5	84.5
7	4-bromoacetophenone	**3** (0.01)	15.5	88
8[c]	4-bromoacetophenone	**1** (0.3)	15.5	66
9[c]	4-bromoacetophenone	**3** (0.3)	18	72
10	4-bromoacetophenone	**3** (0.001)	18	32.5
11	4-bromoanisole	**1** (0.01)	12	77
12	4-bromoanisole	**2** (0.01)	15	79
13	4-bromoanisole	**3** (0.01)	15.5	98
14[d]	4-bromoanisole	**3** (0.01)	15.5	93
15	2-bromotoluene	**1** (0.01)	9	81
16	2-bromotoluene	**2** (0.01)	15	20
17	2-bromotoluene	**3** (0.01)	15	80
18	4-bromotoluene	**1** (0.01)	12	83.5
19	4-bromotoluene	**2** (0.01)	15	89
20	4-bromotoluene	**3** (0.01)	15	96.5
21	4-chloronitrobenzene	**1** (0.01)	18	30.5
22	4-chloronitrobenzene	**3** (0.01)	18	34
23	4-chloronitrobenzene	**1** (0.1)	18	85.5
24	4-chloronitrobenzene	**3** (0.1)	18	88

[a] Reaction conditions: 1.0 mmol aryl halide, 1.5 mmol $PhB(OH)_2$, 2.0 mmol base (K_2CO_3), 5 mL toluene, catalyst added in toluene solution (for **3** 1,4-dioxane was used instead), N_2 atmosphere, 110 °C. [b] Determined by GC against hexadecane internal standard, based on aryl halide. [c] Solvent: 10 mL 1,4-dioxane, 65 °C. [d] Reaction performed in air.

Table 2. Suzuki coupling of aryl halides with phenylboronic acid catalysed by palladium metallocene-based P,C,P-pincer complexes under multiphase conditions.[a]

Entry	Aryl halide	Catalyst [mol-%]	Time [h]	Yield [%][b]
1	4-bromoacetophenone	**1** (0.1)	6.5	100
2	4-bromoacetophenone	**1** (0.01)	4.5	100
3	4-bromoacetophenone	**2** (0.1)	14.5	100
4	4-bromoacetophenone	**2** (0.01)	14.5	11
5	4-bromoacetophenone	**3** (0.1)	6.5	100
6	4-bromoacetophenone	**3** (0.01)	15.5	100
7	4-bromoacetophenone	**3** (0.01)	4.5	100
8[c]	4-bromoacetophenone	**3** (0.01)	2	64
9	4-bromoanisole	**1** (0.01)	15	62
10	4-bromoanisole	**2** (0.01)	15	9
11	4-bromoanisole	**3** (0.01)	15.5	63.5
12	4-bromoanisole	**3** (0.01)	6.5	27.5
13	4-bromotoluene	**1** (0.01)	15	59
14	4-bromotoluene	**2** (0.01)	15	9
15	4-bromotoluene	**3** (0.01)	15	60
16	4-bromotoluene	**3** (0.01)	4	28.5
17	2-bromotoluene	**1** (0.01)	15	49
18	2-bromotoluene	**3** (0.01)	4	47

[a] Reaction conditions: 1.0 mmol aryl halide, 1.5 mmol $PhB(OH)_2$, 2.0 mmol base (K_2CO_3), 5 mL decane, 5 mL H_2O, 1.16 mL 10% solution (w/v) of A336 in isooctane (0.30 mmol A336), catalyst added in toluene solution (for **3** 1,4-dioxane was used instead), N_2 atmosphere, 110 °C. [b] Determined by GC against hexadecane internal standard, based on aryl halide. [c] Reaction performed in air.

Entry 5) and almost inactive under multiphase conditions at a 0.01 mol-% catalyst concentration, as well as in all subsequent multiphase reactions with other aryl bromides. However, higher concentrations of **2** (0.1 mol-%) in the coupling reaction of 4-bromoacetophenone in the multiphase system afforded the product in a 100% yield (Table 2, Entry 3). Complexes **1** and **3** catalyse the coupling of 4-bromoacetophenone (Table 1, Entries 8 and 9) at 65 °C in satisfactory yields with a catalyst loading of 0.3 mol-%. At room temperature, this cross-coupling reaction does not proceed.

Complexes **1**–**3** display sufficient catalytic activity in the coupling of electronically deactivated substrates (4-bromoanisole) under homogeneous conditions (Table 1). In all cases, good yields were observed at a catalyst concentration of 0.01 mol-%. No loss in activity was observed when the coupling reaction was performed in air (Entry 14). The same coupling reaction catalysed by complexes **1** and **3** under multiphase conditions proceeded less efficiently to give the corresponding diphenyl in an approximately 60% yield (Table 2, Entries 9 and 11).

A similar situation was observed for the coupling reaction of 4-bromotoluene: complexes **1**–**3** show good catalytic activity at 0.01 mol-% catalyst loading under homogeneous conditions and moderate activity for **1** and **3** in the multiphase system.

Complexes **1** and **3** show good activity for the coupling of electronically deactivated and sterically hindered 2-bromotoluene under homogeneous conditions and moderate activity in the multiphase system. Complex **2** is not very effective as a catalyst in the reaction of a sterically hindered substrate (Table 1, Entry 16), most likely because the Pd atom is less sterically available than in **1**.

Complexes **1** and **3** catalyse the coupling of activated aryl chloride (4-chloronitrobenzene) and show good activity with a catalyst loading of 0.1 mol-%; they are also active at lower concentrations under homogeneous conditions (Table 1, Entries 21–24). Noteworthy is that no appreciable reaction was observed when Cs_2CO_3 was used as a base instead of K_2CO_3 in dioxane solution; this observation is in contrast to the excellent results obtained for the coupling of different aryl chlorides reported by Bedford and Cazin.[11] In the multiphase catalytic system, the coupling reaction of 4-chloronitrobenzene also does not proceed.

Taking into account a decrease in catalytic activity of complexes **1** and **3** in the coupling reaction of electronically deactivated aryl bromides in a triphase solvent system relative to that under traditional homogeneous reaction conditions, the effect of the phase-transfer catalyst (A336), which presumably takes part in the reaction to form a complex[12] with $PhB(OH)_3^-$, cannot be ruled out. Therefore, the acceleration rate and the high conversion in this case require an increasing concentration of quaternary ammonium salt, that was described for the two-phase Suzuki reaction with a water soluble catalyst and phase-transfer agent[13] and for ligandless $Pd(OAc)_2$ catalysis in water in the presence of $n$$Bu_4NBr$.[12]

Conclusions

In summary, we have demonstrated for the first time that ferrocene-based palladium pincer complexes successfully catalyse Suzuki aryl coupling under homogeneous conditions. Besides, they also show moderate activity under conditions of phase-transfer catalysis.

By comparing the catalytic activity of complexes **1**–**3**, it should be noted that the efficiencies of catalysts **1** and **3** are similar despite different ligand environments at the phosphorus atoms in **1** and **3**. The higher activity of **3** than that of **2** may be attributed to both steric and electronic peculiarities. However, at present we can not exclude the fact that complexes **1** and **3** are more inclined to decompose under the reaction conditions than **2**. They are virtually precatalysts in the reaction system, where reduction of Pd^{II} to Pd^0 takes place, and the catalytic reaction then proceeds with participation of the classical cycle that includes the Pd^{II}/Pd^0 oxidation states.[14] Further investigations for the elucidation of the veritable nature of the catalytic species in related reactions are necessary.

Experimental Section

General Materials and Procedures: All synthetic work was performed under purified argon atmosphere using standard Schlenk techniques. The solvents were dried and degassed by standard methods under an argon atmosphere. $CDCl_3$ was degassed with argon. Commercially available reagents were used as received. Palladium pincer complexes **1** and **2** were prepared according to literature procedures.[2]

Elemental analyses and mass spectra were performed at the A.N. Nesmeyanov Institute of Organoelement Compounds of RAS. ^{1}H-, ^{19}F-, and ^{31}P NMR spectra were recorded at 400.13, 282.40 and 161.98 MHz, respectively, with a Bruker AMX-400 NMR spectrometer. ^{1}H NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{1}H NMR chemical shifts were referred to the residual hydrogen signal of the deuterated solvents. ^{19}F NMR chemical shifts are reported relative to external $CFCl_3$. ^{31}P NMR chemical shifts are reported in parts per million downfield from H_3PO_4 and referred to an external 85-% solution of phosphoric acid in D_2O. Catalytic reactions were monitored by GC, GC/MS analyses. GC analyses were performed on a Varian 3400 by using a fused silica capillary column "Chrompack CP-Sil 24 CB lowbleed/MS" (30 m × 0.25 mm, film thickness 0.25 µm). GC/MS analyses were performed on an Agilent 5973 mass detector coupled to an Agilent 6890NGC with an HP-5MS capillary column (30 m × 0.25 mm, film thickness 0.25 µm).

Preparation of $\{PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]\}OTf$ (3): To an acetone solution (40.0 mL) of $PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]$ (**2**; 0.142 g, 0.221 mmol) was added an acetone solution (5.0 mL) of Me_3SiOTf (0.073 g, 0.331 mmol) at room temperature. The reaction mixture was then stirred at room temperature for 3 h, and the solution was then left for several days. The solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane, the solution was filtered through Celite and the solvent was removed under vacuum. The residue was dissolved in a small amount of dichloromethane, and the solution was then diluted with hexane. Green crystals were obtained by cooling this solution at 0 ºC for several days [0.103 g, 59% yield]. $C_{29}H_{47}ClF_3FeO_3P_2PdS{\cdot}CH_2Cl_2$ (877.29): calcd. C 41.07, H 5.63; found C 41.09, H 5.72. MS: *m*/*z* = 643 [$M^+ - CF_3SO_3^-$]. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, +23 °C): δ = 91.87 (s, 2 P) ppm. ^1H NMR (400.13 MHz, $CDCl_3$, +23 °C): δ = –110.86 (br., 2 H, $C\mathit{H}_AH_BP$), –24.18 (br., 2 H, $CH_A\mathit{H}_BP$), –10.05 [s, 18 H, $C(CH_3)_3$], 6.84 [s, 18 H, $C(CH_3)_3$], 23.15 (br., 5 H, C_5H_5), 27.65 (br., 2 H, C_5H_2) ppm. ^{19}F NMR (282.40 MHz, $CDCl_3$, +23 °C): δ = –85.15 (s, 3 F) ppm.

Typical Procedure for the Suzuki Reaction: To the reactor were added in this order (homogeneous conditions) aryl halide (1.0 mmol), $PhB(OH)_2$ (183 mg, 1.5 mmol), K_2CO_3 (280 mg, 2.0 mmol), toluene (5 mL), solution of catalyst and hexadecane (226 mg, 1.0 mmol; internal standard); (multiphase conditions) aryl halide (1.0 mmol), $PhB(OH)_2$ (183 mg, 1.5 mmol), K_2CO_3 (280 mg, 2.0 mmol), decane (5 mL), H_2O (5 mL), 10% solution (w/v) of A336 (1.16 mL) in isooctane (0.30 mmol A336), solution of catalyst and hexadecane (226 mg, 1.0 mmol; internal standard). The mixture was heated (110 °C in the reactor) in a silicon oil bath for the desired time.

X-ray Crystal Structure Determination: Single crystals of $PdCl[\{2,5\text{-}(tBu_2PCH_2)_2C_5H_2\}Fe(C_5H_5)]SO_3CF_3{\cdot}CH_2Cl_2$ ([**3**]$SO_3CF_3{\cdot}CH_2Cl_2$) were recrystallised from dichloromethane/*n*-hexane, mounted in inert oil and transferred to the cold gas stream of the Bruker SMART APEX II diffractometer. The APEX II software[15] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL[16] for space group and structure determination, refinements, graphics and structure reporting. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation.

Crystal Data: $C_{30}H_{49}Cl_3F_3FeO_3P_2SPd$, M = 877.29, monoclinic, a = 9.4738(6), b = 19.583(1), c = 10.4769(7) Å, β = 105.923(1)°, V = 1869.2(2) Å^3, T = 100 K, space group $P2_1$, Z = 2, μ(Mo-K_α) = 12.69 cm^{-1}, 24551 reflections measured, 10794 unique (R_{int} = 0.0603), which were used in all calculations. The final $wR(F^2)$ was 0.0858 (all data) and $R(F)$ was 0.0454 [8384 observed reflections with $I > 2\sigma(I)$]. It should be noted that the structure can be solved in the centrosymmetric space group $P2_1/m$. In this case, the cation complex and dichloromethane solvate molecule occupy a special position at the mirror plane. However, the OTf anion appears to be disordered over the inversion centre. At the same time, solution and refinement of this structure in the $P2_1$ space group [Flack parameter is 0.46(2)] leads to the disappearing of the disorder as well as to the improvement in the accuracy of the geometrical parameters. CCDC-652131 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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