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Synthetic Methods

An Alternative Approach to PEPPSI** Catalysts: From Palladium Isonitriles to Highly Active Unsymmetrically Substituted PEPPSI Catalysts

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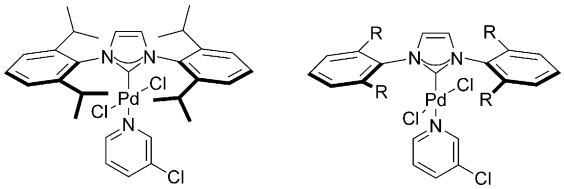
Abstract: A series of new pyridine-enhanced precatalyst preparation, stabilization, and initiation (PEPPSI)-type complexes bearing different types of carbene ligands was prepared by the modular and convergent template synthesis strategy. Nitrogen acyclic carbenes, saturated and unsaturated five-membered NHC, saturated six-membered NHCs, and five-membered N-heterocyclic oxo-carbene (NHOC) ligands on palladium were prepared this way. These new organometallic compounds then were tested in Suzuki and Negishi cross-coupling reactions by using substrates with one or two substituents in *ortho*-position of the new C–C bond being formed. Both aryl chlorides and bromides were tested as coupling partners. In some cases, the new ligands gave results similar to Organ's successful IPr-based and IPent-based PEPPSI derivatives, with aryl bromides 0.05 mol% catalyst load still gave satisfactory results, with aryl chlorides 0.5 mol% were needed.

Introduction

Initially regarded as a curiosity when reported in the late 1960s,[1] N-heterocyclic carbenes (NHCs) have become one of the most important ligand classes in homogeneous transition-metal catalysis. This rise was initiated by Arduengo et al. who were able to isolate the first stable NHC derivative in 1991.[2] Due to their very strong σ-donating properties combined with a weak π-acceptor capability,[3] NHCs form stable complexes especially with late transition metals, resulting in a diverse spectrum of applications.[4] One important field is the use of NHC–Pd complexes as highly active catalysts in Pd-promoted cross-coupling reactions as was reported by groups of Herrmann,[5] Beller,[6] Nolan,[7] Caddick and Cloke,[8] Bellemin-Laponez and Gade,[9] and others. Among the different synthetic strategies for the synthesis of NHC–Pd complexes, most approaches are based either on a free carbene or on the in situ generation of a free carbene, which is derived from an imidazolium salt in the presence of a palladium source and a base.[10]

Pyridine-
Enhanced
Precatalyst
Preparation,
Stabilization (and)
Initiation



Pd-PEPPSI-IPr (**1**)
first generation

Pd-PEPPSI-IBu (**2a**)
Pd-PEPPSI-IPent (**2b**)
Pd-PEPPSI-cPent (**2c**)
second generation

Scheme 1. First and second generation Pd–PEPPSI catalysts.

The Organ group contributed a series of air-stable, user-friendly NHC–Pd^{II} precatalysts, the Pd–pyridine-enhanced precatalyst preparation, stabilization, and initiation (PEPPSI; Scheme 1).[11] These catalysts turned out to be generally applicable in nearly every field of cross-coupling reactions.[12] The 3-chloropyridine ligand of the precatalysts functions as a "throw-away" ligand. Pd–PEPPSI–IPr complex (**1**), the first-generation of the Pd–PEPPSI catalysts, was prepared in almost quantitative yield by heating of the corresponding imidazolium salt with $PdCl_2$ and K_2CO_3 in neat 3-chloropyridine. In the same way, second-generation Pd–PEPPSI complexes (**2**) were synthesized.[13] By increasing the steric bulk at the *ortho* positions of the *N*-phenyl moieties of the NHCs, higher catalyst reactivities could be observed.[12] Based on the aforementioned synthetic strategy for the ligands, this approach has only been applied

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[+] *Crystallographic investigation.*

[**] *PEPPSI = Pyridine-enhanced precatalyst preparation, stabilization, and initiation.*

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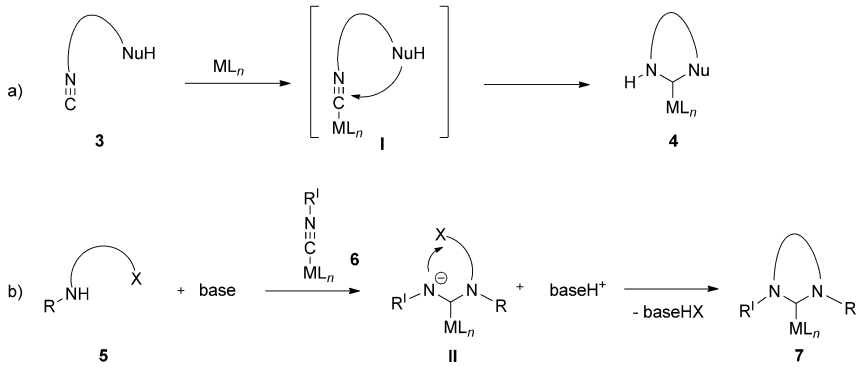
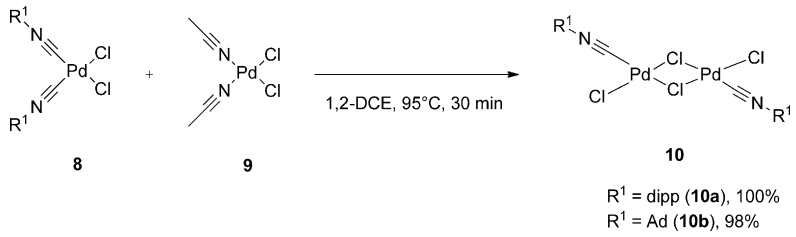
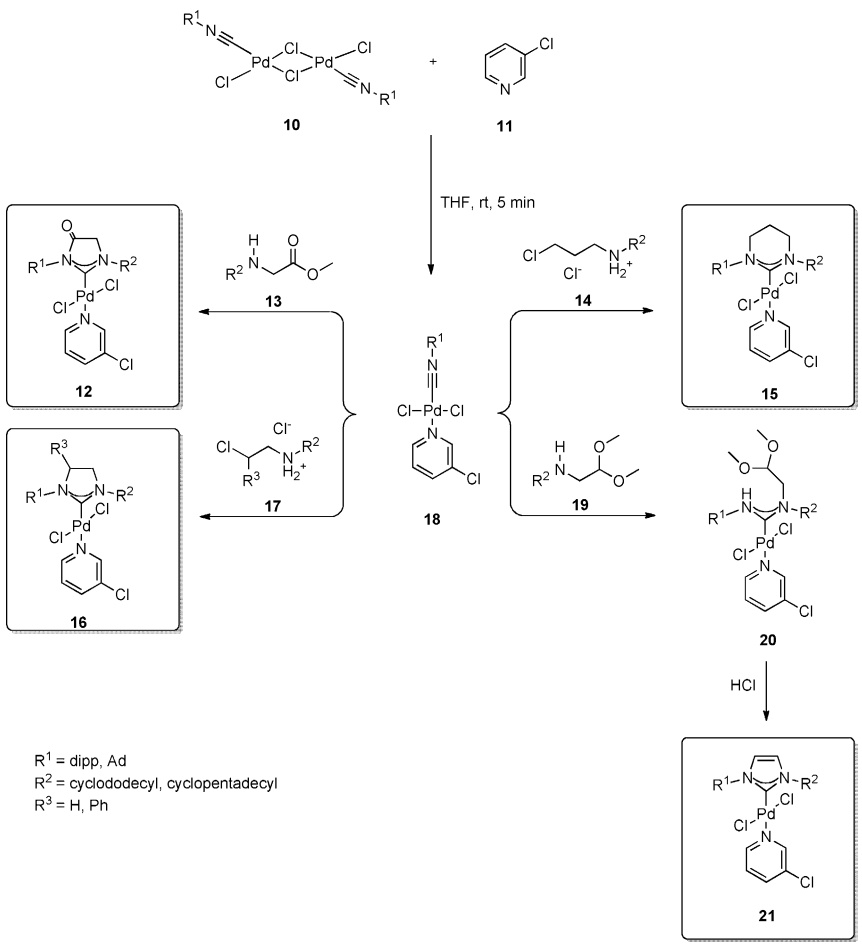


Scheme 2. Different approaches for the formation of NHC complexes from coordinated isonitriles.



Scheme 3. Synthesis of the dimeric precursor **10**.



Scheme 4. Overview of the different routes towards new Pd–PEPPSI complexes in this contribution.

to symmetrically substituted Pd–PEPPSI complexes due to preparative feasibility to date.

The pioneering contributions from the groups of Minghetti and Bonati,[14] as well as Hahn,[15] on the synthesis of metal carbenes starting from metal-coordinated isonitriles, inspired us to develop an alternative strategy for the synthesis of Pd–PEPPSI complexes. Preparing NHC ligands through an isonitrile strategy not only offers a route to unsymmetrically substituted NHC ligands, but also avoids a stepwise pre-synthesis of the corresponding imidazolium salts. Earlier approaches were based on isonitriles bearing tethered nucleophilic functionalities for the ring closure towards the NHC. These strategies have the drawback that one of the NHC nitrogen atoms remains unsubstituted (Scheme 2a). This can be circumvented by an alternative approach, in which the nucleophilic nitrogen atom is attached to a secondary amine **5** instead of being incorporated into the isonitrile backbone. One condition the amine has to fulfill is to bear a leaving group/electrophilic position in an appropriate distance to the nitrogen, which allows nucleophilic ring closure in the following step (Scheme 2b).

Our strategy towards an alternative synthesis of PEPPSI catalysts used the dimeric Pd^{II} complexes **10** as isonitrile precursor for all of the isonitrile-based PEPPSI catalyst syntheses. Compound **10** could be synthesized through the known route in almost quantitative yield by the treatment of $[Pd^{II}Cl_2(CH_3CN)_2]$ (**9**) with the corresponding Pd–isonitrile complexes **8** (Scheme 3).[16] Cleavage of the dimer with 3-chloropyridine gave access to the pyridine-coordinated isonitrile monomers **18**, which could be converted to the desired PEPPSI catalyst deriva-

tives in a synthetically valuable one-pot fashion by simple addition of the appropriate amine.

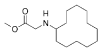
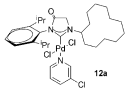
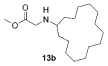
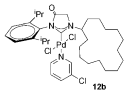
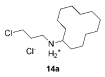
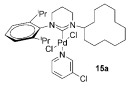
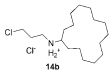
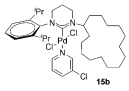
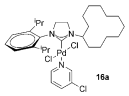
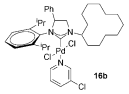
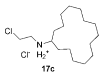
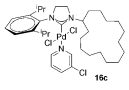
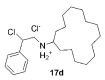
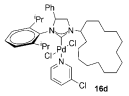
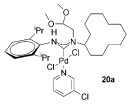
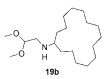
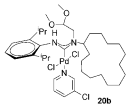
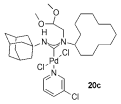
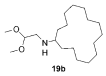
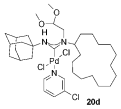
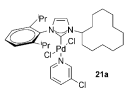
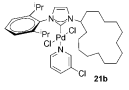
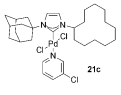
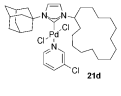
Scheme 4 summarizes the classes of NHC complexes obtained by this route. By variation of the tether length, as well as the electrophilic moieties attached to the reacting amines, four different classes of PEPPSI derivatives were feasible. N-Heterocyclic oxo-carbenes (NHOCs; Scheme 4, top left) were obtained by using an ester moiety as electrophile. 6-Membered (Scheme 4, top right) and 5-membered (Scheme 4, bottom left) NHC–PEPPSI derivatives were obtained by the reaction with amines bearing a chloro substituent as leaving group. Unsaturated NHCs were prepared following a two-step procedure (Scheme 4, bottom right). After formation of the acetal-substituted N-acyclic carbene (NAC) complexes, deprotection of the acetal with hydrochloric acid initiates ring closure and, under elimination of methanol, the unsaturated NHC complexes are formed.

By employing these routes, we gained access to a set of structurally diverse unsymmetrically substituted Pd–PEPPSI complexes. All of the obtained complexes are bearing an aryl or alkyl group on one of the nitrogen atoms of the NHC ring and a 12- or 15-membered ring on the other. The installation of large cyclic aliphatic rings was accomplished when these substituents had a positive influence on catalytic reactivities in previous studies of our group.[17] It is important to note that the ratio of *cis*- and *trans*-isomers of **18** is highly dependent on the reaction conditions. In general, longer reaction times and higher concentration of the reaction mixture led to undesired isomerization reactions.

Table 1 summarizes the results for the complex syntheses. After work-up, which was done by column chromatography, the Pd–PEPPSI complexes were obtained in moderate to excellent yields. The NHOC–Pd complexes **12a** and **b** (entries 1 and 2) were prepared by treating the in situ formed isonitrile complex **18** with an α-amino ester. Reaction times for the NHOC synthesis turned out to be quite long, and yields turned out to be only moderate, which is partly based on the observation that the resulting complexes were hardly soluble in all common solvents, which might explain the moderate yields after isolation by column chromatography.

The addition of γ-substituted amines to **18** yielded the six-membered NHC–Pd complexes **15a** and **b** (Table 1, entries 3 and 4). As was mentioned before, a primary attack of the amine led to the formation of a secondary nucleophilic center (the former isonitrile), which enables intramolecular cyclization by the reaction with the leaving group. Because of the easy handling, we utilized the corresponding ammonium salts in combination with triethylamine for the in situ generation of the 3-(chloropropyl)amines.

Table 1. NHC–Pd–PEPPSI complexes synthesized.

Entry	Nucleophile	Conditions	Pd complex	Yield [%]
1	 13a	THF, rt, 4 d	 12a	56
2	 13b	THF, rt, 4 d	 12b	50
3	 14a	THF, rt, 1 d	 15a	76
4	 14b	THF, rt, 1 d	 15b	45
5	 17a	THF, rt, 1 d	 16a	88
6	 17b	THF, rt, 1 d	 16b	48
7	 17c	THF, rt, 1 d	 16c	72
8	 17d	THF, rt, 1 d	 16d	53
9	 19a	THF, rt, 1 d	 20a	45
10	 19b	THF, rt, 1 d	 20b	66
11	 19a	THF, rt, 2 d	 20c	43
12	 19b	THF, rt, 2 d	 20d	53
13	**20a**	HCl (4 M), CH_2Cl_2, rt, 2 d	 21a	100
14	**20b**	HCl (4 M), CH_2Cl_2, rt, 2 d	 21b	100
15	**20c**	HCl (4 M), CH_2Cl_2, rt, 2 d	 21c	97
16	**20d**	HCl (4 M), CH_2Cl_2, rt, 2 d	 21d	98

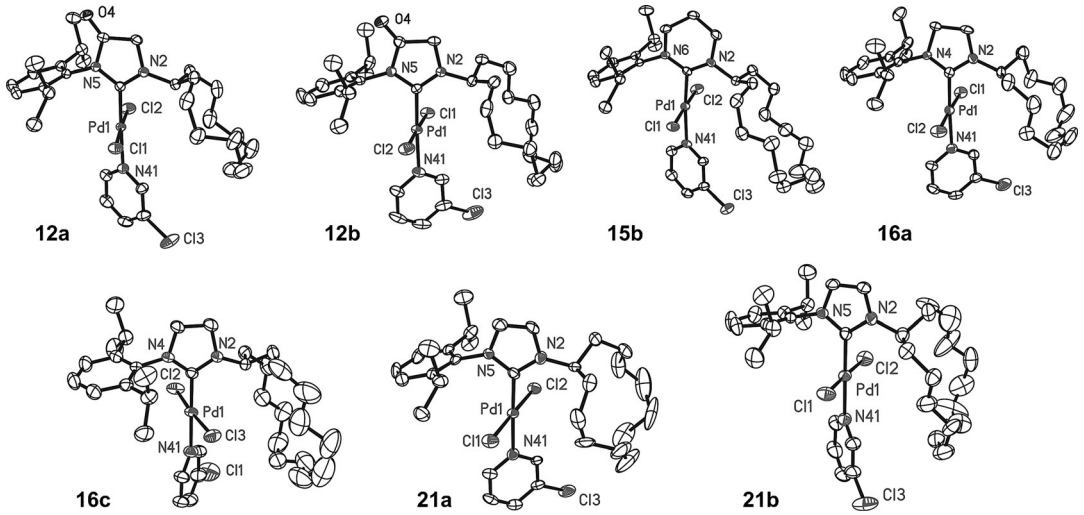


Figure 1. Molecular structures of the NHC–Pd–PEPPSI complexes **12a**, **12b**, **15b**, **16a**, **16c**, **21a**, and **21b** in the solid state.

The corresponding five-membered Pd complexes **16a** and **c** (Table 1, entries 5 and 7) could be obtained in very good yields by applying the same strategy with substituted 2-(chloroethyl)ammonium salts. With secondary halides in the amine tether, it was also possible to introduce a phenyl group in the backbone of the NHC ligand (Table 1, entries 6, 8). An interesting electronic effect was observed in the ^{1}H NMR spectra of **16b** and **16d**. Due to the ring current of the phenyl group in the backbone the signals corresponding to the *iso*-propyl group of the aromatic moieties of the Pd complexes are shifted significantly towards higher field (0.01 ppm instead of the usual 1.15 ppm).

The synthesis of unsaturated NHC–Pd–PEPPSI complexes was accomplished by the treatment of **18** with substituted (2,2-dimethoxyethyl)amines to **20a–d.** Subsequent acid-catalyzed ring closure delivered the desired complexes **21a–d** in quantitative yields. By this procedure, NHC complexes bearing different sterically bulky aliphatic groups at both nitrogen atoms could be synthesized (**21c** and **d**).

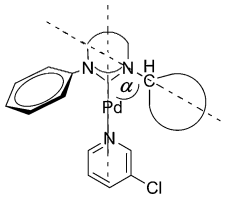
In summary, the broad scope of the isonitrile-based methodology was underlined by the synthesis of these new NHC–Pd–PEPPSI complexes that were accomplished in an one-pot procedure involving the in situ formation of isonitrile complexes **18** and its direct reaction with different ammonium salts and secondary amines. We not only succeeded in the synthesis of different saturated and unsaturated NHC–Pd complexes, but were also able to prepare NHOCs **12** and six-membered NHC complexes **15**.

Fortunately, most of the structures of the synthesized complexes could be unambiguously proven by X-ray structure analysis (Figure 1).[18] Crystals were obtained by vapor diffusion of *n*-pentane into a saturated dichloromethane solution of the Pd complexes. All of the shown complexes possess a *trans*-configuration bearing the 3-chloropyridine ligand opposite to the NHC ligand in a square planar environment around the metal center.

Table 2 schematically illustrates the structure of the complexes shown in Figure 1. The angle between the $C_{carbene}$-Pd-N axis and N–C_{ring} axis (α) was determined and is listed along with selected bond lengths. Furthermore, the percentage buried volume (% V_{bur}) of the NHC ligands bound to palladium have been calculated.[19]

As was expected, the Pd–carbene bond is significantly shorter (1.95–1.98 Å) than the Pd–pyridine distance (2.09–2.12 Å), but variations within the series of complexes are small. The angle between the aliphatic ring of the nitrogen and the $C_{carbene}$-Pd-N axis was determined to verify whether a dependency to the catalytic performance exists, which was tested in selected Suzuki and Negishi cross-coupling reactions (see below). The studies revealed that with the exception of the six-membered NHC complex **15b**, the complexes with the smallest angle (**21b** and **16c**) performed best, whereas com-

Table 2. Comparison of structural parameters in Pd–PEPPSI complexes synthesized.



Complex	Pd–$C_{carbene}$	Pd–$N_{pyridine}$	α [°]	% V_{bur} [a]
12a	1.954(2)	2.092(2)	71.0	38.1
12b	1.954(3)	2.098(3)	69.0	38.0
15b	1.984(3)	2.117(3)	59.8	42.2
16a	1.956(4)	2.106(3)	68.2	37.7
16c	1.958(3)	2.121(3)	67.2	39.1
21a	1.966(6)	2.109(5)	74.5	40.7
21b	1.962(3)	2.114(3)	67.8	38.1

[a] NHC geometries from DFT-optimized $[IrCl(CO)_2(NHC)]$ complexes, bond radii scaled by 1.17, sphere radius $R = 3.5$ Å, M–NHC distance $d = 2.10$ Å, which leads to the % V_{bur} values given in Table 2.[20]

plexes **12a** and **b** showed a low level of activity. Besides, the angle for the complexes with a twelve-membered ring is greater than for the corresponding complexes with a fifteen-membered ring (compare **12a** and **b**, **16a** and **c**, **21a** and **b**), which is also linked to the catalytic performance. This observation is attributed to the fact that a better shielding of the catalytic active center is associated to a higher catalytic performance. The calculated $\%V_{bur}$ as a modular descriptor of the steric properties of the NHC ligands ranged between 37.7 and 42.2. In comparison, the $\%V_{bur}$ value of the commercially available Pd–PEPPSI–IPr is slightly smaller (34.3) than for the values for the herein reported complexes.[21]

As was already mentioned, all synthesized complexes were tested in Suzuki–Miyaura cross-coupling reactions by using chlorobenzene or bromobenzene in combination with 2,5-dimethylphenylboronic acid as coupling partner. Herein, we were interested in the structure–performance relationship of the different catalysts. In addition, the catalytic activity of these complexes was compared with the commercially available Pd–PEPPSI–IPr catalyst. To have robust and user-friendly conditions, all reactions were performed at room temperature by using typical laboratory preparations without the need for handling in a glovebox. All of the reactions proceeded smoothly in technical-grade ethanol without prior degassing, and potassium *tert*-butoxide was found to be the optimal base to ensure high formation of product. The results of these experiments are listed in Figure 2.

The highest yields for the Suzuki cross-coupling reaction with chlorobenzene were obtained with the commercially available Pd–PEPPSI–IPr and the saturated and unsaturated NHC-complexes bearing a 15-membered ring (**16c** and **21b**). On the contrary, NHOC complexes (**12a** and **b**), as well as NHC complexes bearing two aliphatic groups at both nitrogen atoms (**21c** and **d**), showed only low activity. With all other complexes, good to moderate yields (52–85%) could be achieved.

To study the reaction kinetics, ReactIR in situ measurements were conducted. Figure 3 shows the kinetics of the Suzuki–Miyaura cross-coupling of chlorobenzene and 2,5-dimethylphenylboronic acid using complexes **12a**, **15b**, **16c**, and **21a** as catalysts. After a short induction time of a few minutes, **16c** and **21a** permitted the completion of the reaction in approximately 1 h. Complexes **12a** and **15a** showed lower reaction rates and due to catalyst deactivation (that was visible by a fast formation of palladium black), only poor conversions were obtained after 12 h (25 and 52%). This further demonstrates the worse stability issues of these complexes

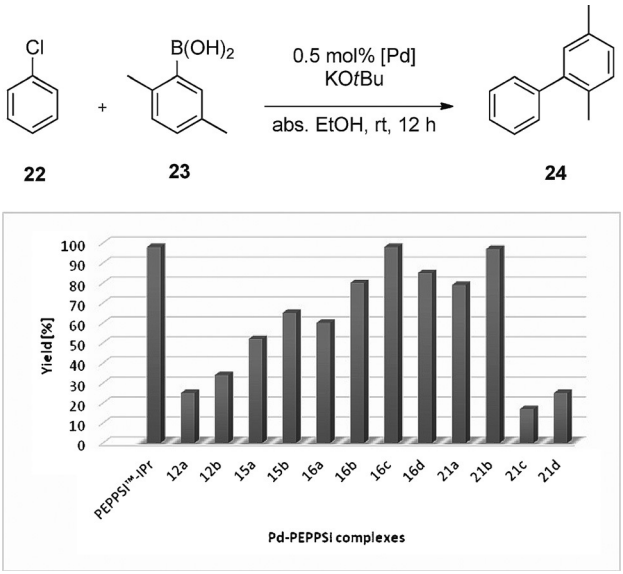


Figure 2. Suzuki–Miyaura cross-coupling of chlorobenzene and 2,5-dimethylphenylboronic acid catalyzed by the new NHC–Pd–PEPPSI complexes. Average of two runs. Reaction conditions: 1.00 mmol of chlorobenzene, 1.20 mmol of boronic acid, 1.20 mmol of KO*t*Bu, 0.5 mol% [Pd], 2.00 mL of EtOH, 12 h, rt. The yield was determined by GC, using *n*-dodecane as internal standard.

compared to complexes with five-membered saturated and unsaturated NHC ligands.

Furthermore, all of the synthesized complexes were tested in a Suzuki cross-coupling reaction using bromobenzene. Because bromobenzenes are more reactive, the amount of catalyst was reduced (0.05 mol%) to obtain distinguishable results. For this transformation, NHC complex **21b** showed an even higher yield than the original Pd–PEPPSI–IPr catalyst, whereas most of the other complexes delivered the desired product **24** in moderate to good yields (54–87%). Once more, the ring size of the attached aliphatic moiety at one of the nitrogen atoms

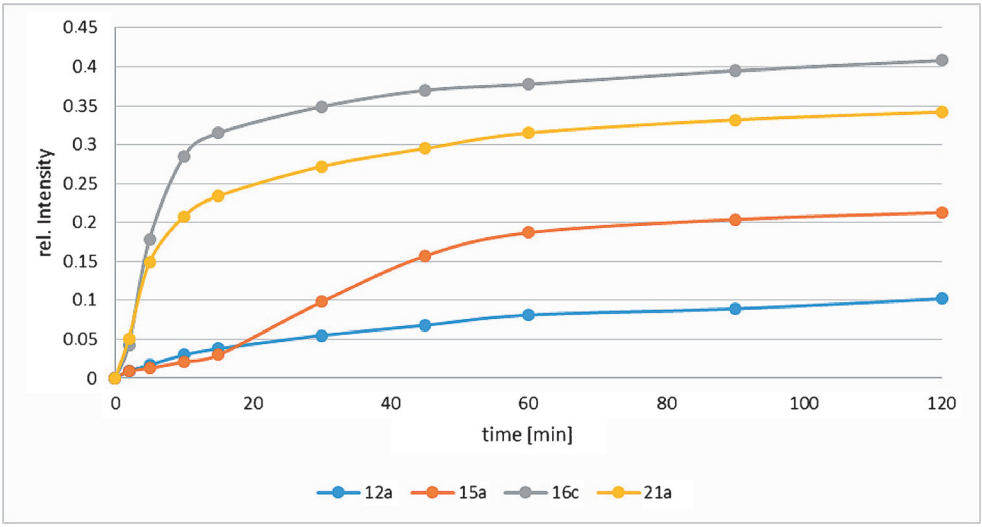


Figure 3. Suzuki–Miyaura cross-coupling of chlorobenzene and 2,5-dimethylphenylboronic acid monitored by ReactIR using complexes **12a**, **15a**, **16c**, and **21a**.

played a key role and an increasing ring size led to an increased yield.

Due to the excellent functional group tolerance and high activity of organozinc reagents, the complexes, which performed best in the Suzuki cross-couplings, were also tested in Negishi reactions and compared with the commercially available catalysts PEPPSI–IPr and PEPPSI–IPent. Herein, a sterically demanding arylzinc reagent, which was generated in situ by transmetalation of mesitylmagnesium bromide to zinc chloride, was effectively coupled with different aryl chlorides and bromides (Figures 4 and 5). All reactions were performed in a THF/*N*-methyl-2-pyrrolidone (NMP) cosolvent system at 70 °C, and the yields were determined by GC by using *n*-dodecane as internal standard.[11b]

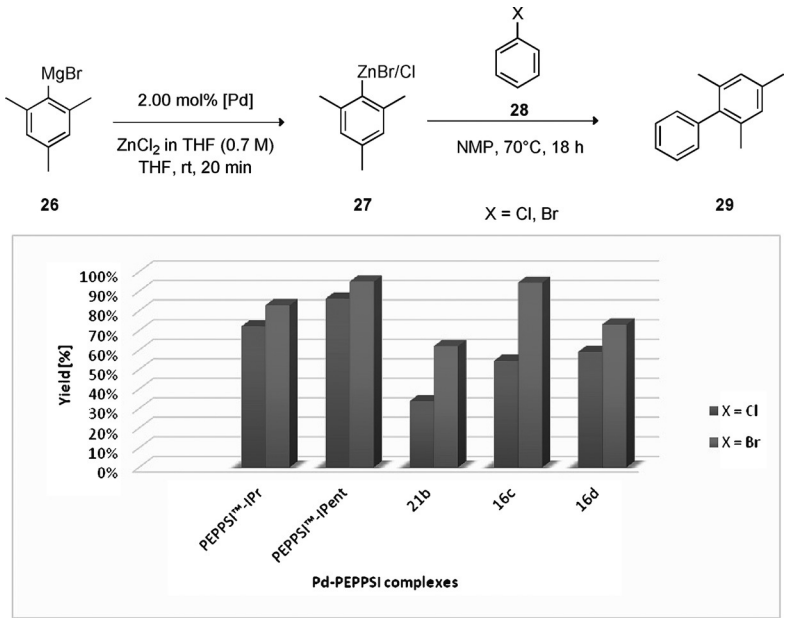


Figure 4. Negishi cross-coupling of chloro- or bromobenzene and mesitylmagnesium bromide by the new NHC–Pd–PEPPSI complexes. Average of two runs. Reaction conditions: 250 μmol of halide, 300 μmol of mesitylmagnesium bromide (1 M in THF), 350 μmol $ZnCl_2$ (0.7 M in THF), 0.4 mL NMP, 2 mol% [Pd], 18 h, 70 °C. The yield was determined by GC, using *n*-dodecane as internal standard.

As depicted in Figure 4, the saturated complexes **16c** and **d** performed better than the corresponding unsaturated analogues (**21b**). An inconsistent effect of the phenyl substituent in the backbone of the ligand was observed. Although in the case of chlorobenzene, the phenyl substituent in the backbone enhanced the catalytic performance in the Negishi cross-coupling reaction, a reverse behavior was observed for bromobenzene. In the case of the Negishi reaction, the commercially available catalysts turned out to be more active for chlorobenzene, but it is noteworthy that complex **16c** gave the same high yield as Pd–PEPPSI–IPent in the reaction with bromobenzene.

Encouraged by these results, the same complexes were tested in another Negishi cross-coupling reaction by using 1-bromonaphthalene and mesitylzinc halide as coupling partner. For this transformation, the desired product **31** could be obtained in good to excellent yields (83–96%). It is clear that a high substrate dependency of the catalyst exists. This is underlined by the observation that in this case, the unsaturated complex **21b** showed superior results.

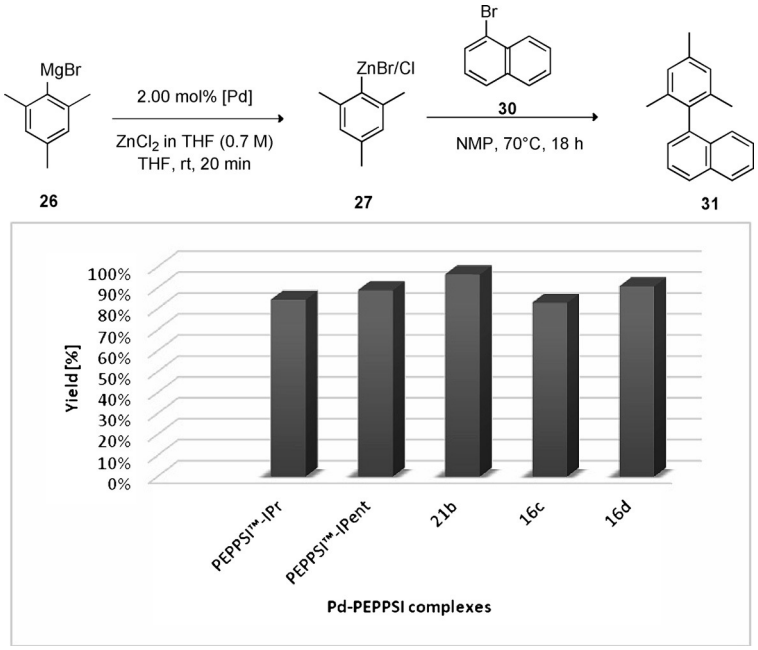


Figure 5. Negishi cross-coupling of 1-bromonaphtalene and mesitylmagnesium bromide by the new NHC-Pd-PEPPSI complexes. Average of two runs. Reaction conditions: 250 μmol of 2-bromonaphthalene, 300 μmol of mesitylmagnesium bromide (1 M in THF), 350 μmol $ZnCl_2$ (0.7 M in THF), 0.4 mL NMP, 2 mol% [Pd], 18 h, 70 °C. The yield was determined by GC, using *n*-dodecane as internal standard.

Conclusion

We have presented a short and efficient route to new unsymmetrically substituted NHC–Pd–PEPPSI complexes based on isonitrile precursors. This methodology allowed the preparation of a diverse set of different catalyst classes, namely, NHOCs, saturated, unsaturated, and six-membered NHC complexes. The modular approach enabled an easy synthesis of different structural motifs concerning the *N*-termini of the carbene complexes. The solid-state molecular structure of most of the synthesized complexes could be determined by X-ray crystallographic analysis. Furthermore, the catalytic activity of the

obtained Pd–PEPPSI complexes was tested and compared in a number of cross-coupling reactions. All reactions were performed by using typical laboratory techniques without the need for glovebox handling. We could show that the catalytic performance depends not only on the catalyst class but also on the ring size of adjacent aliphatic ring. An increasing ring size is associated with a higher degree of conformational freedom of this side group, which might facilitate transmetalation/oxidative addition. The improved stability of the complexes bearing the cyclic aliphatic systems might also be based on the ability of shielding the metal center, which can prevent from catalyst deactivation (this effect is also visible in the solid-state molecular structures, in which the aliphatic moieties point towards the palladium center). On the other hand, the high flexibility can enable a high reactivity, as was mentioned above. In addition, it was shown that a sterically demanding aromatic group at the *N*-termini of the carbene showed a better catalytic performance than the corresponding complexes with an aliphatic group. We also found that a high substrate dependency of the catalysts exists. This fact underlines even more the necessity for modular ligand synthesis like the demonstrated isonitrile route, which enables a fast synthesis of a set of catalysts for screening purposes. Further investigations of this ligand concept and applications in catalysis are part of our ongoing research.

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Keywords: amines · carbenes · cross-coupling · isonitriles · palladium

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[18] CCDC 1021057 (**12a**), 1021058 (**12b**), 1021059 (**15b**) and 1021060 (**16a**), 1021061 (**16c**), 1021062 (**21a**), 1021063 (**21b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

[19] Based on solid state structures, the percentage buried volume have been calculated using the "Samb*V*ca" software on a web application at the URL http://www.molnac.unisa.it/OMtools.php.

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