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Palladium(II) Complexes with Chelating Biscarbene Ligands in the Catalytic Suzuki–Miyaura Cross-Coupling Reaction

Maik Micksch[a] and Thomas Strassner*[a]

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We studied the catalytic activity of palladium(II) complexes with chelating imidazolium and benzimidazolium ligands in the Suzuki–Miyaura cross-coupling reaction. The methylene-bridged systems with aryl substituents carrying sterically and electronically different groups (F, NO_2, OMe, H, Me, *i*Pr) show good to excellent catalytic activities in the Suzuki–Miyaura cross-coupling reaction of aryl bromides. The *p*-methoxyphenyl-substituted bis(NHC)–palladium complex was the most active one under our reaction conditions, also in the context of a wide substrate scope. Several *ortho*- as well as *para*-substituted aryl bromides were coupled in excellent yields under mild reaction conditions.

Introduction

Palladium-catalyzed cross-coupling reactions are one of the most powerful carbon–carbon bond-forming processes[1,2] and have recently been honored with the Nobel Prize for chemistry.[3] The Suzuki–Miyaura cross-coupling reaction has become a very important and widely used method in fine chemical syntheses.[4–8] Examples include the synthesis of 3-arylcoumarins,[9] 5-chloro-1-phenyltetrazoles,[10] isocoumarins[11] and 3(2*H*)-pyridazinones.[12] To improve the catalytic efficiency in these transformations various phosphane-based ligands have been investigated,[13–17] but other ligands[18–23] or even ligand-free catalytic systems[24–29] have also been published. Since Arduengo[30] reported the isolation of a stable free N-heterocyclic carbene (NHC) in 1991, a large number of palladium–NHC complexes has been reported. Even in-situ systems of a palladium source [e.g., $Pd(OAc)_2$] and imidazolium salts show high catalytic activity in a variety of palladium-catalyzed cross-coupling reactions.[31–34] Phosphane-based ligands are often air-sensitive and degrade at higher temperatures.[35,36] Therefore, catalyst systems with these ligands generally require the use of excess ligand.[13,37] Owing to their high tolerance towards air and moisture, NHC ligands were shown to be a promising alternative, although there are several phosphane ligands (e.g., P*t*Bu_3) that reach the same or even higher performance.[38–40]

The remarkably high catalytic activity of a large number of palladium–NHC complexes in the Suzuki–Miyaura cross-coupling reaction and C–C coupling reactions in general is usually explained by the strong σ-donating properties of the carbene ligands.[41,42] Examples are monodentate phenyl-substituted NHC ligands,[43–47] palladium complexes with pyridine coligands,[48] bis(oxazoline)-derived NHC ligands,[49,50] and many other structures possessing an NHC moiety.[32,51–67]

Chelating bis(NHC) complexes combine the strong donating properties of the two carbenes, high steric demand, and good stability even under harsh reaction conditions.[68–73] Chelating NHC complexes also show excellent catalytic activities in cross-coupling reactions at elevated temperatures under air.[32,74–77] Owing to their high stability bis(NHC)–palladium complexes have also been successfully used in other palladium-catalyzed reactions such as the activation of methane,[78–80] which requires oxidative conditions and high reaction temperatures. In particular, *N*-phenylbis(NHC)–palladium complexes substituted with electron-donating groups such as methoxy and butoxy groups turned out to be very active catalysts.[81]

We were therefore interested in whether electronic and steric effects can also be observed in the Suzuki–Miyaura cross-coupling reaction.

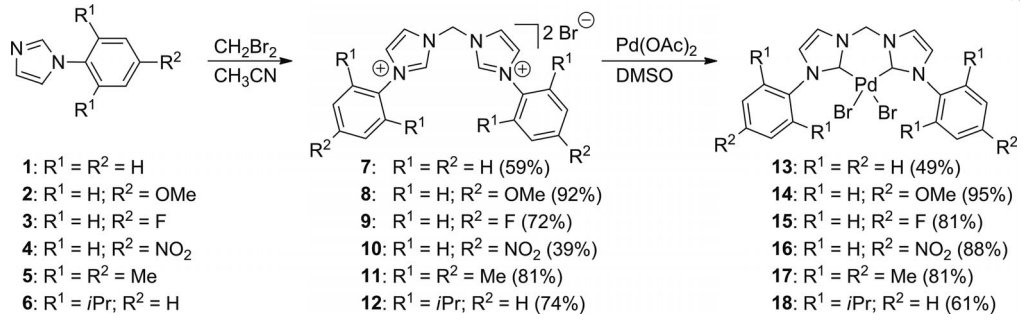
Results and Discussion

Preparation of Bis(NHC)–Palladium Complexes

To investigate electronic and steric effects of substituted ligands, we prepared a set of *N*-phenyl-substituted bis(NHC)–palladium complexes with electron-donating, electron-withdrawing and sterically demanding groups by using the general synthetic route shown in Scheme 1.

Phenyl-substituted imidazoles **1**–**6** were prepared according to literature procedures.[82] The reaction of **1**–**6** with dibromomethane in acetonitrile yielded the methylene-bridged bis(imidazolium) salts **7**–**12** in good yields

[a] Fachrichtung Chemie und Lebensmittelchemie, Technische Universität Dresden
Bergstr. 66, 01069 Dresden, Germany
Fax: +49-351-463-39679
E-mail: thomas.strassner@chemie.tu-dresden.de
Homepage: http://www.chm.tu-dresden.de/oc3/



Scheme 1. Synthesis of the bis(NHC)–palladium complexes **13**–**18**.

(Scheme 1). The bis(NHC)–palladium complexes **13**–**18** were synthesized from the bis(imidazolium) salts with $Pd(OAc)_2$ in dimethyl sulfoxide (DMSO).

The investigated bis(NHC)–palladium bromide complexes **13**–**18** include ligands with electron-donating (**14**) as well as electron-withdrawing groups (**15** and **16**). To investigate steric effects some complexes with sterically demanding *ortho*-substituted phenyl groups (**17** and **18**) as well as non-bulky ligands **19**[83–85] and **20**[86] were prepared (Figure 1).

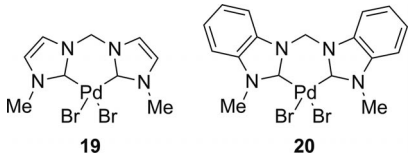


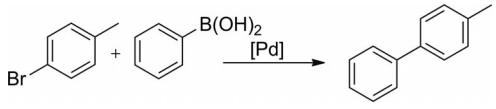
Figure 1. *N*-Methyl-substituted bis(NHC)–palladium complexes **19** and **20**.

We compared the catalytic activities of the investigated bis(NHC)–palladium complexes **13**–**20** for the reaction of 4-bromotoluene with phenylboronic acid (Table 1). Preliminary experiments of the Suzuki–Miyaura cross-coupling reaction with the investigated bis(NHC)–palladium complexes identified the solvent/base system toluene/K_3PO_4 as superior to various combinations of other solvents (methanol, ethanol, 2-propanol, dioxane, THF) and bases (Cs_2CO_3, K_2CO_3, KO*t*Bu, KOH, NaOMe).

With the exception of **13**, all investigated bis(NHC)–palladium complexes achieve good to excellent yields under mild conditions within a short reaction time of 1 h. The best results were obtained with the *p*-methoxy-substituted **14** and the benzimidazole-derived complex **20**, which led to yields of 95%, followed by the methyl-substituted complex **19** with a yield of 92%. After the yields for 1 h of reaction time, we examined the reaction time required for the full conversion of 4-bromotoluene. All complexes led to high conversions (> 96%) after 24 h; however, full conversion was not observed with **18** and **20**. Even longer reaction times of up to 72 h did not increase the conversion. Complexes **14** and **19** required the shortest reaction times of 3 and 5 h, respectively. We studied the reaction rates in detail, and these experiments are discussed later.

We also tested the in-situ system of $Pd(OAc)_2$ and bis(imidazolium) salt **8**, but it shows a significantly lower yield (22%) compared to the corresponding bis(NHC)–palladium complex **14**. This is not surprising since the preparation of **14** requires reaction temperatures from 60 to 130 °C, which makes the in-situ formation of complex **14** improbable under the reaction conditions of the cross-coupling reaction.

Table 1. Comparison of the catalytic activities of the bis(NHC)–palladium complexes **13**–**20** in the Suzuki–Miyaura cross-coupling reaction.[a]



[Pd]	Yield[b] (after 1 h) [%]	Conv.[c] (after 24 h) [%]	Reaction time[c] [h]
13	44	100	24 (100)
14	95	100	2 (100)
15	77	97	48 (100)
16	63	100	24 (100)
17	79	100	24 (100)
18	83	98	72 (98)
19	92	100	5 (100)
20	95	97	72 (97)
$Pd(OAc)_2$ + **8**	22	not determined	
$Pd(OAc)_2$	35	not determined	

[a] Reaction conditions: aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), [Pd] (1 mol-%), K_3PO_4 (1.95 mmol), toluene (5 mL), 40 °C, argon. [b] GC–MS yields determined by using diethylene glycol dibutyl ether as internal standard, average of two runs. [c] For maximum conversion. Conversion of 4-bromotoluene was measured in a separate run by using *n*-dodecane as internal standard by GC–MS. Maximum conversion is given in parentheses.

Another control experiment, the use of $Pd(OAc)_2$ without bis(imidazolium) salt led to a higher yield (35%) than the reaction with the ligand precursor, in which the presence of the bis(imidazolium) salt **8** might decelerate the preactivation of $Pd(OAc)_2$.

In most cases, the substituents will exert an electronic as well as steric influence on the reaction. It is therefore hard to distinguish which effect is responsible for observed activity differences or whether they influence the same step of the catalytic cycle. However, when comparing the results for **13**–**16** the electronic effect should prevail (Table 1). It indicates that electron-donating groups show a positive effect, as the *p*-methoxy-substituted **14** leads to significantly better results than the *p*-fluoro- and *p*-nitro-substituted **15**

and **16**, respectively. One reason might be that the electron-withdrawing groups decelerate the oxidative addition of the aryl bromide, which in turn results in lower yields.

The steric demand of the ligands certainly plays an important role in the case of the *ortho*-substituted complexes **17** and **18** and seems to have a negative effect as the complexes with nonbulky alkyl ligands **19** and **20** are more active. We suspect that the mesityl- and 2,6-diisopropylphenyl-substituted ligands **17** and **18**, respectively, have less of an electronic effect as we expect that the plane of the phenyl ring is orthogonal and not conjugated with the imidazole core. One way to evaluate the electron density at the metal atom is by cyclic voltammetry experiments, which have recently been conducted with **13**, **19**, and **20**. It was found that the electron density at the metal atom in **19** and **20** is lower than that in **13**.[87] For **17** and **18** we need to discuss steric and electronic effects, because one would expect a more active catalyst based on the positive inductive effect, whereas the steric demand should lower the activity.

Based on these results it is hard to say which step of the catalytic cycle is rate-determining or whether the rate-determining step is the same for all catalysts. For the complexes with electron-withdrawing groups (**15** and **16**), the oxidative addition might be rate-determining, whereas for more active complexes the oxidative addition seems not to be rate-determining. A detailed investigation of the rate-determining step for **14** is discussed later in the paper. Complex **14** seems to be a good compromise between steric demand and electronic effects, which leads to its high catalytic activity.

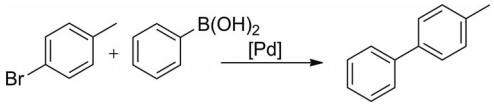
Optimal Reaction Temperature

To optimize the reaction conditions, we first investigated the reaction temperature (Table 2) for the previously described reaction catalyzed by **14**. Starting at room temperature up to refluxing toluene (111 °C), we found that 40 °C seems to be the temperature of choice (Table 2, Entry 4). Even with short reaction times (Table 2, Entries 5–7) excellent yields were achieved. Temperatures higher than 60 °C and lower than 40 °C resulted in lower yields (Table 2, Entries 1, 2, 8 and 9).

Stoichiometry of the Reactants

For comparison we had used 1 mol-% catalyst for all experiments (Table 1), but were interested to see whether lower concentrations of **14** (Table 3) would also lead to full conversion. With 1 mol-% a quantitative yield was achieved after 3 h (Table 3, Entry 2), whereas it took 6 h with 0.5 mol-% of **14** (Table 3, Entry 4). The cross-coupling reaction with 0.2 and 0.1 mol-% led to good yields of 84% and 74%, respectively, after 2 h at 40 °C (Table 3, Entries 5 and 7). To obtain a quantitative yield with 0.2 mol-% of **14** an increased reaction time and temperature were required (Table 3, Entry 6). When the amount of catalyst was reduced to 0.1 mol-% of **14**, only a good yield of 90% was obtained (Table 3, Entry 8). It can be concluded that **14** gives good to excellent yields (Table 3, Entries 3–8) even in low concentrations, although an increased reaction temperature and/or time might be required.

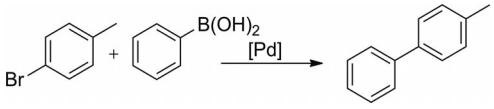
Table 2. Suzuki–Miyaura cross-coupling of 4-bromotoluene with phenylboronic acid catalyzed by **14**.[a]



Entry	Temperature [°C]	Time [h]	GC yield[b] [%]
1	111	4	93[c]
2	80	4	98[c]
3	60	4	100
4	40	4	100
5	40	3	100
6	40	2	99
7	40	1	95
8	32	4	95
9	r.t.	4	65

[a] Reaction conditions: aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), **14** (1 mol-%), K_3PO_4 (1.95 mmol), toluene (5 mL), argon. [b] GC–MS yields determined by using diethylene glycol dibutyl ether as internal standard, average of two runs. [c] Formation of palladium black.

Table 3. Suzuki–Miyaura cross-coupling of 4-bromotoluene with phenylboronic acid catalyzed by different concentrations of **14**.



Entry	mol-% **14**	Temperature [°C]	Time [h]	Yield [%]
1	1	40	2	99[a]
2	1	40	3	100[a]
3	0.5	40	2	86[b]
4	0.5	40	6	100[b]
5	0.2	40	2	84[b]
6	0.2	60	72	100[b]
7	0.1	40	2	74[b]
8	0.1	60	72	90[b]

[a] Reaction conditions: aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), **14** (as indicated), K_3PO_4 (1.95 mmol), toluene (5 mL), argon, GC–MS yields determined by using diethylene glycol dibutyl ether as internal standard, average of two runs. [b] Reaction conditions: aryl bromide (2 mmol), phenylboronic acid (3 mmol), **14** (as indicated), K_3PO_4 (3.9 mmol), toluene (10 mL), argon, isolated yields, average of two runs.

We generally ran all cross-coupling reactions with a 1.5-fold excess of phenylboronic acid (relative to 4-bromotoluene). To check whether smaller amounts of phenylboronic acid could also be used without a decrease of the reaction rate, we ran the cross-coupling reaction with 0.8–2.0 equiv. of phenylboronic acid with 1 mol-% of **14** at 40 °C. The conversions of the reactions were determined after fixed periods of time (Figure 2a). We observed a strong dependence of the reaction rate on the amount of phenylboronic acid. Only reactions with ≥ 1.3 equiv. of phenylboronic acid led to full conversion of 4-bromotoluene. The reaction

with 1.0 equiv. led to a conversion of 74% after 24 h; longer reaction times did not increase the conversion.

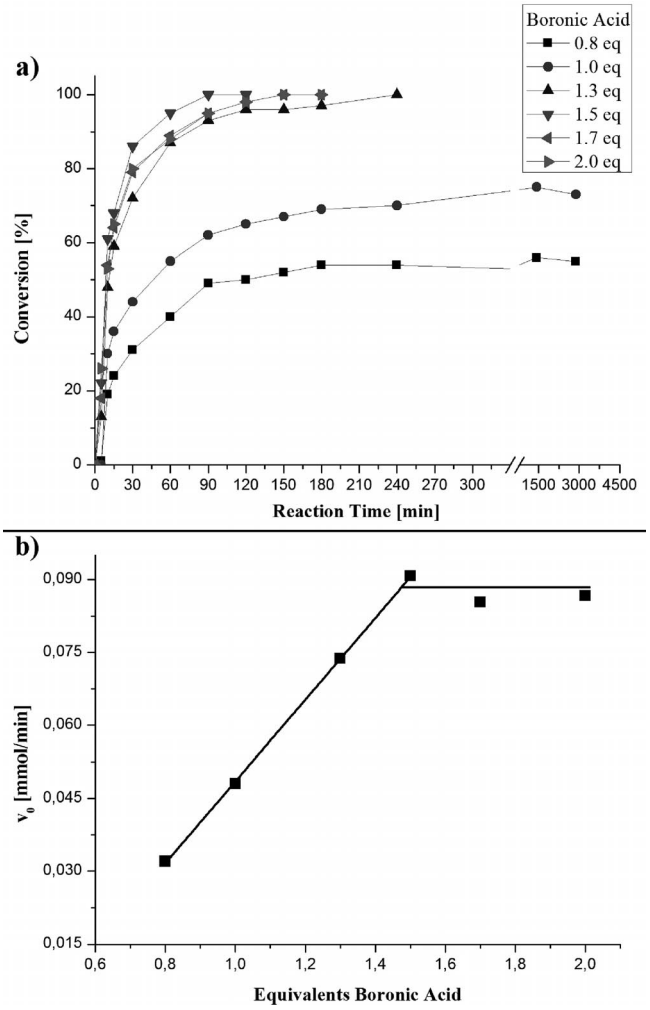


Figure 2. (a) Conversion of 4-bromotoluene in the Suzuki–Miyaura cross-coupling reaction with different amounts of phenylboronic acid. (b) Initial reaction rates (v_0) of Suzuki–Miyaura cross-coupling reactions of 4-bromotoluene with different equivalents of phenylboronic acid. Reaction conditions: aryl bromide (2 mmol), phenylboronic acid, **14** (1 mol-%), K_3PO_4 (3.9 mmol), *n*-dodecane (internal standard), toluene (10 mL), argon.

The correlation of the measured initial reaction rates (v_0) and the equivalents of phenylboronic acid are shown in Figure 2b. The initial reaction rates were determined by the conversion after 15 min. This correlation shows a linear dependence up to 1.5 equiv. Higher concentrations of phenylboronic acid did not increase the initial reaction rate. The linear dependence of the initial reaction rate on the concentration of phenylboronic acid indicates that the transmetalation is the rate-determining step in the Suzuki–Miyaura cross-coupling reaction with bis(NHC)–palladium complex **14**. We postulate the transmetalation to be rate-determining for the more active complexes (complexes that are not substituted with electron-withdrawing groups), which is also a likely explanation for the negative effect of the sterically demanding ligands (in **17** and **18**) since the transmetalation might be hindered by their steric demand (Table 1).[88–90]

Another important parameter in the reaction might be the base used in the cross-coupling reaction. We checked different bases and obtained the best results for K_3PO_4. We therefore investigated in detail the optimal concentration of the base and tested the cross-coupling reaction with amounts of K_3PO_4 ranging from 1.7 to 2.3 equiv. (Figure 3) and found the highest reaction rate for 1.95 equiv.

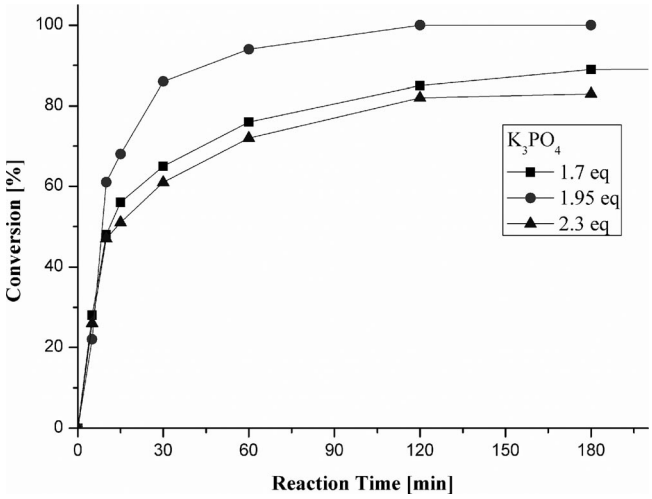


Figure 3. Conversions of 4-bromotoluene in the Suzuki–Miyaura cross-coupling with different amount of K_3PO_4. Reaction conditions: aryl bromide (2 mmol), phenylboronic acid (3 mmol), **14** (1 mol-%), K_3PO_4, *n*-dodecane (internal standard), toluene (10 mL), argon.

Side Reactions

Unwanted side reactions often decrease the reaction yield. We were, therefore, interested in whether typical side reactions such as protodebromination,[91,92] homocoupling of phenylboronic acid[55,93,94] and protodeboronation[94–99] can be found for these catalysts. Therefore, we investigated in detail **13**, **14** and **18**, which had shown different performances (Table 1).

First, we investigated the conversion of 4-bromotoluene in the Suzuki–Miyaura cross-coupling (Figure 4) and found that the measured aryl bromide conversions of 37 (**13**), 95 (**14**), and 87% (**18**) were in good agreement with the observed product yields of 44 (**13**), 95 (**14**), and 83% (**18**) after 1 h (Table 1).

We did not observe induction periods at the beginning of each reaction. Complexes **14** and **18** showed high initial reaction rates, and for the reaction with **14** no 4-bromotoluene was detected in the reaction mixture after 90 min. Certainly, **18** showed a lower reaction rate after 60 min, but after 24 h 98% conversion was obtained. Contrary to both other complexes, **13** gave a low, but constant, reaction rate from the beginning of the reaction until full conversion was reached after 24 h.

The agreement between conversions and yields is an indication of the absence of protodebromination in the Suzuki–Miyaura cross-coupling with the investigated bis(NHC)–

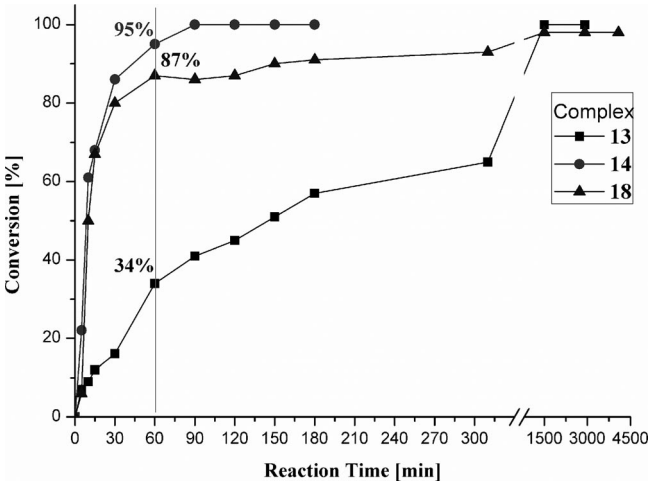
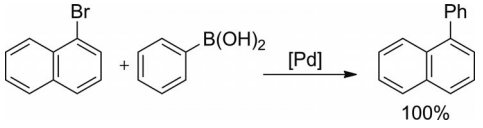


Figure 4. Conversions of 4-bromotoluene in the Suzuki–Miyaura cross-coupling with **13**, **14** and **18**. Reaction conditions: aryl bromide (2 mmol), phenylboronic acid (3 mmol), [Pd] (1 mol-%), K_3PO_4 (3.9 mmol), *n*-dodecane (internal standard), toluene (10 mL), argon. Stated conversions were obtained after 60 min.

palladium complexes. To verify that no protodebromination occurs, we ran the cross-coupling reaction with 1-bromonaphthalene (Scheme 2) as we would be able to detect the corresponding product (naphthalene) by GC–MS.



Scheme 2. Suzuki–Miyaura cross-coupling reaction of 1-bromonaphthalene and phenylboronic acid. Reaction conditions: aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), [Pd] (1 mol-%), K_3PO_4 (1.95 mmol), toluene (5 mL), 40 °C, 2 h (for **14**), 16 h (for **13** and **18**), argon, isolated yield.

All complexes led to a quantitative yield of the corresponding product, and the reaction mixtures were analyzed by GC–MS. The quantitative yield and the observation that no naphthalene could be detected are evidence for the absence of protodebromination in the Suzuki–Miyaura cross-coupling with the investigated bis(NHC)–palladium complexes.

Another possible side reaction, the homocoupling of phenylboronic acid can be excluded as well, because no biphenyl was detected in the reaction mixtures. To check for protodeboronation reactions, we measured the conversion of phenylboronic acid by determination of unreacted phenylboronic acid, which (after an aqueous workup) was quantified by ^{1}H NMR with nitromethane as internal standard. The conversions of the reactants and the product yields for **13**, **14** and **18** are given in Table 4.

The conversions of the reactants and the product yields are in agreement for **14** and **18**, although we cannot exclude that a small amount of phenylboronic acid is lost in the cross-coupling reaction with **18**. However, for **13** there is a large difference between the amount of reacted 4-bromotoluene and phenylboronic acid. As no biphenyl could be detected, the homocoupling of phenylboronic acid could be ruled out, and protodeboronation is the most likely reason for the loss of phenylboronic acid in the reaction mixture.

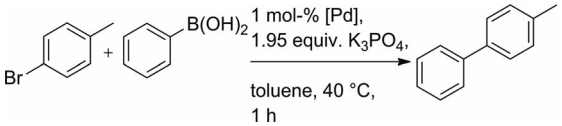
The results indicate that common side reactions of the Suzuki–Miyaura cross-coupling do not take place in case of the bis(NHC)–palladium complexes **14** and **18**, but certainly for the less active complex **13** protodeboronation is a likely side reaction, which might also contribute to its low initial reaction rate.

Substrate Scope

To study the influence of substituents on the aryl bromide we used different *para*-substituted aryl bromides for the investigation of electronic effects as well as *ortho*-substituted aryl bromides for their steric effects (Table 5).

Complex **14** was able to catalyze the Suzuki–Miyaura cross-coupling reactions of different aryl bromides with electron-withdrawing as well as electron-donating groups in the *para* position in excellent yields. 4-Bromotoluene (Table 5, Entry 1), 4-bromoanisol (Table 5, Entry 2), and 4-bromoacetophenone (Table 5, Entry 3) were coupled in yields of 95–98% at 40 °C in 2 h (Table 5, Entries 1–3). Owing to the low solubility of 1-bromo-4-nitrobenzene in toluene, a slightly increased reaction temperature was required (Table 5, Entries 5 and 6), which then afforded excellent yields too. For all studied aryl bromides with different *para*

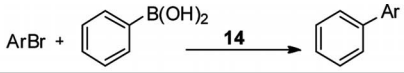
Table 4. Comparison of the conversions of the reactants with product yields for **13**, **14** and **18**.

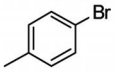
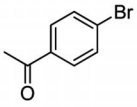
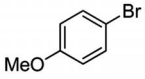
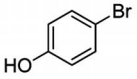
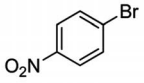
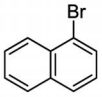
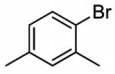
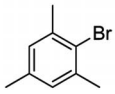
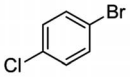
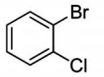


[Pd]	Conv. of 4-bromotoluene[a] [mmol]	Conv. of phenylboronic acid[b] [mmol]	GC yield of 4′-methylbiphenyl[c] [mmol]
13	0.34	1.13	0.44
14	0.95	1.05	0.95
18	0.87	1.13	0.83

[a] Conversion of 4-bromotoluene was measured by GC–MS using *n*-dodecane as internal standard. [b] Conversion of phenylboronic acid was measured by ^{1}H NMR spectroscopy in a separate run by using nitromethane as internal standard. [c] GC–MS yields were measured by using diethylene glycol dibutyl ether as internal standard.

Table 5. Suzuki–Miyaura cross-coupling reactions of aryl bromides and phenylboronic acid.[a]



Entry	ArBr	Time [h]	Temperature [°C]	Yield[b] [%]	Reaction time[c] [h]
1		2	40	95	3 (100)
2		2	40	98	2 (100)
3		2	40	95	6 (100)
4		2	40	87[d]	4 (100)
5		2	40	64	–
6		2	60	96	2 (100)
7		2	40	100	2 (100)
8		2	40	77	–
9		2	60	94	4 (100)
10		2	40	62	–
11		18	60	91	48 (95)
12		2	40	85	–
13		6	60	99	6 (100)
14		2	40	87	–
15		6	60	99	6 (100)

[a] Reaction conditions: aryl bromide (1 mmol), **14** (1 mol-%), phenylboronic acid (1.5 mmol), K_3PO_4 (1.95 mmol), toluene (5 mL), argon. [b] Isolated yields, average of two runs. [c] For maximum conversion, given in parentheses. Conversion of 4-bromotoluene was measured in a separate run using *n*-dodecane as internal standard by GC–MS. [d] Formation of palladium black.

substituents we obtained almost the same yield, so the very active catalyst did not discriminate between the different electronic effects of the substituents. This result is not surprising as the transmetalation was found to be the rate-determining step.

Certainly, the presence of *ortho* substituents at the aryl bromide has an effect on the reaction rate. Although 4-bromotoluene was coupled in a 95% yield (Table 5, Entry 1), under the same reaction conditions bromoxylene led to a yield of 77% (Table 5, Entry 8) and bromomesitylene to a yield of 62% (Table 5, Entry 10). This effect could also be explained by the transmetalation being the rate-determining step. However, high yields for these aryl bromides could be obtained by increasing the reaction time and temperature (Table 5, Entries 9 and 11).

The good selectivity toward bromo electrophiles allows to distinguish between chloro and bromo substituents. Coupling of chloro-substituted aryl bromides could be accomplished in good yields (Table 5, Entries 12–15). Even the *ortho*-chloro-substituted aryl bromide led to the same yield as the *para*-chloro-substituted aryl bromide. No side products such as the corresponding biphenyl bromides or terphenyls were observed.

Furthermore, we investigated the reaction parameters required for full conversion of the substrates. We were able to obtain full conversion for all but one of the investigated aryl bromides. *para*-Substituted aryl bromides generally needed reaction times of 2–6 h for full conversion under standard conditions. Only the sterically demanding bromomesitylene (Table 5, Entries 10 and 11) did not reach full conversion using our standard reaction conditions (1 mol-% **14**, 1.5 equiv. of phenylboronic acid).

Conclusions

We report the high catalytic activity of bis(NHC)–palladium complexes in the Suzuki–Miyaura cross-coupling reactions with aryl bromides. All investigated bis(NHC)–palladium complexes give good to excellent yields under mild reaction conditions (40 °C). The *p*-methoxyphenyl-substituted **14**, the methyl-substituted **19** and the benzimidazole-derived **20** turned out to be the most active catalysts. Even with low catalyst loadings, excellent yields were obtained. We found that complexes carrying ligands substituted with electron-donating groups led to higher yields, whereas sterically demanding ligands gave lower yields in the Suzuki–Miyaura cross-coupling of aryl bromides. Our results indicate that the transmetalation is the rate-determining step in the cross-coupling reaction, at least for the electron-rich, sterically unhindered catalysts, which is in agreement with a negative effect of sterically demanding ligands, because the transmetalation reaction is hindered in these cases.

In addition, we were able to exclude common side reactions like protodebromination, homocoupling of phenylboronic acid and protodeboronation for the most active complex **14**. Furthermore the substrate scope of the reaction of aryl bromides catalyzed by **14** was investigated. Several *para*- as well as *ortho*-substituted aryl bromides were coupled in excellent yields. Electron-withdrawing as well as electron-donating groups in the *para* position showed only a small effect in contrast to groups in the *ortho* position. For *ortho*-substituted and *ortho*,*ortho*-disubstituted aryl bromides, an increased reaction temperature and time was generally required to achieve excellent yields.

Experimental Section

General Considerations: All chemicals were used as received. Toluene was distilled under argon from calcium hydride prior to use and stored over molecular sieves. ^1H, ^{13}C and ^{19}F NMR spectra were obtained with a Bruker AC 300 P at 300.13, 75.45 and 282.40 MHz, respectively. Chemical shifts (δ) are given in parts per million and are internally referenced to the solvent resonances. Elemental analyses were performed by the microanalytical laboratory of our institute with a Hekatech EA 3000 Euro Vector CHNSO

elemental analyzer. 1-(4-Methoxyphenyl)imidazole (**2**),[82] 1-(4-nitrophenyl)imidazole (**4**),[82] 1-(2,4,6-trimethylphenyl)imidazole (**5**), 1-(2,6-diisopropylphenyl)imidazole (**6**),[82] imidazolium salts **8**,[100] **10**,[100] **12**,[101] and complexes **13**[81,102] **14**,[81] **17**,[83] **19**,[83–85] and **20**[86] were prepared according to literature procedures.

1-Phenylimidazole (1): Aniline (18.6 g, 0.2 mol) in MeOH (50 mL) was treated with 30% aqueous glyoxal (32.4 mL, 0.2 mol) at room temperature for 10 min to form a yellow mixture. NH_4Cl (21.4 g, 0.4 mol) was added followed by 37% aqueous formaldehyde (32 mL, 0.4 mol). The mixture was diluted with MeOH (400 mL) and heated to reflux for 1 h before H_3PO_4 (28 mL, 85%) was slowly added. The resulting mixture was then stirred at reflux for another 8 h. After removal of the solvent, the dark residue was poured onto ice (300 g) and neutralized with 40% aqueous KOH solution until the solution was at pH = 9. The resulting mixture was extracted with dichloromethane (3× 300 mL). The organic phases were combined and dried ($MgSO_4$). The solvent was removed, and after distillation a yellow oil was obtained (24.69 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.12 (s, 1 H, NCHN), 7.32 (m, 1 H, ar), 7.48 (m, 2 H, ar), 7.60 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, NCHCHN), 7.73 (s, 1 H, ar), 8.22 (s, 1 H, ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 118.0, 120.3, 126.9, 129.1, 129.9, 135.6, 136.2 ppm. $C_9H_8N_2$ (144.18): calcd. C 74.98, H 5.59, N 19.43; found C 74.61, H 5.70, N 19.51.

1-(4-Fluorophenyl)imidazole (3): 4-Fluoroaniline (11.1 g, 0.1 mol) in MeOH (50 mL) was treated with 30% aqueous glyoxal (16.2 mL, 0.1 mol) at room temperature for 16 h to form a yellow mixture. NH_4Cl (10.7 g, 0.2 mol) was added followed by 37% aqueous formaldehyde (16 mL, 0.2 mol). The mixture was diluted with MeOH (400 mL) and heated to reflux for 1 h. H_3PO_4 (14 mL, 85%) was added slowly. The resulting mixture was then stirred at reflux for another 8 h. After removal of the solvent, the dark residue was poured onto ice (300 g) and neutralized with 40% aqueous KOH solution until the solution was at pH = 9. The resulting mixture was extracted with dichloromethane (3× 300 mL). The organic phases were combined and dried ($MgSO_4$). The solvent was removed, and the residue was subjected to sublimation in vacuo. After purification by column chromatography on silica gel (ethyl acetate), a white solid was obtained (12.1 g, 75%). M.p. 20 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.11 (s, 1 H, ar), 7.18 (s, 1 H, ar), 7.25 (m, 2 H, ar), 7.38 (m, 2 H, ar), 7.79 (s, 1 H, NCHN) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 116.6 (d, J = 23.0 Hz), 118.5, 123.4 (d, J = 8.6 Hz), 130.5, 133.5 (d, J = 2.8 Hz), 135.7, 161.0 (d, J = 247.2 Hz) ppm. $C_9H_7FN_2$ (162.17): calcd. C 66.66, H 4.35, N 17.27; found C 66.61, H 4.34, N 17.51.

3,3′-Bisphenyl-[(1,1′-diimidazolium)methane] Dibromide (7): In comparison with the previously published syntheses,[102] the change of the solvent from toluene to acetonitrile led to a significant increase of the product yield: To a solution of imidazole **1** (0.7 g, 5.0 mmol) in acetonitrile (5 mL) in an ACE pressure tube, CH_2Br_2 (0.3 mL, 4.0 mmol) was added. A colorless precipitate formed after the solution had been heated at 110 °C for 24 h. The precipitate was filtered and washed with THF (3× 5 mL). A colorless powder was obtained after the product had been dried in vacuo (0.6 g, 59%). M.p. 315 °C (dec.). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 6.95 (s, 2 H, NCH_2N), 7.67 (m, 6 H, ar), 7.84 (d, $^3J_{H,H}$ = 7.4 Hz, 4 H, NCHCHN), 8.45 (dt, $^3J_{H,H}$ = 8.0, 1.6 Hz, 4 H, NCHCHN), 10.41 (s, 2 H, NCHN) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO, 25 °C): δ = 58.4, 121.6, 122.0, 123.1, 130.2, 130.0, 134.5, 137.4 ppm. $C_{19}H_{18}Br_2N_4 \cdot 0.5H_2O$ (471.19): calcd. C 48.43, H 4.06, N 11.89; found C 48.37, H 3.68, N 11.86.

3,3′-Bis(4-fluorophenyl)-[(1,1′-diimidazolium)methane] Dibromide (9): To a solution of imidazole **3** (0.8 g, 5.0 mmol) in acetonitrile (5 mL) in an ACE pressure tube, CH_2Br_2 (0.3 mL, 4.0 mmol) was added. A colorless precipitate formed after the solution had been heated at 130 °C for 24 h. The precipitate was filtered and washed with THF (3× 5 mL). A colorless powder was obtained after the product had been dried in vacuo (0.9 g, 72%). M.p. > 330 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 6.92 (s, 2 H, NCH_2N), 7.60 (m, 4 H, ar), 7.91 (m, 4 H, ar), 8.42 (s, 4 H, ar), 10.35 (s, 2 H, ar) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 58.3, 117.2, 121.9, 122.9, 124.7 (d, J = 9.5 Hz), 130.9 (d, J = 2.5 Hz), 137.5, 162.4 (d, J = 247.9 Hz) ppm. ^{19}F NMR (282.4 MHz, [D$_6$]DMSO, 25 °C): δ = –110.76 (d, J = 5.8 Hz) ppm. $C_{19}H_{16}Br_2F_2N_4$ (495.17): calcd. C 45.81, H 3.24, N 11.24; found C 45.45, H 2.97, N 11.46.

3,3′-Bis(2,4,6-trimethylphenyl)-[(1,1′-diimidazolium)methane] Dibromide (11): In comparison to the previously published syntheses,[83,101] the change of the solvent from toluene or THF, respectively, to acetonitrile led to a significant increase in the product yield: To a solution of imidazole **5** (0.9 g, 5.0 mmol) in acetonitrile (5 mL) in an ACE pressure tube, CH_2Br_2 (0.3 mL, 4.0 mmol) was added. A colorless precipitate formed after the solution had been heated at 130 °C for 24 h. The precipitate was filtered and washed with cooled THF (3× 5 mL). A colorless powder was obtained after the product had been dried in vacuo (1.1 g, 81%). M.p. 307 °C (dec.). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 2.05 (s, 12 H, o-CH_3), 2.35 (s, 6 H, p-CH_3), 6.89 (s, 2 H, NCH_2N), 7.19 (s, 4 H, ar), 8.10 (t, $^3J_{H,H}$ = 1.8 Hz, 2 H, NCHCHN), 8.38 (t, $^3J_{H,H}$ = 1.8 Hz, 2 H, NCHCHN), 9.86 (d, $^3J_{H,H}$ = 1.4 Hz, 2 H, NCHN) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 16.9, 20.6, 67.0, 122.8, 124.8, 129.4, 130.8, 134.2, 139.1, 140.6 ppm. $C_{25}H_{30}Br_2N_4 \cdot H_2O$ (544.08): calcd. C 53.35, H 5.71, N 9.93; found C 53.21, H 5.72, N 9.93.

3,3′-Bis(4-fluorphenyl)-[1,1′-diimidazolin-2,2′-diylidene)methane]-palladium(II) Dibromide (15): A solution of $Pd(OAc)_2$ (122 mg, 0.55 mmol) and bisimidazolium salt **9** (302 mg, 0.61 mmol) in DMSO (10 mL) was heated at 60 °C for 2 h, 80 °C for 2 h, 100 °C for 2 h, and 130 °C for 1 h. The solvent was removed under reduced pressure, and the colorless residue was washed with methanol (2× 5 mL) and acetonitrile (2× 5 mL) and dried in vacuo (267 mg, 81%). M.p. > 330 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 6.52 (m, 2 H, NCH_2N), 7.51 (m, 4 H, NCHCHN), 7.81 (m, 8 H, ar) ppm. Owing to the low solubility of **15**, no ^{13}C NMR spectra could be obtained. $C_{19}H_{14}Br_2F_2N_4Pd$ (602.55): calcd. C 37.87, H 2.34, N 9.30; found C 38.06, H 2.03, N 9.65.

3,3′-Bis(4-nitrophenyl)-[1,1′-diimidazolin-2,2′-diylidene)methane]-palladium(II) Dibromide (16): A solution of $Pd(OAc)_2$ (117 mg, 0.52 mmol) and bisimidazolium salt **10** (302 mg, 0.58 mmol) in DMSO (10 mL) was heated at 60 °C for 2 h, 80 °C for 2 h, and 100 °C for 2 h. The solvent was removed under reduced pressure, and the yellow residue was washed with methanol (2× 5 mL) and acetonitrile (2× 5 mL) and dried in vacuo (300 mg, 88%). M.p. > 330 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 6.55 (m, 2 H, NCH_2N), 7.93 (s, 4 H, NCHCHN), 8.14 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, ar), 8.58 (d, $^3J_{H,H}$ = 8.8 Hz, 4 H, ar) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 63.4, 122.6, 122.8, 124.4, 126.5, 144.4 146.8, 160.2 ppm. $C_{19}H_{14}Br_2N_6O_4Pd$ (656.58): calcd. C 34.76, H 2.15, N 12.80; found C 34.65, H 1.76, N 13.04.

(3,3′-Bis(2,6-diisopropylphenyl)-[1,1′-diimidazolin-2,2′-diylidene)-methane]palladium(II) Dibromide (18): A solution of $Pd(OAc)_2$ (177 mg, 0.79 mmol) and bisimidazolium salt **12** (551 mg, 0.87 mmol) in DMSO (14 mL) was heated at 60 °C for 3 h, 80 °C for 3 h, and 110 °C for 2 h. The solvent was removed under reduced pressure, and the colorless residue was washed with acetonitrile (2× 5 mL) and dried in vacuo (351 mg, 61%). M.p. 290 °C (dec.).

^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.03 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 1.27 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH_3), 1.35 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, CH_3), 2.34–2.65 (m, 4 H, CH), 7.92 (s, 2 H, NCH_2N), 6.51–6.59 (m, 2 H, ar), 7.17–7.61 (m, 8 H, ar) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 25 °C): δ = 22.9, 23.3, 24.9 25.0, 28.0, 28.4, 62.1, 121.2, 122.1, 123.5, 123.9, 127.6, 129.8, 136.0, 136.5, 144.6, 146.0, 144.6 ppm. $C_{31}H_{40}Br_2N_4Pd$ (734.89): calcd. C 50.66, H 5.49, N 7.62; found C 50.30, H 5.48, N 7.30.

General Procedure for Suzuki–Miyaura Cross-Coupling Reactions (with Determination of Isolated or GC–MS Yields): A 2-neck flask containing a magnetic stir bar was charged with the bis(NHC)–palladium complex, phenylboronic acid (183 mg, 1.5 mmol), and powdered anhydrous K_3PO_4 (414 mg, 1.95 mmol). The flask was capped with a septum, evacuated, and filled with argon three times. The aryl bromide (1 mmol) dissolved in dry toluene (5 mL) was added through the septum with a syringe, and the resulting mixture was stirred as indicated. The solvent was removed under reduced pressure. For the determination of GC–MS yields, the residue was diluted with dichloromethane (5 mL) and filtered through a thin pad of silica gel [elution with dichloromethane (100 mL)]. Diethylene glycol dibutyl ether (170 mg) was added as internal standard. The isolated yields were determined after purification by column chromatography (petroleum ether/ethyl acetate) on silica gel. For the determination of the conversion of phenylboronic acid, the residue after the removal of toluene was dissolved in ethyl acetate (20 mL) and washed with saturated NH_4Cl solution (20 mL). The aqueous phase was extracted with EtOAc (2 × 15 mL). The organic phases were combined and dried (Na_2SO_4). The solvent was removed in vacuo. Nitromethane (61 mg) was added, the mixture was dissolved in DMSO (2 mL), and analyzed by ^{1}H NMR spectroscopy.

General Procedure for Suzuki–Miyaura Cross-Coupling Reactions (with Determination of the Conversion): A 2-neck flask containing a magnetic stir bar was charged with the bis(NHC)–palladium complex, phenylboronic acid (183 mg, 1.5 mmol), and powdered anhydrous K_3PO_4 (414 mg, 1.95 mmol). The flask was capped with a septum, evacuated, and filled with argon three times. The aryl bromide (1 mmol) and *n*-dodecane (172 mg) dissolved in dry toluene (5 mL) were added through the septum with a syringe, and the resulting mixture was stirred as indicated. Aliquots (0.1 mL) were removed from the reaction mixture after a fixed period of time and filtered through a silica gel filled pipette by using dichloromethane (7 mL), followed by GC–MS analysis.

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