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# Active catalysts for the Suzuki coupling: Palladium complexes of tetrahydropyrimid-2-ylidenes☆

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**Abstract**

An alternative way to synthesize a mixed N-heterocyclic carbenes (NHC) phosphine palladium(II) complex is described in this work. A free carbene, generated by deprotonation of a tetrahydro-pyrimidinium salt, was reacted with $Pd(PPh_3)_2Cl_2$ to yield the desired mixed NHC phosphine palladium(II) complex.

In this work, we have combined the superior activity of mixed NHC phosphine palladium complexes in Suzuki-coupling reactions with the additional advantage of a stronger σ-donating ligand. The combination of these two effects results in an increased catalytic activity in Suzuki reactions than found for corresponding mixed imidazole–ylidene phosphine complexes.

Using this new class of catalysts, TONs of approximately 1 Mio. after a reaction time of 14 h can be achieved. Desactivated bromoarenes could also be coupled efficiently, using quite a low amount of catalyst (0.005 mol%). Even aryl chlorides can be coupled: TONs of approximately 6000 can be reached after only 14 h without any detectable catalyst deterioration using only 0.01 mol% of catalyst.


*Keywords:* N-heterocyclic carbene; Tetrahydropyrimid-2-ylidene; Palladium; Suzuki coupling; Carbon–carbon bond formation

## 1. Introduction

Palladium complexes have widely been used as catalysts for carbon–carbon bond forming reactions [1]. These reactions are key steps in many syntheses of organic chemicals, natural products, as well as in a variety of industrial processes [1]. One important example of this type of catalysis is the Suzuki–Miyaura reaction [2].

Palladium(II) complexes of N-heterocyclic carbenes (NHC) are well known, and various routes to obtain them have been published [3]. Often times they are thermally stabile and display high dissociation energies regarding the Pd–NHC bond [4]. These complexes have been successfully applied to Heck-type C,C-coupling reactions [5].

Phosphine complexes of palladium(II) are even better known and easily prepared from palladium(II) salts and an excess of phosphine ligand [6]. With these complexes, the catalytic activity of palladium in various reactions including C,C-coupling has been established [1]. Despite their activity as potential catalysts, these complexes suffer from easy ligand dissociation, resulting in deactivation [1b]. There have been many efforts to avoid this unwanted degradation processes [7].

Herrmann et al. have repeatedly shown that the replacement of a phosphine ligand by a stronger σ-donating NHC ligand alters the electron density on the palladium centre, thus facilitating the halogen aryl activation [5a]. Therefore, mixed NHC phosphine complexes of palladium proved to be more efficient than bis(carbene) or bis(phosphine) complexes in C,C-coupling catalysis, especially in the Suzuki–Miyaura reaction [8]. To maximize this effect, much interest is presently dedicated to novel, strongly electron-donating N-heterocyclic carbene ligands.

The acyclic bis(dialkylamino)carbenes published by Alder et al. [9] are the strongest σ-donating carbene ligands known so far [10]. However, their metal complexes suffer from peculiar deactivation phenomena [10]. For this reason, the six-membered tetrahydropyrimid-2-ylidenes were investigated since they expect to be comparable in their σ-donor strength [10], but may form more stable metal complexes.

☆ N-heterocyclic carbenes, 41. Mitteilung. – 40. Mitteilung: Lit. [16].

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It could be shown in literature that ruthenium complexes with isopropyl and mesityl substituted tetrahydropyrimid-2-ylidene ligands are active catalysts in olefin metathesis. Grubbs-type catalysts [11] as well as Grubbs–Hoveyda-type catalysts [12] were reported in this regard. Also certain silver(I)–carbene complexes with this particular ligand were recently reported [13].

In the present paper, we report that tetrahydropyrimid-2-ylidene ligands form exceptionally active palladium(II) catalysts for the Suzuki–Miyaura reaction.

## 2. Experimental part

### 2.1. General comments

NMR spectra ($^1$H, $^{13}$C) were recorded either on a Jeol JMX-GX 400, on a Jeol JMX-GX 270 or on a Bruker DPX 400 instrument. Chemical shifts are given in ppm. The spectra are calibrated to the residual protons of the solvent ($^1$H) or to the 13-carbon signals of the solvent ($^{13}$C). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, q = quintet, m = multiplet. Coupling constants *J* are given in Hz. FAB-MS spectra were measured at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer (xenon/*p*-nitrobenzyl alcohol). Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. GC spectra were measured on a Hewlett-Packard gas chromatograph GC 6890 A equipped with a FID.

Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques. All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. Other chemicals were obtained from commercial sources and used without further purification.

### 2.2. *trans*-Chloro(1,3-diisopropyltetrahydropyrimid-2-ylidene)bis(triphenylphosphine)palladium(II)-chloride ***3***

In 30 ml of THF 250 mg (0.97 mmol, 1 eq.) **1**, 43 mg (0.38 mmol, 0.4 eq.) KO$^t$Bu and 425 mg (17.7 mmol, 18.2 eq.) NaH were mixed and stirred for 2 h at room temperature. The formed free carbene was extracted with 15 ml *n*-hexane, which after removal of the solvent, remains as a colourless oil. This oil is solved in 15 ml of dry THF, and then canulated to a suspension of 375 mg (0.35 mmol) *trans*-Pd(PPh$_3$)$_2$Cl$_2$ in THF.

After stirring for 3 h, the solvent was removed in vacuo and the residue was washed with 50 ml of hexane. The crude product is extracted with 50 ml of acetonitrile. After removal of the solvent, the crude product is solved in dichloromethane and precipitated with pentane. Product: colourless powder: 270 mg (yield: 89%).

$^1$H NMR (270.2 MHz, CDCl$_3$): $\delta$ = 7.70–7.04 (m, 30H, ArH), 5.35 (septett, 2H, *J* = 7.0 Hz, NCHMe$_2$), 3.14 (t, 4H, *J* = 5.6 Hz, NCH$_2$), 2.20 (quintet, 2H, *J* = 5.6 Hz, CCH$_2$C), 0.42 (d, 12H, *J* = 7.0 Hz, CH$_3$).

$^{13}$C{$^1$H} NMR (67.9 MHz, CDCl$_3$): $\delta$ = 182.1 (t, *J* = 5.6 Hz, NCN), 134.7–128.9 (m, ArC), 60.2 (NCHMe$_2$), 40.8 (NCH$_2$), 29.7 (CH$_3$), 19.2 (CCH$_2$C).

$^{31}$P{$^1$H} NMR (109.4 MHz, CDCl$_3$): $\delta$ = 22.2 (s).

MS (FAB-MS): *m/z* (relative intensity) 833 [M]$^+$ (**5**); 572 [M − PPh$_3$]$^+$ (12); 536 [M − PPh$_3$ − Cl]$^+$ (4).

### 2.3. *cis*-Dichloro(1,3-diisopropyltetrahydropyrimid-2-ylidene)(triphenylphosphine) palladium(II) ***4***

200 mg (0.23 mmol) of **3** were dissolved in 40 ml of toluene and stirred for 2 h at 120 °C yielding a white precipitate. The precipitated product was filtered off and was washed with 25 ml of toluene. Drying in vacuo affords 129.7 mg (yield: 93%) of a colourless solid, which could be identified as **4**.

$^1$H NMR (399.8 MHz, CDCl$_3$): $\delta$ = 7.96–7.35 (m, 15H, ArH), 5.84 (septett, 2H, *J* = 7.2 Hz, NCHMe$_2$), 3.21 (m, 2H, NCH$_2$), 2.71 (m, 2H, NCH$_2$), 1.73 (m, 2H, CCH$_2$C), 1.56 (d, 6H, CH$_3$), 0.43 (d, 6H, CH$_3$).

$^{13}$C{$^1$H} NMR (100.5 MHz, CDCl$_3$): $\delta$ = 183.6 (d, *J* = 28.8 Hz, NCN), 135.2–128.5 (m, ArC), 59.5, 59.2, 29.6, 19.7, 18.8.

$^{31}$P{$^1$H} NMR (161.8 MHz, CDCl$_3$): $\delta$ = 26.6 (s).

MS (FAB-MS): *m/z* (relative intensity) 571 [M − Cl]$^+$ (9); 535 [M − 2Cl]$^+$ (3).

Anal. Calcd. for 4 × C$_{28}$H$_{35}$Cl$_2$N$_2$PPd + 1 × CHCl$_3$: C, 53.20; H, 5.57; N, 4.39. Found: C, 53.14; H, 5.31; N, 4.14.

### 2.4. Suzuki reaction

A total of 1.2 equivalents of phenylboronic acid (293 mg, 2.4 mmol) and 1.5 equivalents of potassium carbonate (415 mg, 3 mmol) are placed in a Schlenk tube equipped with a stirring bar. The vessel is put under an argon atmosphere and 1.0 equivalent of aryl halide (2.0 mmol, e.g. 374 mg bromoanisole), 100 mg diethyleneglycol-di-*n*-butylether and 2 ml degassed xylene are added. After thermostating at 130 °C for 10 min, the required amount of the catalyst stock solution is added against a positive stream of argon. To finish the reaction, the mixture is allowed to cool to room temperature and 3 ml of water are added. The water phase is extracted three times with 2 ml of diethylether and the organic phases are dried with MgSO$_4$. The reaction products were identified and quantified by a Hewlett-Packard gas chromatograph GC 6890 A equipped with an FID detector, using diethylenglykole-di-*n*-butylether as internal standard.

#### 2.4.1. Catalyst stock solution

0.02 mmol of catalyst were solved (**3** or **4**) in 10 ml of dimethylacetamide (DMAc) and stored in the freezer. The concentration was chosen in order to make sure that for our experimental setup 0.1 ml of the stock solution equals a catalyst/substrate ratio of 0.01 mol% catalyst. For the experiments with extremely low catalyst concentrations, the initial stock solution was further diluted with DMAc.

### 2.5. Crystallography

#### 2.5.1. Crystal structure analysis of compound **4**

$C_{28}H_{35}Cl_2N_2PPd$, $3(CHCl_3)$, $M_r = 965.97$, colourless plate (0.25 mm × 0.51 mm × 0.81 mm), orthorhombic, $Pca2_1$ (No.: 29), $a = 19.3191(2)$, $b = 11.2720(1)$, $c = 38.2844(4)$ Å, $V = 8337.00(14)$ Å$^3$, $Z = 8$, $d_{calc} = 1.539$ g cm$^{-3}$, $F_{000} = 3888$, $\mu = 1.214$ mm$^{-1}$. Preliminary examination and data collection were carried out on a kappa-CCD device (NONIUS MACH3) with an Oxford Cryosystems cooling device at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection were performed at 123 K within the $\Theta$ range of $1.06^\circ < \Theta < 25.35^\circ$. A total of 108,810 reflections were integrated, corrected for Lorentz, polarization, and arising from the scaling procedure, corrected for latent decay and absorption effects. After merging ($R_{int} = 0.028$), 14,593 [13,126: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 838 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions (riding model). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with $R1 = 0.0282$ [$I_o > 2\sigma(I_o)$], $wR2 = 0.0662$ [all data], GOF = 1.028 and shift/error < 0.001. The final difference-Fourier map shows no striking features ($\Delta e_{min/max} = +0.71/-0.51$ e Å$^{-3}$). The unit cell contains two crystallographically independent molecules **A** and **B** and six solvent molecules $CHCl_3$ [17].

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthesis of the tetrahydropyrimidinium salt **1** is achieved according to Saba et al. [14] by reaction of *N*,*N*-diisopropylpropane diamine with triethyl orthoformiate and ammonium tetrafluoroborate. In order to make a mixed phosphine carbene complex, a halobridged derivative according to Herrmann et al. [8] had to be prepared, which can subsequently be split using a phosphine to yield the desired product. Unfortunately, the well-known reaction to synthesize imidazolylidene palladium(II) complexes by treating an imidazolium salt with $Pd(OAc)_2$, KO$^t$Bu and NaI in acetonitrile [8] failed when it was applied to the saturated 6-membered tetrahydropyrimidinium salts, probably due to the low acidity of the azolium-H. The reaction of the free carbene **2**, derived according to Alder et al. by reacting the tetrahydropyrimidinium salt with NaH and catalytic amounts of KO$^t$Bu [15] with $Pd(PPh_3)_2Cl_2$ in THF, afforded compound **3**. This compound could then be transformed to compound **4** by refluxing a toluene solution of **3** (Scheme 1). Compound **3** already contains traces of **4**. The latter complex is already formed during the reaction of the free carbene **2** with the palladium precursor.

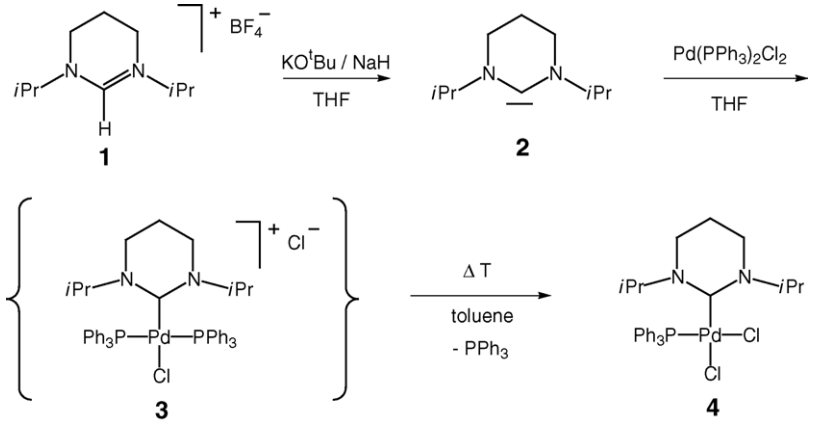
The reaction of **2** with common Pd(II) precursors like $Pd(CH_3CN)_2Cl_2$ failed, as the free carbenes of the six-membered ring carbenes are strong reducing agents as compared to their unsaturated, five-membered ring analogues [11]. For example, the $Pd(CH_3CN)_2Cl_2$ was reduced to palladium black upon addition of the free carbene to a suspension of the palladium(II) precursor in THF.

Complexes **3** and **4** are soluble in polar solvents like dichloromethane or chloroform. However, they are insoluble in non-polar solvents like *n*-pentane, *n*-hexane and diethylether. Compound **3** is soluble in hot toluene and **4** is insoluble.

**4** can be obtained after recrystallization from chloroform/*n*-pentane as colourless plates. The molecular structure of **4** was determined by X-ray diffraction techniques.

All compounds were identified by $^1$H and $^{13}$C NMR spectroscopy, elemental analysis and FAB-MS.

The carbene carbon signal of **3** appears at 182.1 ppm as a triplet with a coupling constant of ca. 5.6 Hz, indicating two phosphine groups in a *trans* arrangement. The two phosphine groups, are thus equivalent and show a single resonance at 22.2 ppm. The protons of the isopropyl groups also give rise to only one set of signals, as expected for a *trans* arrangement of the two-phosphine ligands. The carbene carbon signal of **4** appears at 183.6 ppm as doublet with a coupling constant of about 28.8 Hz indicating only one phosphine group. The $^{31}$P NMR spectrum contains only one resonance with a chemical shift of 26.6 ppm. The protons of the isopropyl groups show two




Scheme 1. Synthetic procedure; Ph = $C_6H_5$, *i*Pr = *i*-$C_3H_7$, $^t$Bu = *t*-$C_4H_9$.

different sets of signals, also indicating the *cis* arrangement of the phosphine and the carbene ligand. This *cis* arrangement is also in line with the X-ray crystal structure of complex **4**.

For the Pd(II) carbene complex **3**, the most prominent peak in the mass spectrum is the $[M - PPh_3]^+$ fragment. The molecular peak $[M]^+$ with $m/z = 571$ is also present. A third peak at 535 $[M - PPh_3{}^-Cl]^+$ indicates the molecular structure of **3**. The peaks at 571 $[M - Cl]^+$ and at 535 $[M - 2Cl]^+$ are also detected in the FAB-MS of **4**. The molecular peak is missing which is in line with the fact, that **4** is neutral, and therefore the loss of an anion is necessary to reach a fragment which is detectable in the FAB-MS. In both spectra (for **3** and **4**), the isotope patterns are in accord with palladium carbene fragments.

### 3.2. X-ray crystal structure of the six-membered N-heterocyclic carbene complex *4*

The molecular structure of the square-planar Pd(II) complex **4** in the solid state is shown in Fig. 1. Selected bond lengths and angles are depicted in Table 1. To our knowledge, this is the first X-ray structure determination of a mixed phosphine tetrahydropyrimid-2-ylidene palladium(II) complex. It is especially noteworthy to mention that **4** is one of the very few cases of mixed carbene–phosphine complexes with a *cis*-arrangement of the two ligands. In most of the known imidazol-based examples, the phosphine and the carbene are in *trans* position to each other [8]. Another example of such an arrangement is a corresponding dimethylpyrazol-2-ylidene palladium(II) complex recently reported by our group [16]. The *cis*-structure of **4** is in accord with the solution-phase geometry, cf. the above NMR data.

The complexes **4** and **5** (Fig. 2) enable us to compare the structural differences between imidazolin-2-ylidene and tetrahydropyrimid-2-ylidene complexes. The transition from the five-membered to the six-membered ring geometry causes a widening of the $NC_{carbene}N$-bond angle from ca. 106° in **5** to 120.5° in **4**. This results in a compression of the α-angle $C_RNC_{carbene}$ from 131° in the imidazole complex [8] to 121° in **4** (Table 1; Fig. 2). The $C_{carbene}$–Pd distance of 2.00 Å in **4** is slightly shorter than the one reported for the corresponding imidazol-2-ylidene compound (2.03 Å) (Table 1; [8]).

Table 1
Selected bond lengths [Å] and bond angles [°] in **4** and **5** [X = Cl (**A**,**B**), X = I (**5**)]

| | **4**·**3**$CHCl_3$ | | **5** [8] |
|---|---|---|---|
| | **A** | **B** | |
| Pd—$C_{Carbene}$ | 2.003(4) | 1.999(4) | 2.031(4) |
| Pd—P | 2.2648(9) | 2.2642(9) | 2.334(1) |
| Pd—X1 | 2.3660(8) | 2.3660(8) | 2.6325(8) |
| Pd—X2 | 2.3649(9) | 2.3647(8) | 2.6175(8) |
| N1—$C_{Carbene}$ | 1.339(5) | 1.338(5) | 1.362 |
| N2—$C_{Carbene}$ | 1.328(5) | 1.338(5) | 1.361 |
| $C_{Carbene}$—Pd—X1 | 176.60(10) | 176.45(10) | 86.43 |
| $C_{Carbene}$—Pd—X2 | 87.25(10) | 86.92(10) | 89.81 |
| $C_{Carbene}$—Pd—P | 92.09(10) | 92.40(10) | 175.5 |
| X2—Pd—P | 179.33(3) | 179.18(3) | 90.19 |
| N1—$C_{Carbene}$—N2 | 120.5(3) | 120.1(3) | 105.7(3) |
| $C_R1$—N1—$C_{Carbene}$ | 121.4(3) | 120.8(3) | 130.4 |
| $C_R2$—N2—$C_{Carbene}$ | 121.0(3) | 121.1(3) | 130.6 |

### 3.3. Catalysis

Phosphine-based systems and NHC-based complexes are among the most active catalysts for the Suzuki–Miyaura reaction. Despite the high activities reported for phosphine-based systems [1], NHC-based catalysts are much more stable under

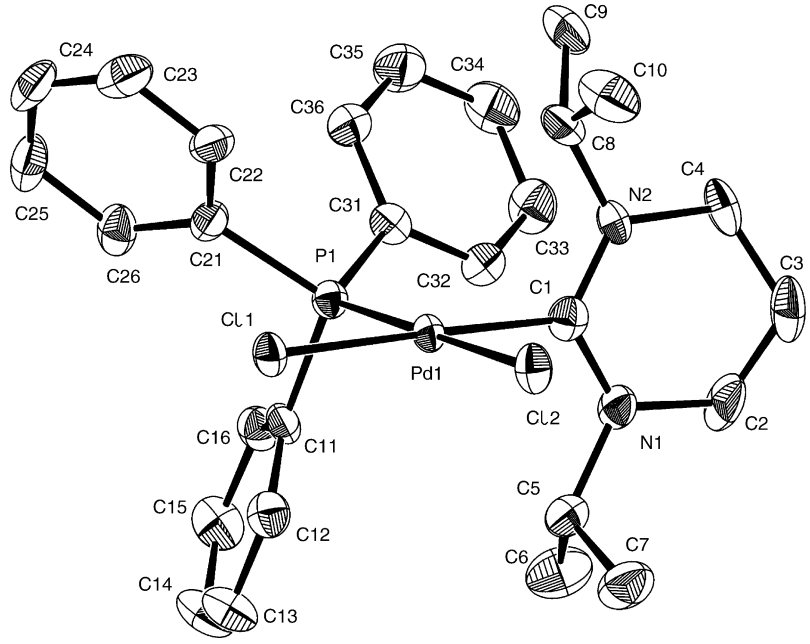



Fig. 1. ORTEP style plot of molecule **A** in the solid state of compound **4**. Thermal ellipsoids are drawn at the 50% probability level.

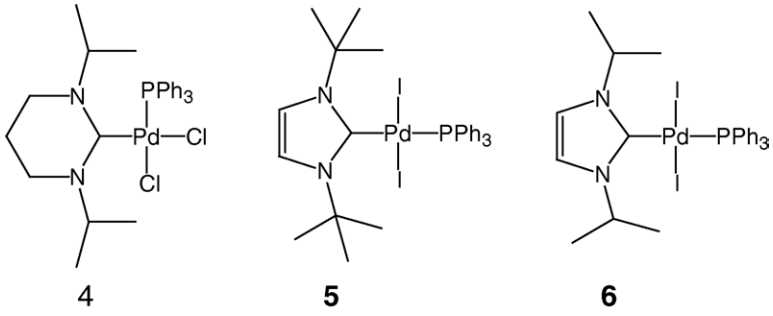



Fig. 2. NHC-complexes for comparison.

the relevant reaction conditions; they also can be recycled and reused. Moreover, higher reaction temperatures are an option of the NHC-based catalysts.

The data obtained for the Suzuki–Miyaura reaction of aryl bromides and chlorides with phenylboronic acid are summarized in Table 2. The results show that **4** is indeed a an excellent catalyst for the coupling of activated as well as deactivated aryl bromides; turnover numbers of 1 Mio. can be reached after 14 h (entries 3 and 4, Table 2).

Deactivated bromoarenes can also be coupled with low amounts of catalysts. The optimum concentration of catalyst was minimized in this case to 0.005 mol% (entry 11), this is unexpected in case of deactivated bromoarenes [5a].

Even aryl chlorides can be coupled with only 0.01 mol% of catalyst **4** (entry 21, Table 2) no catalyst deterioration is observed. TONs of 6000 after only 14 h can be reached.

Catalyst **4** reveals to be superior to its congener **3**. However, the differences are not dramatic. The difference is possibly caused by the lower stability of **3** under the catalytic conditions applied. Pd black occurred faster when **3** instead of **4** was used as catalyst.

It is known that the use of alkylphosphines instead of arylphosphines strongly enhances the activity of such mixed NHC phosphine catalysts, especially in the Suzuki reaction [8,10]. We expect the tricyclohexylphosphine derivative to give even more improved activities. Experiments are under way.

To put the results in a proper context, time conversion experiments were performed to compare the activity of **4** with the corresponding imidazolylidene palladium(II) complex **6** (Fig. 2), which was generated according to Herrmann et al. [8].

In order to evaluate the differences in activity, the coupling of 4-chloroacetophenone with phenylboronic acid was followed over time (Fig. 3).

It can be seen that **4** is more active than **6**. It is remarkable that the initial activity of **4** is much higher than for **6**, cf. Figs. 2 and 3. There is no induction period, thus indicating a quick formation of the catalytically active $Pd^0$ species. Complex **6** clearly shows a lower starting activity combined with a weaker overall performance. This is probably due to the stronger σ-donating ligand present in **4**, which might help in the reduction step forming the active species. We explain the superior performance of **4** as

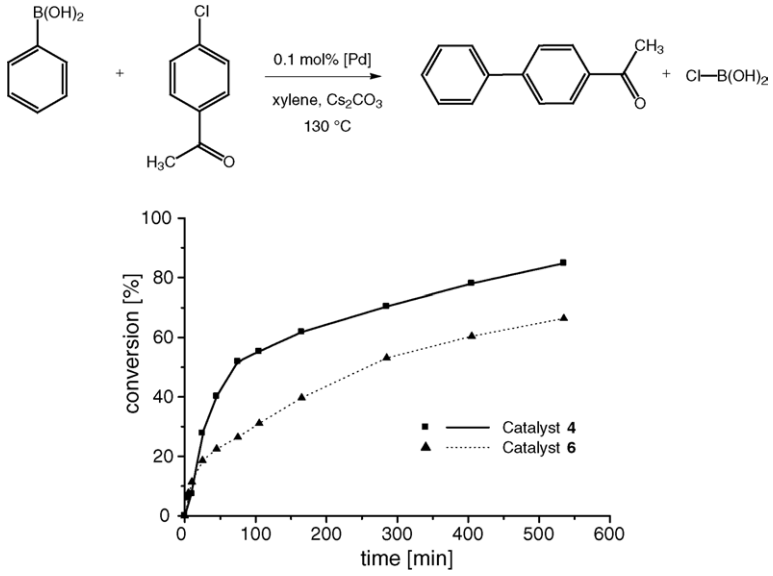
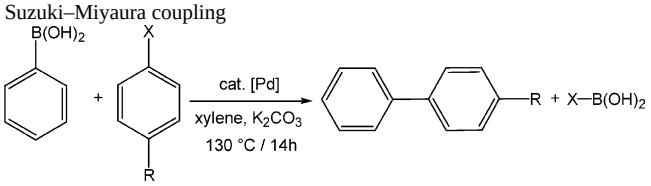



Fig. 3. Time-conversion diagram of the Suzuki–Miyaura reaction.

Table 2
Suzuki–Miyaura coupling




| Entry | *R* | *X* | Pd (mol%) | Catalyst | Yield (%) | TON |
|---|---|---|---|---|---|---|
| 1 | $C(O)CH_3$ | Br | 0.01 | **4** | 100 | $10^4$ |
| 2 | $C(O)CH_3$ | Br | 0.001 | **4** | 100 | $10^5$ |
| 3 | $C(O)CH_3$ | Br | 0.0001 | **4** | 100 | $10^6$ |
| 4 | $C(O)CH_3$ | Br | $10^{-5}$ | **4** | 10 | $10^6$ |
| 5 | $C(O)CH_3$ | Br | 0.001 | **3** | 100 | $10^5$ |
| 6 | $C(O)CH_3$ | Br | 0.0001 | **3** | 63 | $6.3 \times 10^5$ |
| 7 | H | Br | 0.01 | **4** | 100 | $10^4$ |
| 8 | H | Br | 0.001 | **4** | 100 | $10^5$ |
| 9 | H | Br | 0.0001 | **4** | 100 | $10^6$ |
| 10 | H | Br | $10^{-5}$ | **4** | 3 | $3 \times 10^5$ |
| 11 | H | Br | 0.001 | **3** | 100 | $10^5$ |
| 12 | H | Br | 0.0001 | **3** | 80 | $8 \times 10^5$ |
| 13 | OMe | Br | 0.1 | **4** | 91 | $9.1 \times 10^2$ |
| 14 | OMe | Br | 0.01 | **4** | 80 | $8 \times 10^3$ |
| 15 | OMe | Br | 0.005 | **4** | 89 | $1.78 \times 10^4$ |
| 16 | OMe | Br | 0.001 | **4** | 63 | $6.3 \times 10^4$ |
| 17 | OMe | Br | 0.01[b] | **4** | 100 | $10^4$ |
| 18 | OMe | Br | 0.1 | **3** | 88 | $8.8 \times 10^3$ |
| 19 | OMe | Br | 0.01 | **3** | 85 | $8.5 \times 10^4$ |
| 20 | $C(O)CH_3$ | Cl | 0.1[a] | **4** | 87 | $8.7 \times 10^3$ |
| 21 | $C(O)CH_3$ | Cl | 0.01[a] | **4** | 60 | $6 \times 10^4$ |
| 22 | $C(O)CH_3$ | Cl | 0.1[a] | **3** | 65 | $6.5 \times 10^3$ |

[a] $Cs_2CO_3$ as the base.

compared to **6** with the stronger σ-donating properties of the tetrahydropyrimid-2-ylidene ligands.

## 4. Conclusion

Tetrahydropyrimid-2-ylidenes form excellent palladium catalysts for the Suzuki coupling, particularly when the N-heterocyclic carbenes are combined with phosphines at the metal centre. Especially remarkable is the fact that even chloro arenes work well with the new catalysts, with concentrations of the latter in the order of 0.01 mol% being fully sufficient. A further optimization of NHC-derived C,C-coupling catalysts seems possible. As already mentioned above, this optimization could probably be achieved by employing catalysts bearing stronger basic phosphanes, e.g. tricyclohexylphosphane in the reported Suzuki coupling. Different palladium precursors like $Pd(PCy_3)_2Cl_2$ have to be investigated in this regard. Also the variation of the N-substituent in the carbene ligand may alter the activity of these catalysts in a positive way too. Active work in this area is on the way.

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## References

[1] (a) J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, 1995; (b) W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, second ed., VCH, Weinheim, 2002.
[2] (a) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457; (b) A. Suzuki, Pure Appl. Chem. 63 (1991) 419.
[3] (a) W.A. Herrmann, Angew. Chem. 114 (2002) 1342; W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 41 (2002) 1290; (b) W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256; W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162; (c) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, Chem. Eur. J. 2 (1996) 772; (d) W.A. Herrmann, J. Schwarz, M.G. Gardiner, M. Spiegler, J. Organomet. Chem. 575 (1999) 80.
[4] J. Schwarz, V.P.W. Böhm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, Chem. Eur. J. 6 (2000) 1773.
[5] (a) W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. 107 (1995) 2602; W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. Int. Ed. Engl. 34 (1995) 2371; (b) W.A. Herrmann, K. Öfele, D.v. Preysing, S.K. Schneider, J. Organomet. Chem. 687 (2003) 229; (c) D. Enders, H. Gielen, G. Raabe, J. Runsink, J.H. Teles, Chem. Ber. 129 (1996) 1483; (d) D.S. McGuinness, M.J. Green, K.J. Cavell, B.W. Skelton, A.H. White, J. Organomet. Chem. 572 (1999) 239.
[6] F. Ozawa, in: S. Komiya (Ed.), Synthesis of Organometallic Compounds, Wiley, Sussex, 1997, p. 249 ff.
[7] Examples; (a) M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Broßmer, Angew. Chem. 107 (1995) 1992; M. Beller, H. Fischer, W.A. Herrmann, K. Öfele, C. Broßmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 1848; (b) A.F. Littke, G.C. Fu, Angew. Chem. 110 (1998) 3586; A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. Engl. 37 (1998) 3387; (c) D.W. Old, J.P. Wolfe, S.L. Buchwald, J. Am. Chem. Soc. 120 (1998) 9722.
[8] W.A. Herrmann, V.P.W. Böhm, C.W.K. Gstöttmayer, M. Grosche, C.-P. Reisinger, T. Weskamp, J. Organomet. Chem. 617–618 (2001) 616.
[9] R.W. Alder, P.R. Allen, M. Murray, A.G. Orpen, Angew. Chem. Int. Ed. Engl. 35 (1996) 1121.
[10] W.A. Herrmann, K. Öfele, D.v. Preysing, E. Herdtweck, J. Organomet. Chem. 684 (2003) 235.
[11] (a) M. Sakamoto, S. Okada, Y. Tsunokai, S. Ikeda, W.A. Herrmann, K. Öfele, Nippon Zeon Co. Ltd, JP 2003089689, 2003; (b) W.A. Herrmann, K. Öfele, S. Okada, S. Ikeda, M. Sakamoto, Y. Tsunokai, WO 03027079, 2005; (c) J. Yun, E.R. Marinez, R.H. Grubbs, Organometallics 23 (2004) 4172.
[12] L. Yang, M. Mayr, K. Wurst, M.R. Buchmeiser, Chem. Eur. J. 10 (2004) 5761.
[13] (a) W.A. Herrmann, S.K. Schneider, K. Öfele, M. Sakamoto, E. Herdtweck, J. Organomet. Chem. 689 (2004) 2441; (b) M. Mayr, K. Wurst, K.-H. Ongania, M.R. Buchmeiser, Chem. Eur. J. 10 (2004) 1256; (c) M. Mayr, M.R. Buchmeiser, Macromol. Rapid Commun. 25 (2004) 231.
[14] S. Saba, A.-M. Brescia, M.K. Kaloustian, Tetrahedron Lett. 32 (1991) 5031.
[15] R.W. Alder, M.E. Blake, C. Bortolotti, S. Bufali, C.P. Butts, E. Linehan, J.M. Oliva, A.G. Orpen, M.J. Quale, Chem. Commun. (1999) 241.
[16] G.D. Frey, W.A. Herrmann, J. Organomet. Chem. 690 (2005), in press.
[17] (a) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-281521

(4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk);
(b) Data Collection Software for Nonius kappa-CCD devices, Delft, The Netherlands, 2001;
(c) Z. Otwinowski, W. Minor, Methods in Enzymology 276 (1997) 307ff;
(d) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR92, J. Appl. Crystallogr. 27 (1994) 435;
(e) International Tables for Crystallography, vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2, in: A.J.C., Wilson, (Ed.), Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992;
(f) A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2001;
(g) G. M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1998.