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Square-planar dichloro palladium complexes with *trans*-configurated phosphine ligands avoiding *ortho*-metallation: Ligand design, complex synthesis, molecular structure and catalytic potential for Suzuki cross-coupling reactions

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Abstract

The square-planar palladium complexes *trans*-[$PdCl_2(PPh_2$-CH_2-2,4,6-$C_6H_2Me_3)_2$] (**1**) and *trans*-[$PdCl_2(\eta^2$-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-$PPh_2)$] (**2**) have been synthesized from [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene) and the corresponding new phosphine or diphosphine ligands. The single-crystal X-ray structure analysis reveals for both complexes a *trans* arrangement of the two chlorine and of the two phosphorus atoms. In both cases, *ortho*-metallation leading to palladacycles is not possible, since all *ortho* positions in the benzylic rings of **1** and **2** are blocked by methyl substituents. Both complexes are found to catalyze Suzuki cross-coupling reactions of deactivated and even bulky arene substrates.
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Keywords: Suzuki cross-coupling; Palladium complexes; Ligand rigidity; Ligand flexibility

1. Introduction

The Suzuki cross-coupling (Suzuki-Miyaura reaction) catalyzed by various palladium complexes, is among the most powerful synthetic tools for the generation of carbon–carbon bonds [1]. Although many different palladium(II) or palladium(0) complexes catalyze this coupling reaction, significant efforts have been put on the design of suitable ligands that can increase the catalytic activity of the palladium center. Despite the still lacunary mechanistic knowledge, a simplified catalytic cycle involving palladium(0) or palladium(II) complexes according to Scheme 1 is generally accepted: The oxidative addition of the aryl halide to a Pd(0) complex to give a Pd(II) species is followed by a transmetallation step involving arylboronic acid and a base to give a Pd(II) complex containing two aryl ligands, and finally by a reductive elimination step to give the product and a Pd(0) species [2].

As the oxidative addition step is supposed to give rise to a *cis*-Pd(II) complex [3], and as the reductive elimination step seems to involve a *cis*-Pd(II) complex [4], it has been assumed that palladium(II) complexes containing two phosphine ligands would be more active in the *cis* than in the *trans* form. Accordingly, diphosphine ligands that impose a *cis* geometry on the palladium center, such as diphenylphosphinomethane (dppm), diphenylphosphinoethane (dppe) or diphenylphosphinoferrocene (dppf) have been used as co-catalysts (ligands) in Suzuki cross-coupling reactions [5]. Moreover, some of the most active Suzuki catalysts are palladium complexes susceptible to *ortho*-metallation or palladacycle formation [6,7]. The influence of the phosphine ligands on the catalytic activity used in Suzuki cross-coupling reactions has been studied systematically by Buchwald and co-workers [8], which allowed a

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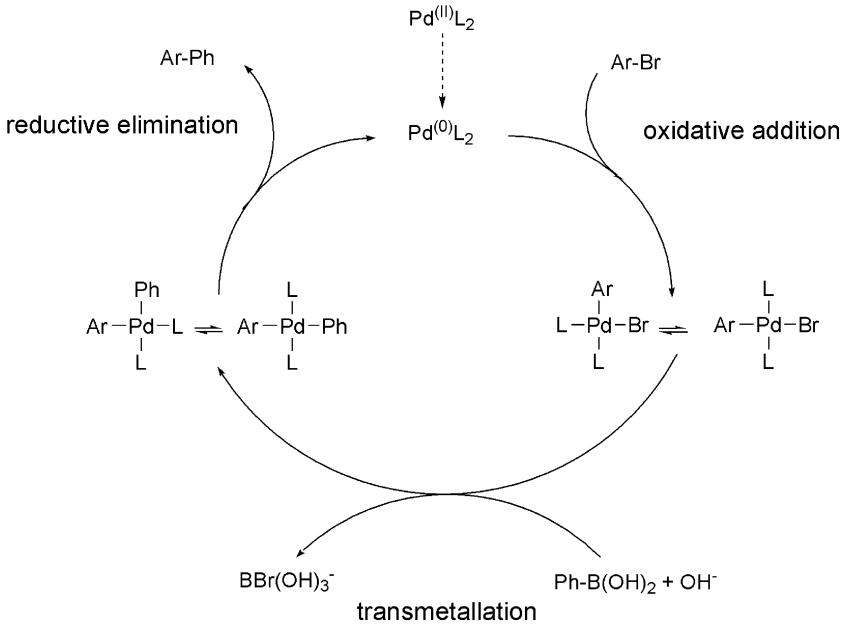


Scheme 1. Catalytic cycle of Suzuki cross-coupling adapted for the coupling of an arylbromide with phenylboronic acid.

rational design of a universal Suzuki catalyst [9]. However, the precise geometries and possible isomerization processes of the catalytically active species are not known.

Recently, several palladium(II) complexes containing *trans*-spanning diphosphine ligands, that contain a rigid ligand backbone, have been synthesized [10,11,16]. Thus, *trans*-[$PdCl_2$(SPANphos)] reported by van Leeuwen does not show any tendency to *cis-trans* isomerization [10], the complex *trans*-[$PdCl_2$(diphos)] (diphos = 2,6-bis(2-((diphenylphosphino)methyl)phenyl)benzene) reported by Protasiewicz [11] has been successfully used as Heck and Suzuki catalyst, in spite of the rigid *trans*-geometry [12]. With the diphosphine Xantphos, developed by van Leeuwen [13] and used as a ligand for Suzuki reactions, palladium complexes with *trans*-standing alkyl and chloro ligands [14] and with *trans*-standing aryl and bromo ligands [15] have been isolated and characterized by X-ray crystallography.

In this paper we report two new *trans*-palladium(II) complexes and their use as Suzuki catalysts. In both complexes, the formation of palladacycles via *ortho*-metallation is not possible thanks to two newly designed phosphine ligands. However, the two complexes differ in the rigidity of their structures: While *trans*-[$PdCl_2$(PPh_2-CH_2-2,4,6-$C_6H_2Me_3$)$_2$] (**1**) with two monophosphine ligands is more flexible, the diphosphine ligand in *trans*-[$PdCl_2$(η^2-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2)] (**2**) increases the steric bulk of the complex.

2. Results and discussion

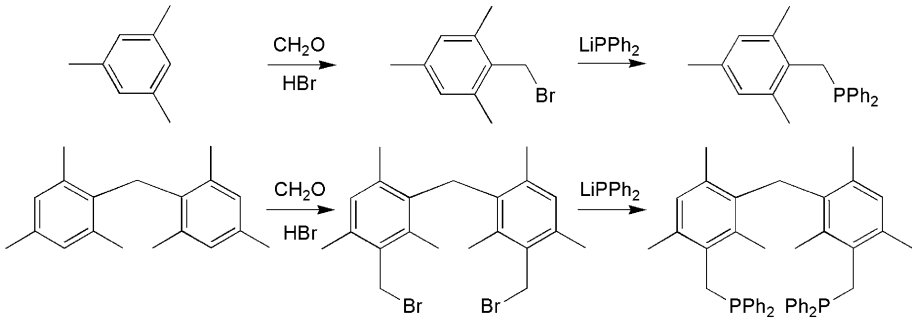
One of the problems encountered in palladium phosphine coordination chemistry is the *ortho*-metallation, which results in the formation of a palladium-carbon bond in addition to the palladium-phosphorus bond. Carbon atoms susceptible to reaction are the *ortho*-carbon atoms of aryl substituents in β-position with respect to the phosphorus atom (e.g. benzyl), since in this case a stable five-membered palladacycle can be formed. By contrast, α-aryl substituents (e.g. phenyl) do not undergo *ortho*-metallation at palladium [20].

For this reason we designed two new phosphine ligands, the *ortho*-positions in the β-aryl substituents of which are blocked by methyl groups: the monophosphine PPh_2-CH_2-2,4,6-$C_6H_2Me_3$ and the analogous diphosphine PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2, which can be expected to allow to bite angle (P–Pd–P) close to 180° upon coordination to palladium (*trans* geometry).

2.1. Synthesis of the new phosphines diphenyl-(2,4,6-trimethylbenzyl)phosphine and bis(3-((diphenylphosphino)methyl)-2,4,6-trimethylphenyl)methane

The new aryl phosphines PPh_2-CH_2-2,4,6-$C_6H_2Me_3$ and PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2 are accessible in two steps (Scheme 2), the first step being the bromomethylation of the mesityl group with hydrogen bromide and paraformaldehyde in glacial acetic acid at 50 °C as reported by Niehues et al. [17]; then the bromo derivatives obtained are reacted with lithium diphenylphosphide in tetrahydrofurane at 0 °C to give the target molecules and lithium bromide.

The synthesis and isolation of the products must be carried out with rigorous exclusion of air, in order to avoid oxidation of the phosphine groups. Both compounds have been characterized by correct NMR (^{1}H, ^{13}C, ^{31}P) and



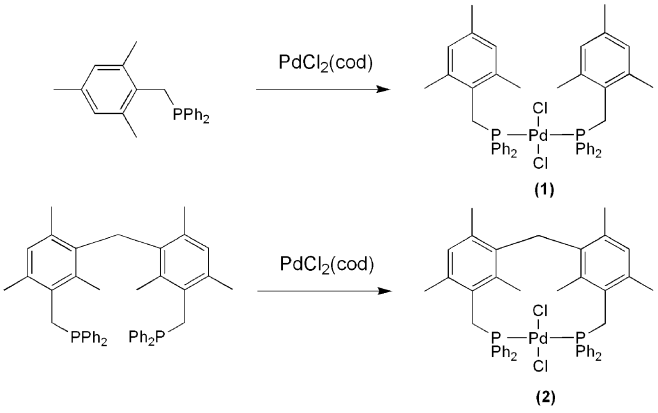
Scheme 2. Synthesis of the new phosphines PPh_2-CH_2-2,4,6-$C_6H_2Me_3$ and PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2–2,4,6-C_6HMe_3-CH_2-PPh_2.

mass-spectroscopic data as well as by satisfactory elemental analysis data.

2.2. Synthesis and molecular structure of the palladium complexes *trans*-[$PdCl_2$(PPh_2-CH_2-2,4,6-$C_6H_2Me_3$)$_2$] (**1**) and *trans*-[$PdCl_2$(η^2-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2)] (**2**)

The palladium complexes *trans*-[$PdCl_2$(PPh_2-CH_2-2,4,6-$C_6H_2Me_3$)$_2$] (**1**) and *trans*-[$PdCl_2$(η^2-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2)] (**2**) are obtained by reacting [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene) with the new aryl phosphines PPh_2-CH_2-2,4,6-$C_6H_2Me_3$ and PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2 in methylene chloride at room temperature. Both complexes **1** and **2,** isolated as air stable yellow powders, have been characterized by correct NMR (^{1}H, ^{13}C, ^{31}P) and mass-spectroscopic data, by satisfactory elemental analysis data and by single-crystal X-ray structure analysis (see Scheme 3).

The molecular structures of **1** and **2** show the palladium atom to be in a square-planar geometry, surrounded by two chlorine atoms and two phosphorus atoms in a *trans* coordination geometry, see Figs. 1 and 2, respectively. In **2**, the coordination of the chelating diphosphine ligand imposes a significant distortion of the planar geometry:



Scheme 3. Synthesis of the palladium complexes *trans*-[$PdCl_2$(PPh_2-CH_2-2,4,6-$C_6H_2Me_3$)$_2$] (**1**) and *trans*-[$PdCl_2$(η^2-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2)] (**2**).

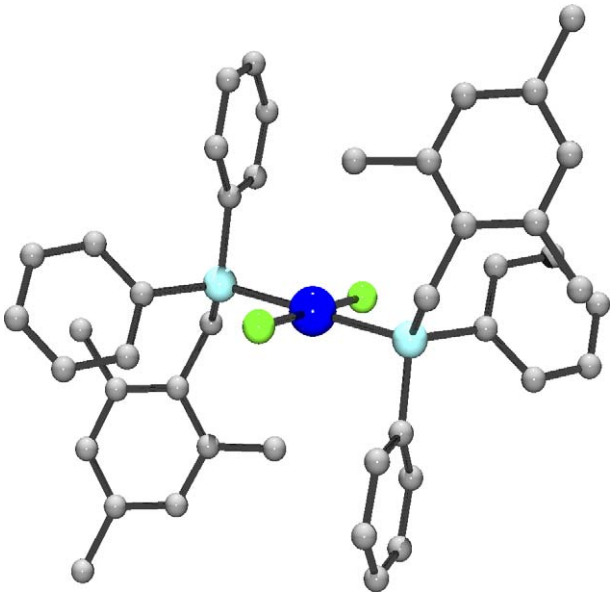


Fig. 1. POV-ray view of **1**, hydrogen atoms are omitted for clarity.

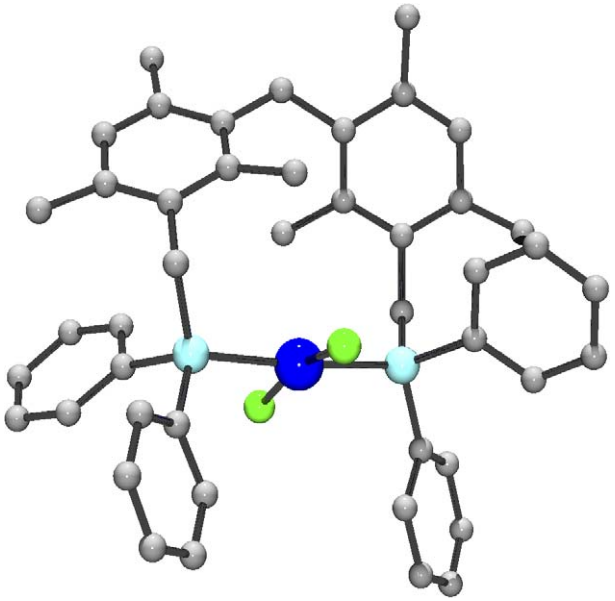


Fig. 2. POV-ray view of **2**, $CHCl_3$ molecules and hydrogen atoms are omitted for clarity.

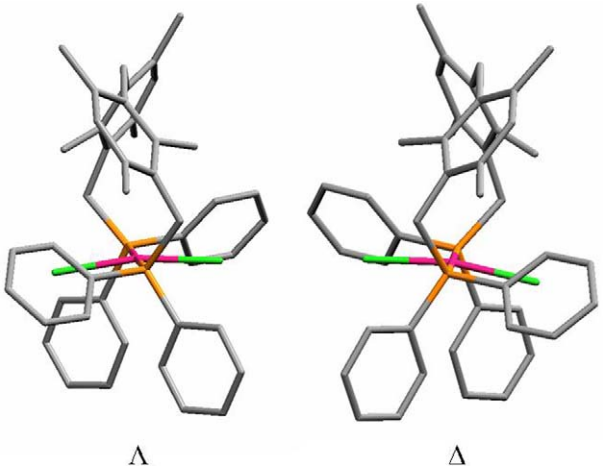


Fig. 3. Capped stick representations, along the -CH_2–P–Pd–P-CH_2– axis, of the two enantiomers of **2**.

Indeed, unlike **1**, where the Cl–Pd–Cl and P–Pd–P axes are perfectly linear, the corresponding angles in **2** are 167.4(1) and 175.5(1)°, respectively.

It is noteworthy that in **2** the rigid diphosphine backbone generates chirality upon coordination. According to the sense of the –CH_2-P-Pd-P-CH_2– torsion angle, two enantiomers Δ-**2** and Λ-**2** can be distinguished in the same crystal, see Fig. 3.

The ^{1}H NMR spectra of **1** and **2** are as expected, except for the signals of the methylene groups bound to phosphorus, which are complicated by virtual coupling. In **1**, the two equivalent protons of the two equivalent CH_2 groups, for which a doublet (due to ^{31}P-^{1}H coupling) is expected, show up as pseudo-triplet (a doublet of doublet) due to the coupling not only with the α-P atom but also with the γ-P atom (through palladium). This type of virtual coupling has also been observed in [{(Ph-CH_2)Ph_2P}$_2$$PdCl_2$] [18] and in [($Me_3$P)$_2$$PdCl_2$] [19]. Accordingly, the methylene triplet in the ^{1}H NMR spectrum of **1** collapses to give a singlet upon {^{31}P} decoupling.

The situation is even more complex in **2**, in which the rigid diphosphine backbone causes the non-equivalence of the two vicinal protons in both CH_2 groups. The ^{1}H NMR spectrum shows for the methylene protons in $CDCl_3$ (400 MHz) a doublet of triplets centered at 3.68 ppm and a second doublet of triplets superimposed by a broad singlet at 4.30 ppm, which is assigned to the methylene bridge between the two aromatic rings. In C_6D_6 (400 MHz) it is possible to resolve the three signals for the methylene protons: a doublet of triplets at 3.51 ppm [J(^{1}H–^{1}H) 13.0 Hz, J(^{31}P–^{1}H) 4.2 Hz], a doublet of triplets at 4.45 ppm [J(^{1}H–^{1}H) 13.0 Hz, J(^{31}P–^{1}H) 4.2 Hz] and a singlet at 2.76 ppm. Selective proton–proton decoupling as well as COSY and NOESY experiments show that the vicinal protons of the two phosphorus-bound CH_2 groups couple with each other and that there is no other ^{1}H–^{1}H coupling. Accordingly, upon {^{31}P} decoupling, the two doublets of triplets signals collapse to the two expected doublets, confirming a ^{1}H–^{1}H coupling of 13 Hz.

*2.3. Molecular structure dynamics of complexes **1** and **2** studied by variable-temperature NMR*

The ^{1}H and ^{31}P{^{1}H} NMR spectra of **1** and of **2** were studied in toluene-d_8 over a temperature range of −40 °C to +90 °C. In the case of **1**, no significant spectral change was observed except a slight shift of the signals. Thus, the single ^{31}P signal of **1** varies from 12.43 ppm (−40 °C) via 13.50 (+25 °C) and to 13.78 (+90 °C). While the characteristic ^{1}H signal of the benzyl CH_2 groups shows up as a virtual triplet at 4.24 ppm (see above) at +25 °C, this signal is only slightly shifted to 4.22 ppm at −40 °C and to 4.25 ppm at +90 °C, but in both cases it appears as a broad signal without triplet structure, due to the loss of resolution. No signal of another compound can be detected over the whole temperature range, suggesting that **1**, which has a *trans* configuration in the solid state, maintains this geometry in solution up to +90 °C. This interpretation is supported by the comparison with the benzyl-diphenyl phosphine analogue [($PhCH_2$-PPh_2)$_2$$PdCl_2$], for which the *cis* and *trans* isomers are known: Whereas the ^{31}P signal of the *trans* isomer is observed at 20.06 ppm, this *cis* isomer gives rise to a signal at 30.27 ppm ($CDCl_3$, +25 °C), the shift difference being 10 ppm [18].

In contrast to **1**, the more rigid diphosphine complex **2** shows the appearance of a new species above +70 °C.

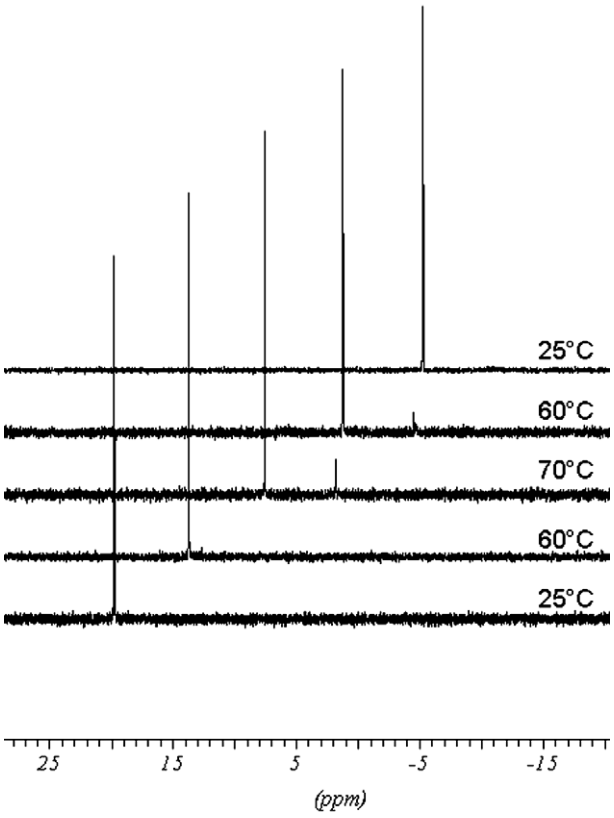


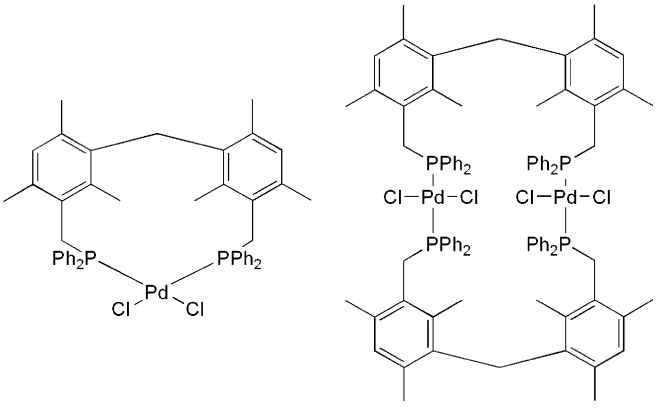
Fig. 4. Variable-temperature ^{31}P{^{1}H} NMR spectra of **2** in C_6D_6 over temperature range from 25 °C to 70 °C and back to 25 °C.

The ^{31}P signal of **2** at 19.71 ppm (+25 °C) shifts to 19.34 ppm at −40 °C and to 20.02 ppm at +90 °C, a second ^{31}P resonance emerging above +70 °C is observed at 14.16 ppm (+90 °C), representing 5–10% of signal intensity. The ^{31}P NMR signals are better resolved in benzene-d_6, even if the temperature range is more restricted in this case. Fig. 4 displays the variable-temperature $^{31}P\{^1H\}$ NMR spectra of **2** in C_6D_6 over the temperature range from +25 °C to +70 °C and back to +25 °C. The cooling experiment shows that the species formed above +70 °C disappears again upon cooling down. In the ^1H NMR spectra, the temperature dependant shift of the benzylic CH_2 signals at 4.35 and 3.48 ppm (+25 °C) to 4.29 and 3.39 (−40 °C) and to 4.33 and 3.53 (+90 °C) is clearly visible, however, the new species formed above +70 °C (seen in the ^{31}P spectrum) cannot be detected unambiguously in the ^1H NMR spectrum, due to the low concentration of 5–10% and the complexity of the ^1H NMR spectrum. Given the reversibility of the reaction, the species formed in low concentration from *trans*-[$PdCl_2(\eta^2$-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2)] (**2**) may either be the *cis* isomer or a *trans* dimer, see Scheme 4. The ^{31}P resonance of 14.16 ppm (90 °C) does not allow discrimination between the two possibilities.

2.4. Catalytic activity of complexes *1* and *2* for Suzuki cross-coupling reactions

The two *trans*-complexes *trans*-[$PdCl_2(PPh_2$-CH_2-2,4,6-$C_6H_2Me_3)_2$] (**1**) and *trans*-[$PdCl_2(\eta^2$-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2)] (**2**) have been studied as catalyst precursors for Suzuki coupling reactions.

Two Suzuki-type reactions have been studied with complexes **1** and **2**: On the one hand, the cross-coupling of phenyl boronic acid with 4-bromotoluene, which is a deactivated bromo derivative, and on the other hand, the cross-coupling phenyl boronic acid with 2,4,6-trimethylphenyl bromide, which is both, deactivated and sterically hindered.

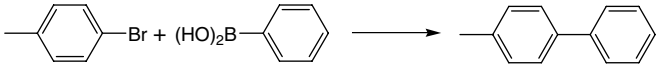


Scheme 4. Possible structures of the high-temperature species formed reversibly from **2** above 70 °C.

The most significant results for the cross-coupling of 4-bromotoluene and phenyl boronic acid are summarized in Table 1. As the catalytic turnover numbers after 18 h indicate, there is no significant difference in the catalytic productivity at 90 °C. The two complexes are less active at lower temperatures: At 30 °C, a catalyst/substrate ratio of 1:1000 is required to observe catalytic activity, the direct comparison of **1** and **2** shows that the more flexible complex *trans*-[$PdCl_2(PPh_2$-CH_2-2,4,6-$C_6H_2Me_3)_2$] (**1**) is 15 times more active that the analogous rigid complex *trans*-[$PdCl_2(\eta^2$-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-PPh_2)] (**2**).

For the cross-coupling of phenyl boronic acid with the sterically hindered 2,4,6-trimethylphenyl bromide, the results are summarized in Table 2. At 90 °C, both complexes **1** and **2** are highly active, the turnover numbers (36500 and 38700 for a catalyst/substrate ratio of 1:100000) being comparable. By contrast, at lower temperatures, the rigid diphosphine complex **2** is less active than

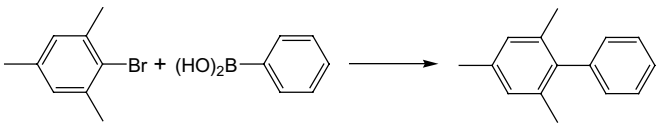
Table 1
Catalytic turnover numbers (TON), indicating the moles of product formed per mol of catalyst used after 18 h, for the Suzuki cross-coupling of 4-bromotoluene and phenyl boronic acid, catalyzed by **1** and **2**



T (°C)	Catalyst/substrate	**1**	**2**
30	1:1000	300	21
30	1:10000	0	0
30	1:100000	0	0
60	1:1000	1000	1000
60	1:10000	9400	8900
60	1:100000	44500	1000
90	1:1000	1000	1000
90	1:10000	10000	10000
90	1:100000	99000	98700

Solvent toluene, base K_2CO_3, reaction time 18 h.

Table 2
Catalytic turnover numbers (TON), indicating the moles of product formed per mol of catalyst used after 18 h, for the Suzuki cross-coupling of 2,4,6-trimethyl-phenyl bromide and phenyl boronic acid, catalyzed by **1** and **2**



T (°C)	Catalyst/substrate	**1**	**2**
30	1:1000	283	0
30	1:10000	0	0
30	1:100000	0	0
60	1:1000	960	872
60	1:10000	4235	5200
60	1:100000	15000	0
90	1:1000	926	1000
90	1:10000	6330	8770
90	1:100000	36500	38700

Solvent toluene, base K_2CO_3, reaction time 18 h.

the analogous bis(monophosphine) complex **1**, which even shows a turnover of 283 at 30 °C for a catalyst/substrate ratio of 1:1000.

3. Conclusion

The *trans*-complexes **1** and **2**, in which *ortho*-metallation is impossible because of the methyl substituents in the *ortho*-positions, show both a good catalytic performance, but differ at low temperatures. In the range of 30–60 °C, with catalyst/substrate ratios between 1000 and 100,000, **1** is more active than **2** in each reaction, suggesting that the rigidity of the ligand reduces the catalytic performance at low temperature. Nevertheless, at 90 °C, the catalytic performance of **1** is similar to that of **2**. The slightly superior performance of **2** for the cross-coupling of the sterically hindered bromide at 90 °C, may be explained by the emergence of a high-temperature species, reversibly formed from **2** above 70 °C. This high-temperature species, observed by variable-temperature ^{31}P NMR spectroscopy (see 2.3), may be either an isomer of **2**, namely *cis*-[$PdCl_2(\eta^2$-PPh_2-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6H-Me_3-CH_2-$PPh_2)$], or a dimer of **2**, namely *trans*, *trans*-[$PdCl_2(PPh_2$-CH_2-2,4,6-C_6HMe_3-CH_2-2,4,6-C_6HMe_3-CH_2-$PPh_2)]_2$ (Scheme 4). As this species converts back to **2** at temperatures below 70 °C, it is not possible to isolate this complex.

4. Experimental

All reactions were carried out by using standard Schlenk techniques under argon atmosphere. The solvent tetrahydrofuran (thf) was distilled from sodium benzophenone under N_2 to avoid water and oxygen contaminations. Toluene, *n*-hexane and diethyl ether were purchased from Merck (puriss p.a.) and were as well as distilled water, argon-saturated prior to use. Methylene chloride was distilled over CaH_2 and saturated with N_2. The [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene) was purchased from Strem Chemicals. Deuterated chloroform was used as received, and all NMR spectra were performed with a Bruker spectrometer (400 MHz for ^1H, 81 MHz for ^{31}P, and 100 MHz for ^{13}C). All gas chromatography analyses were done on a GC DANI 86.10, equipped with a fused silica capillary column OPTIMA δ-3 (0.5 μm, 30 m × 0.25 mm) and an integrator SP-4400.

4.1. Synthesis of diphenyl(2,4,6-trimethylbenzyl)phosphine

To a solution of butyl-lithium (2.86 mL, 1.4 M in hexane) in 30 mL of thf, diphenylphosphine (796 μL, 4 mmol) was added dropwise at 0 °C. Then the solution, which turns red, was stirred for 2 h. A solution of (bromomethyl)-2,4,6-trimethylbenzene (0.852 g, 4 mmol), dissolved in a minimum of thf, was then added dropwise to the solution. The mixture, which became colorless, was stirred overnight at room temperature. Then, 60 mL of an ether/water (1:1) mixture was added. After intense shaking, the organic layer was separated, dried with $MgSO_4$ and evaporated *in vacuo*. *n*-Hexane (10 mL) was added, and the solution was filtrated though a canula equipped with filter paper. The filtrate was dried *in vacuo* to give a colorless oil (yield 80%). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.51$–7.37(m, 10H), 6.88(s, 2H), 3.48(s, 2H), 2.36(s, 3H), 2.06(s, 6H). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -15.96$ (s). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 133.60$(Ar), 133.24(Ar), 129.27 (Ar), 129.23(Ar), 128.99(Ar), 128.70(Ar), 128.56(Ar), 31.95(C2), 21.21(C1), 20.53(C1). Anal. Calc.: C, 82.99; H, 7.28. Found: C, 82.65; H, 7.24%.

4.2. Synthesis of bis(3-(bromomethyl)-2,4,6-trimethylphenyl)methane

A 33 wt.% HBr-AcOH solution (5 mL) was rapidly added to a mixture of bis(mesityl)methane (3.15 g, 12.5 mmol), paraformaldehyde (0.750 g, 25 mmol) and 20 mL of glacial acetic acid. The mixture was stirred at 50 °C for one night and then poured into 50 mL of water. The pH of the mixture was raised to 7 by addition of K_2CO_3 (2M), and then 50 mL of dichloromethane were added. The organic layer was extracted, dried with $MgSO_4$ and evaporated *in vacuo* to give a white powder, which was purified by recrystallization from diethyl ether (yield 80%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.86$(s, 2H), 4.58(s, 4H), 4.09(s, 2H), 2.39(s, 6H), 2.14(s, 6H), 2.13(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.87$(C4), 137.01(C4), 136.83 (C4), 135.26(C3), 131.31(C4), 32.61(C2), 31.33(C2), 21.67 (C1), 19.65(C1), 16.27(C1). Mass: EI-$m/z = 358.1$ $[M–Br]^+$ Anal. Calc.: C, 57.55 ; H, 5.98. Found: C, 57.67; H, 6.03%.

4.3. Synthesis of bis(3-((diphenylphosphino)methyl)-2,4,6-trimethylphenyl)methane

To a solution of butyl-lithium (1.25 mL, 1.6 M in hexane) in 30 mL of thf, diphenylphosphine (350 μL) was added dropwise at 0 °C. Then the solution, which turns red, was stirred for 2 h. Bis((bromomethyl)-2,4,6-trimethylbenzene)methane (0.438 g, 1 mmol) was dissolved in a minimum of thf and then added dropwise to this solution. The mixture, which became colorless, was stirred overnight at room temperature. Then, 60 mL of an ether/water (1:1) mixture was added. After intense shaking, the organic layer was separated, dried with $MgSO_4$ and evaporated *in vacuo*. The crude product was washed with hot *n*-hexane (10 mL) and dried (yield 50%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$–7.25(m, 20H), 6.73(s, 2H), 3.96(s, 2H), 3.47(bs, 4H), 2.06(bs, 6H), 1.92(s, 6H), 1.82(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 136.78$, 136.01, 134.68, 134.64, 133.63, 133.44, 131.03, 129.06, 128.74, 128.67, 33.15, 30.34, 21.51, 20.78, 17.25. ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -14.80$ (s). Mass: APCI-$m/z = 681.1$ $[648 + O_2 + H]^+$ (bisoxidation product). Anal. Calc.: C, 83.31; H, 7.15. Found: C, 83.03; H, 7.12%.

Table 3
Crystallographic and selected experimental data of complexes **1** and **2**

	1	**2** · 2$CHCl_3$
Chemical formula	$C_{44}H_{46}Cl_2P_2Pd$	$C_{47}H_{48}Cl_8P_2Pd$
Formula weight	814.05	1064.79
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$C2/c$
Crystal colour and shape	Yellow plate	Yellow rod
Crystal size	$0.48 \times 0.42 \times 0.2$	$0.18 \times 0.10 \times 0.05$
a (Å)	10.5553(8)	26.079(5)
b (Å)	17.5232(14)	13.993(3)
c (Å)	10.3940(9)	15.307(3)
α (°)	90	90
β (°)	92.516(9)	120.98(3)
γ (°)	90	90
V (Å^3)	1920.6(3)	4789.0(17)
Z	2	4
T (K)	203(2)	173(2)
D_c (g cm^{-3})	1.408	1.477
μ (mm^{-1})	0.736	0.933
Scan range (°)	$3.92 < 2\theta < 51.86$	$3.96 < 2\theta < 51.96$
Unique reflections	3661	4493
Reflections used [$I > 2\sigma(I)$]	2977	2631
R_{int}	0.0791	0.0620
Final R indices [$I > 2\sigma(I)$][a]	0.0328, wR_2 0.0816	0.0554, wR_2 0.1266
R indices (all data)	0.0416, wR_2 0.0847	0.1044, wR_2 0.1440
Goodness-of-fit	0.985	0.895
Max, Min $\Delta\rho$/e (Å^{-3})	0.801, −1.484	1.615, −1.345

[a] Structures were refined on F_o^2 : $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

4.4. Synthesis of diphenyl(2,4,6-trimethylbenzyl)phosphine palladium dichloride (*1*)

In 40 mL of dichloromethane, diphenyl(2,4,6-trimethylbenzyl)phosphine (1 mmol, 0.259 g) and $PdCl_2$(cod) (0.142 g, 0.5 mmol) were stirred at room temperature for 2 days. Then, the solvent was evaporated and the residue was purified by column chromatography on silica gel with dichloromethane (yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$–7.50(m, 8H), 7.41(t, $J = 7.4$ Hz, 4H), 7.31–7.24(m, 8H), 6.65(s, 4H), 4.21(t, J = 3.6 Hz, 4H), 2.22(s, 6H), 2.02(s, 12H). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 13.68$(s). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.23$, 134.87, 134.81, 134.75, 130.70, 129.22, 128.08, 128.04, 27.42(C2), 22.07(C1), 21.19(C1). Anal. Calc.: C, 64.91; H, 5.70. Found: C, 64.65; H, 5.67%.

4.5. Synthesis of bis(3-((diphenylphosphino)methyl)-2,4,6-trimethylphenyl)methane palladium dichloride (*2*)

In 100 mL of dichloromethane, bis(3-((diphenylphosphino)methyl)-2,4,6-trimethylphenyl)methane (0.4 mmol, 0.259 g) and $PdCl_2$(cod) (0.12 g, 0.4 mmol) were stirred at room temperature for 2 days. Then, solvent was evaporated and the residue was purified by column chromatography on silica gel with dichloromethane (yield 70%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.99$–7.91(m, 4H), 7.55–7.48(m, 6H), 7.32(t, $J = 7.5$ Hz, 2H), 7.13(t, $J = 7.5$ Hz, 4H), 6.78–6.71(m, 6H), 4.35–4.26(m, 4H), 3.68(dt, $J = 13.0$ and 4.2 Hz, 2H), 2.48(s, 6H), 2.40(s, 6H), 1.17(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.02$(C4), 136.67(C4), 135.37(C3), 134.94(C4), 134.20(C3), 130.91 (C4), 130.64(C3), 128.86(C4), 128.33(C4), 127.26(C3), 33.75(C2), 28.62(C2), 24.15(C1), 21.98(C1), 19.63(C1). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 20.56$ (s). Mass: ESI-$m/z = 787.4$ [M–Cl–H]. Anal. Calc.: C, 65.42; H, 5.61. Found: C, 65.19; H, 5.58%.

4.6. Catalytic reactions

In a Schlenk tube, the catalyst was added (in the molar ratio given in Table 1 or 2) to a solution of 138 mg (0.5 mmol) of $K_2CO_3 \cdot 1.5\ H_2O$, 91 mg (0.75 mmol) of phenylboronic acid and 0.5 mmol of the aryl bromide in 5 mL of toluene. Then, the mixture was heated to the desired temperature (Table 1 or 2) and stirred for 18 h. After cooling, the solution was filtrated over a small silica gel column then eluted with ether (20 mL). The filtrate was combined with the ether washings, and the solution was analyzed by GC.

4.7. X-ray crystallographic study

Crystals of **1** and **2** were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–200°, increment of 1.2 and 1 respectively, 2θ range from 2.0 to 26°, $D_{max} - D_{min} = 12.45$–$0.81$ Å. All the structures were solved by direct methods using the program SHELXS-97 [21]. Refinement and all further calculations were carried out using SHELXL-97 [22]. In **1** and **2** the H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. In all cases the non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 3. Figures of **1** and **2** were drawn with POV-ray [23] and Fig. 3 with MERCURY [24].

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Appendix A. Supplementary data

CCDC-602844 **1** and 602845 **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc. cam.ac.uk]. Supplementary data associated with

this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.020.

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