C–C coupling

DOI: 10.1002/anie.200701804

Short, Facile, and High-Yielding Synthesis of Extremely Efficient Pincer-Type Suzuki Catalysts Bearing Aminophosphine Substituents**

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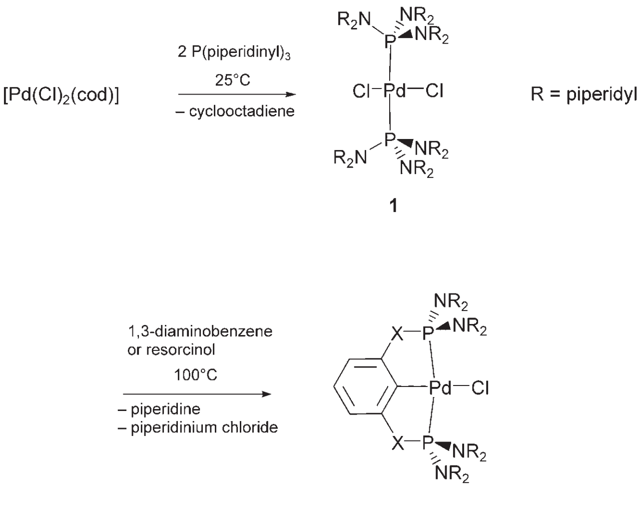
The Suzuki reaction is one of the most efficient methods for forming C–C bonds,[1,2] and is nowadays an indispensable tool in organic synthesis for the formation of symmetric and nonsymmetric biaryl compounds by catalysis.[3] Many palladium complexes have been used to promote the Suzuki–Miyaura cross-coupling reaction and, whilst some are very efficient and allow the use of sterically hindered substrates and even aryl chlorides at very low catalyst loadings and sometimes at room temperature, many suffer from poor thermal stability as well as poor stability towards air and moisture.[4–7] Moreover, the catalyst syntheses are often time consuming, difficult, and/or require the use of expensive starting materials.

After pincer-type complexes were successfully introduced as highly efficient and thermally stable catalysts in the Heck reaction,[8] interest in developing pincer-based Suzuki catalysts increased considerably.[9] For example, just recently 1,3-diaminobenzene-derived phosphine pincer palladium complexes were applied in Suzuki–Miyaura cross-coupling reactions.[10] Remarkably, these systems showed significantly increased levels of activity relative to the xylene- and resorcinol-derived analogues. Although recent catalysts have shown considerable increase in activity in the Suzuki reaction, typical Suzuki–Miyaura cross-coupling reactions still require prolonged reaction times. Therefore, we were intrigued by the possibility of developing catalytically active systems which would lead to high conversion rates in very short reaction times and low catalyst loadings. We have also focused on short, facile, and high-yielding syntheses of catalysts from inexpensive starting materials.

We present here a new concept for the synthesis of aminophosphine-based pincer complexes of palladium with the general formula $[Pd(Cl)(C_6H_3(XP(piperidinyl)_2)_2]$ (X = NH or O), which were formed by facile activation of C–H and P–N bonds. The conceptual novelty of their syntheses include the use of the readily prepared dichloro(bis(1,1′,1″-(phosphinetriyl)tripiperidine))palladium complex as a template for reactions with 2,6-diaminobenzene or resorcinol to build up the aromatic pincer core directly on the metal center, thus making the independent synthesis and purification of the air- and moisture-sensitive ligand systems unnecessary. The prepared pincer complexes turned out to be extremely efficient catalysts in the Suzuki reaction and led to high conversion rates and yields within several minutes. Experimental observations suggest that Pd^0 species (palladium nanoparticles, for example) are probably not the active form of the catalysts.

The addition of two equivalents of 1,1′,1″-(phosphinetriyl)tripiperidine to solutions of $[Pd(Cl)_2(cod)]$ (cod = cycloocta-1,5-diene) in toluene under N_2 at room temperature leads to the immediate and exclusive formation of dichloro(bis(1,1′,1″-(phosphinetriyl)tripiperidine))palladium (**1**), which can be isolated in quantitative yield.[11] Reaction mixtures of **1** can be used for subsequent transformations without purification. For example, facile activation of P–N and C–H bonds occurred when equimolar amounts of 1,3-diaminobenzene or resorcinol were added under N_2 to solutions of **1** in toluene and stirred at 100 °C for 45 and 15 minutes, respectively. This resulted in the exclusive formations of chlorobis[(dipiperidinylphosphino)amino]phenyl and 1,3-phenylene bis[dicyclohexyl(phosphinite)] palladium complexes with the general formula of $[Pd(Cl)(C_6H_3(XP(piperidinyl)_2)_2]$ (X = NH **2**; X = O **3**; Scheme 1). Removal of the volatiles under reduced pressure and subsequent extractions with diethyl ether gave pure **2** and **3** in high yields.[11] Complexes **2** and **3** are thermally very stable and no decomposition was observed within a week when *N*-methylpyrrolidone (NMP) or xylene solutions were heated at temperatures up to 150 °C. Similarly, no decomposition was



X = NH **2**; X = O **3**

Scheme 1. Synthesis of **2** and **3**.

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[**] This research was supported by the University of Zurich and the Swiss National Science Foundation (SNSF).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

noticed when **2** or **3** were heated at 100 °C in an oxygen atmosphere for more than a week. In contrast, when a few drops of water were added to solutions of **2** or **3** in dioxane (1 mL), partial palladium deposition was observed in both systems after heating at 100 °C for 24 h.

The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra of **2** and **3** showed sharp singlets at $\delta = 120.8$ and at $\delta = 146.1$ ppm, respectively. The signals attributable to the piperidinyl units appeared in the $^{1}\mathrm{H}$ NMR spectra as unresolved triplets at $\delta = 3.19$ and 1.56 ppm (**2**) and well-defined triplets at $\delta = 3.25$ and 1.56 ppm with coupling constants of $^{3}J_{\mathrm{HH}} = 4.3$ Hz (**3**). The NH protons of **2** gave a broad singlet at $\delta = 4.41$ ppm. The $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum of **2** displayed an unresolved triplet at $\delta = 123.3$ ppm, which was assigned to the palladium-coordinated carbon atom of the pincer core. The $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum of **3** is similar, and the triplet signal at $\delta = 128.6$ ppm ($^{2}J_{\mathrm{PC}} = 7.8$ Hz) confirmed the cyclometalation process. Complexes **2** and **3** were additionally characterized by X-ray crystallography (Figure 1). Their solid-state structures are very similar and exhibit slightly distorted square-planar geometries around the $\mathrm{Pd^{II}}$ centers. The Pd1–C1 and Pd1–Cl1 bond lengths of **2** are 1.994(8) and 2.401(2) Å, respectively, while those of complex **3** are 2.017(6) and 2.384(2) Å, and hence are of the expected lengths.[12] All the P–N bond lengths of **2** are in the range 1.619(8)–1.681(8) Å. The P1–O1 and P2–O2 bond lengths of **3** are 1.652(6) and 1.643(6) Å, respectively, whereas the P–N bond lengths vary in the range 1.621(8)–1.669(7) Å.

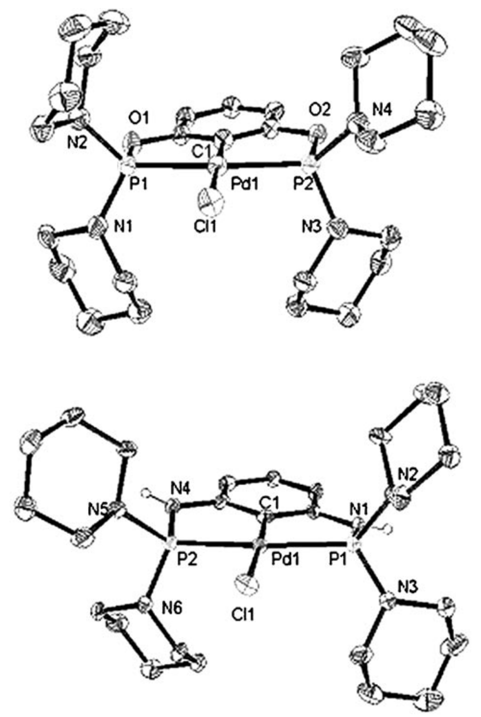

Figure 1. Ortep drawings of **2** (bottom) and **3** (top) in the crystal; thermal ellipsoids were set at 30% probability. All H atoms except H1 and H2 of **2** have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Complex **2**: Pd1-C1 1.994(8), Pd1-P2 2.277(2), Pd1-P1 2.299(2), Pd1-Cl1 2.401(2), P1-N3 1.619(8), P1-N1 1.669(7), P1-N2 1.680(7), P2-N6 1.660(7), P2-N4 1.676(7), P2-N5 1.681(8); P2-Pd1-P1 163.06(8), C1-Pd1-Cl1 176.9(3). Complex **3**: Pd1-C1 2.017(6), Pd1-P2 2.279(2), Pd1-P1 2.290(2), Pd1-Cl1 2.384(2), P1-N1 1.621(8), P1-N2 1.651(8), P1-O1 1.652(6), P2-N3 1.630(8), P2-O2 1.643(6), P2-N4 1.669(7); P2-Pd1-P1 160.21(8), C1-Pd1-Cl1 178.9(3).[13]

Complex **2** proved to be an extremely efficient catalyst for the Suzuki–Miyaura cross-coupling reaction, and led to very high reaction rates and yields in extremely short reaction times and with very low catalyst loadings (Table 1). Remarkably, complex **3** generally shows significantly lower activities than **2**. Since the steric congestions in **2** and **3** are almost identical (Figure 1), the higher catalytic activity of complex **2** over **3** is attributed to electronic factors, the metal center of **2** being more electron-rich than **3**. The CO stretching frequency of their cationic carbonyl derivatives is indicative of the significantly higher electron density at the metal center of $[\mathrm{Pd(CO)(C_6H_3(NHP(piperidinyl)_2)_2][BF_4]}$ (**4**; 2106 $\mathrm{cm^{-1}}$) as compared with its resorcinol derivative **5** (2133 $\mathrm{cm^{-1}}$).[11] As a consequence of the extremely high catalytic activities of **2** and **3**, Suzuki–Miyaura cross-coupling reactions can be carried out in toluene of technical quality in flasks open to air with almost the same reaction rates and yields as reactions performed under $\mathrm{N_2}$ and in freshly distilled toluene. This is possible since biaryl formation is much faster than water-induced catalyst degradation. Moreover, catalyst solutions of **2** and **3** can be prepared in "one pot" by sequential addition of 1,1′,1″-(phosphinetriyl)tripiperidine and 1,3-diaminobenzene or resorcinol to solutions of $[\mathrm{Pd(Cl)_2(cod)}]$ in toluene under $\mathrm{N_2}$.[11] The

Table 1: Suzuki cross-coupling reaction of aryl halides with phenylboronic acid catalyzed by $[\mathrm{Pd(Cl)(C_6H_3(XP(piperidinyl)_2)_2]}$ (X = NH **2**; X = O **3**).[a]

Entry	Aryl halide	Catalyst (mol %)	Conv. [%][b]	*t* [min]	TOF[c]	TON[d]
1	bromobenzene	**2** (0.001)	100	5	1 200 000	100 000
2	bromobenzene	**2** (0.0001)	100	55	1 090 909	1 000 000
3	bromobenzene	**3** (0.001)	98	10	588 000	294 000
4	4′-bromoacetophenone	**2** (0.001)	100	4	1 500 000	100 000
5	1,3-dibromobenzene	**2** (0.001)	100	10	600 000	50 000
6	4-bromoanisole	**2** (0.001)	95	5	1 140 000	95 000
7	4-bromoanisole	**3** (0.001)	96	10	576 000	96 000
8	2-bromotoluene	**2** (0.001)	83	5	996 000	83 000
9	2-bromo-*m*-xylene	**2** (0.001)	62	15	248 000	62 000
10	2-bromo-*m*-xylene	**3** (0.001)	92	30	184 000	92 000
11	chlorobenzene	**2** (0.1)	99	90	653	980
12	chlorobenzene	**3** (0.1)	31	90	207	276
13	4′-chloroacetophenone	**2** (0.01)	92	90	6133	9200
14	2-chloro-*m*-xylene	**2** (0.1)	11	180	37	110
15	4-chloroanisole	**2** (0.1)	8	180	27	80

[a] Reaction conditions: aryl halide (4.0 mmol), $\mathrm{PhB(OH)_2}$ (6.0 mmol), $\mathrm{K_3PO_4}$ (8.0 mmol), toluene (12 mL, technical quality), catalyst (synthesized in one pot and used without purification) were added in solution and the reactions were performed in air at 100 °C. [b] Determined by GC/MS, based on the aryl halide. [c] Defined as mol product per mol of catalyst per hour. [d] Defined as mol product per mol of catalyst.

resulting catalyst solutions were used for catalytic reactions without purification and remain stable in solution for several months at room temperature, and afford the coupling products at essentially the same conversion rates and yields as freshly prepared catalyst solutions from pure **2** and **3**, respectively.[14] For example, bromobenzene and phenylboronic acid in the presence of K_3PO_4 underwent complete C–C coupling in toluene at 100 °C with only 0.001 mol % of catalyst **2** within 5 minutes (Table 1, entry 1). No induction period was required; approximately 40 % conversion was observed after one minute. Higher conversion rates were realized with **2** when activated aryl bromides were used as substrates (Table 1, entry 4). Coupling reactions performed with 1,3-dibromobenzene yielded 76 % 1,1′:3′,1″-terphenyl and 24 % 3-bromobiphenyl after five minutes, while complete conversion into 1,1′:3′,1″-terphenyl was achieved after ten minutes (Table 1, entry 5). The activity only slightly decreases with increasing electron density on the aryl bromide. For example, when the electronically deactivated 4-bromoanisole was employed, 95 % conversion was obtained within five minutes (Table 1, entry 6). A further decrease in activity was obtained by using sterically hindered substrates. While coupling reactions with 2-bromotoluene led to 83 % conversions within 5 minutes, 62 % conversion was obtained after 15 minutes using 2-bromo-*m*-xylene as the substrate (Table 1, entries 8 and 9). Reactions carried out with 4′-chloroacetophenone or chlorobenzene also showed high conversion rates in short reaction times (Table 1, entries 11–13). For example, complete conversions of chlorobenzene at 100 °C with 0.1 mol % catalyst **2** was observed after 90 minutes (Table 1, entry 11). In contrast, coupling reactions with deactivated or sterically hindered aryl chlorides were less successful and only led to approximately 10 % conversions after 3 h (Table 1, entries 14 and 15). Nevertheless, in most of the examples of the Suzuki–Miyaura cross-coupling reactions performed (in particular when aryl bromides as well as activated and unactivated aryl chlorides were employed), catalysts **2** (and to a minor extent **3**) were more efficient than the reference systems of $[Pd(Cl)(C_6H_3(NHP(Ph)_2)_2]$,[10] $[Pd_2(Cl)_2(C_6H_2(t\mathrm{Bu})_2O)P(OR)_2)_2]$,[6g,15] and $Pd(OAc)_2/PCy_2Ar$.[2h] Comparisons with the extremely active air- and moisture-stable NHC-bearing $[Pd^{II}(Cl)(R\text{-allyl})]$ (NHC = N-heterocyclic carbene)[16] complexes are difficult, since the Suzuki reactions were generally performed at room temperature.[7k] However, because of the high conversions obtained within a few minutes and the facile syntheses of **2** and **3**, these systems belong to the most convenient Suzuki catalysts reported to date.

The Suzuki reaction is strongly influenced by the solvent and base. For example, replacing toluene with NMP and/or K_3PO_4 with K_2CO_3 or Cs_2CO_3 led to a substantial drop in the reaction rate. The same trend was observed by lowering the reaction temperature, which led to 30 % conversion after 12 h and 58 % conversion after 24 h with 0.01 mol % of catalyst **2** at 50 °C. Almost no activity was observed at room temperature.

Although the reaction mechanism has not been studied in detail, transformations of **2** (or **3**) into another, catalytically active species (palladium nanoparticles, for example) appears to be unlikely since **2** and **3** did not require an induction period. Further evidence for this was gained from the addition of tetrabutylammonium bromide (ca. 15 mol %)—a salt known to stabilize palladium nanoparticles—to catalytic reaction mixtures with **2** and **3**: no influence on the conversion rate or yield was observed. The same findings were made in the mercury drop test,[17] thus suggesting that the catalytic active species has a homogeneous nature, since heterogeneous catalysts would form an amalgam, thereby poisoning it. Finally, the formation of biphenyl-2,6-diamine was not detected (by GC/MS) in catalytic reactions with 0.1 mol % catalyst and bromo- or chlorobenzene as substrates after hydrolytic workup. This finding suggests that the Pd–C bond remains intact during catalysis. The only change observed at the end of a catalysis reaction performed with phenyl bromide, for example, is substitution of the chloride ligand to give the corresponding palladium bromide complex, as shown by $^{31}P\{^1H\}$ NMR spectroscopy.[11] Hence, the catalysts remain highly active after the reaction is complete and catalysis is resumed, upon addition of more substrates, to afford coupling products at essentially the same rates. Similar to the Heck reaction catalyzed by pincer-type complexes, where mechanisms based on Pd^{II}/Pd^{IV} have been postulated,[8,18] mechanisms involving Pd^{IV} species in the Suzuki reaction may need to be taken into account.[19]

In summary, a new concept for the facile, short, and high-yielding synthesis of complexes with the general formula $[Pd(Cl)(C_6H_3(XP(\text{piperidinyl})_2)_2]$ (X = NH **2** or O **3**) has been developed, which may be applicable to other metal centers and aminophosphines. These complexes were found to be extremely efficient catalysts in the Suzuki reaction. Moreover, catalyst solutions of **2** and **3** can be prepared in a one-pot reaction and are stable for several months, and lead to coupling products at essentially the same reaction rates and yields as freshly prepared catalyst solutions of pure **2** and **3**, respectively. Activation processes including the cleavage of the palladium–carbon bond and/or the formation of palladium nanoparticles as the active form of the catalysts are unlikely. Further investigations aimed at clarifying the scope and mechanism of these catalysts are in progress.

Received: April 24, 2007
Revised: June 6, 2007
Published online: July 24, 2007

Keywords: C–C coupling · P ligands · palladium · phosphanes · Suzuki reaction

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[19] The electronic properties of aminophosphines could provide a possible explanation for the high catalytic activities of **2** and **3** if Pd^{IV} intermediates are involved in the catalytic cycle. The high σ-donor strength of the P atom of aminophosphines is thought to arise from donation of electron density towards the P atom from the lone pairs of electrons on the N atom. This property could facilitate the accessibility of Pd^{IV} intermediates by additional electron donation to the P atom, possibly accompanied by temporary shortening of the P–N bond lengths.[20]

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