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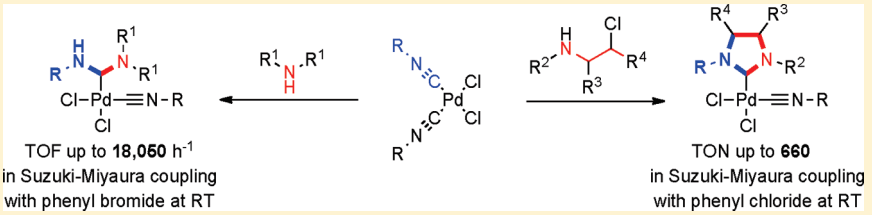
From Isonitriles to Carbenes: Synthesis of New NAC− and NHC−Palladium(II) Compounds and Their Catalytic Activity

A. Stephen K. Hashmi,* Christian Lothschütz, Constantin Böhling, and Frank Rominger

Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69221 Heidelberg, Germany

Supporting Information

ABSTRACT:



A series of NAC− and their structurally related NHC−palladium(II) isonitrile complexes, including examples of dinuclear complexes, were prepared. In a second series, NHC−palladium complexes bearing an aryl group on one nitrogen of the NHC ring and different cycloalkyl groups ranging from six- to 15-membered rings have been synthesized. The good yields document the value of the very short route to new palladium(II) NHC complexes. The stuctures have been investigated by crystal structure analyses of some representatives; in addition conformational studies by NMR were conducted. The reactivity in Suzuki cross-coupling reactions was investigated, showing turnover frequencies of up to 18 050 h^{-1} and a clear correlation of the size of the cycloalkyl moiety with the turnover number achieved for the coupling of chlorobenzene and 2,5-dimethylphenylboronic acid.

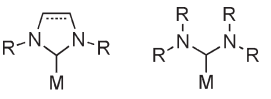
INTRODUCTION

During the last decades N-heterocyclic carbenes (NHCs) have revolutionized modern organometallic chemistry.[1] Initially considered as a curiosity, NHC−metal complexes found broad application in a number of different reactions.[2] NHCs form stable complexes with a large number of elements, resulting in a diverse field of applications.[3] Nonetheless, NHC−Pd(II) compounds can be considered as one of the most prominent classes of NHC−metal complexes. In this field the pioneering contributions from the groups of Herrmann,[4] Nolan,[5] Organ,[6] and Glorius[7] should be mentioned. Structurally related but less apparent in the literature, another group of carbene ligands exists, the so-called nitrogen-acyclic carbenes (NACs).[8] These compounds stand out by the absence of the backbone, resulting in a number of interesting characteristics (Scheme 1).

Depending on the number and type of substituents, NACs can form diastereoisomers with different N−C−N bond angles and therefore differing electron-donating abilities.[9] The first NAC−Pt(II) complex was synthesized by Chugaev and co-workers in 1915, but was inadvertently formulated as a dimeric hydrazine-bridged complex.[10] Later Shaw and co-workers were able to assign the correct structure.[11] The groups of Richards and Belluco were next to investigate NAC−Pd(II) complexes in the late 1960s.[12] The synthesis of these complexes can be easily accomplished by the reaction of a nucleophile with a metal-coordinated isonitrile, commonly resulting in the acyclic carbene in high yields. In addition to the use of nitrogen nucleophiles, oxygen nucleophiles also found broad application in this concept.[13] In addition to this method, there exist other procedures that for example start from formamidinium or chloramidinium salts.[14] In a recent publication, the catalytic activity in Suzuki−Miyaura cross-coupling reactions of special NAC−Pd(II) compounds, resulting from the addition of hydrazones to bis(isonitrile)palladium(II) complexes, was described.[15] Preceding reports dealt with the use of NAC−Pd(II) complexes in Sonogashira, Heck, and Suzuki−Miyaura reactions.[16]

In our latest work we addressed the probably simplest synthesis of unsymmetrical substituted NHC metal complexes and their catalytic activity.[17] In this article we expand our initial findings and for the first time compare structurally related NHC−Pd(II) and NAC−Pd(II) complexes with respect to their catalytic activity and structural parameters.

Scheme 1. Structural Comparison of NHCs and NACs



RESULTS AND DISCUSSION

The synthesis of both NAC− and NHC−Pd(II) compounds utilizes the addition of a nitrogen nucleophile to the coordinated

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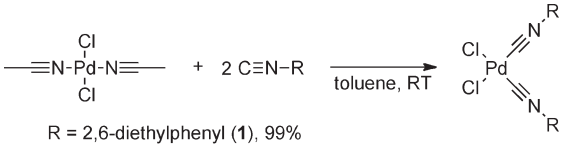
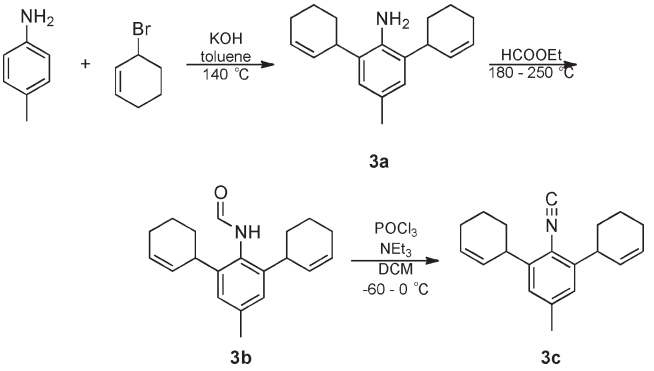
Scheme 2. Synthesis of Bis(isonitrile)palladium(II) Complexes

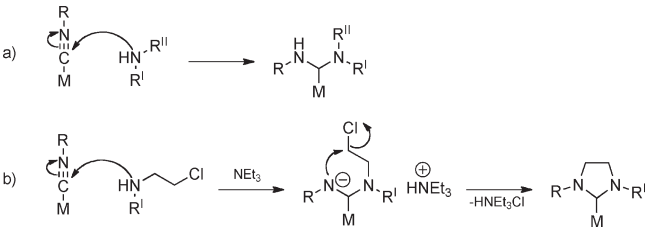


R = 2,6-diethylphenyl (**1**), 99%
R = 2,6-diisopropylphenyl (**2**),82%
R = 2,6-di(cyclohex-2-ene-1yl)-4-methylphenyl (**3**), 96%
R = ^{t}Bu (**4**), 89%

Scheme 3. Synthesis of 3c from *p*-Toluidine and 3-Bromocyclohexene



Scheme 4. Formation of NAC and NHC Complexes

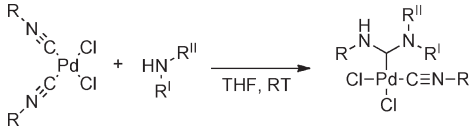


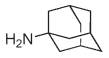
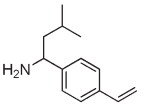
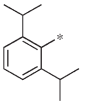
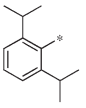
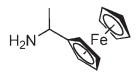
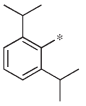
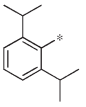
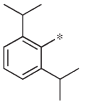
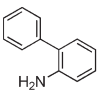
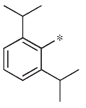
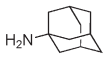
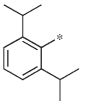
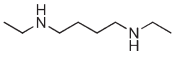
isonitrile ligand. On coordination of an isonitrile to a metal such as palladium(II), platinum(II), or gold(I), the IR stretching frequency shows a hypsochromic shift in the range of more than 100 cm^{-1}, indicating an activation for the reaction with a nucleophile. This spectroscopic property identifies the isonitrile ligands as virtually pure donor ligands. Moreover, isonitriles are isoelectronic to NHCs so that the isonitrile−metal bond can be characterized as a carbene-type bond. The synthesis of the bis(isonitrile)palladium(II) complexes was simply achieved by the treatment of $(CH_3CN)_2Cl_2Pd(II)$ with two equivalents of the corresponding isonitrile in toluene.

In the case of **3** the isonitrile was synthesized by two consecutive 3,3-sigmatropic rearrangements of in situ generated *N*-(cyclohex-2-en-1-yl)-4-methylbenzene, forming the corresponding aniline derivative **3a**. This compound can be transformed into the isonitrile **3c** by standard procedures.

On addition of a simple primary or secondary amine to bis(isonitrile)palladium(II) complexes, the outcome is a NAC−Pd(II) complex (Scheme 4a). When substituted 2-(chloroethyl)amines are used, the primary attack of the amine causes the formation of a secondary nucleophilic center on the nitrogen atom of the isonitrile, closing the heterocycle by a

Table 1. Synthesis of the NAC−Palladium Complexes 5−17



Entry	R	Amine[a]	NAC-complex (yield)
1			**5** (63%)
2			**6** (72%)
3			**7** (96%)
4			**8** (67%)
5			**9** (94%)
6			**10** (79%)
7			**11** (38%)
8			**12** (42%)
9			**13** (21%)
10			**14** (34%)
11			**15** (52%)
12			**16** (34%)
13			**17** (64%)[b]

[a] For the syntheses of the amines see Supporting Information. [b] In case of this amine 2.00 equiv of the palladium precursor were used in order to form the dimeric NAC−Pd(II) complex.

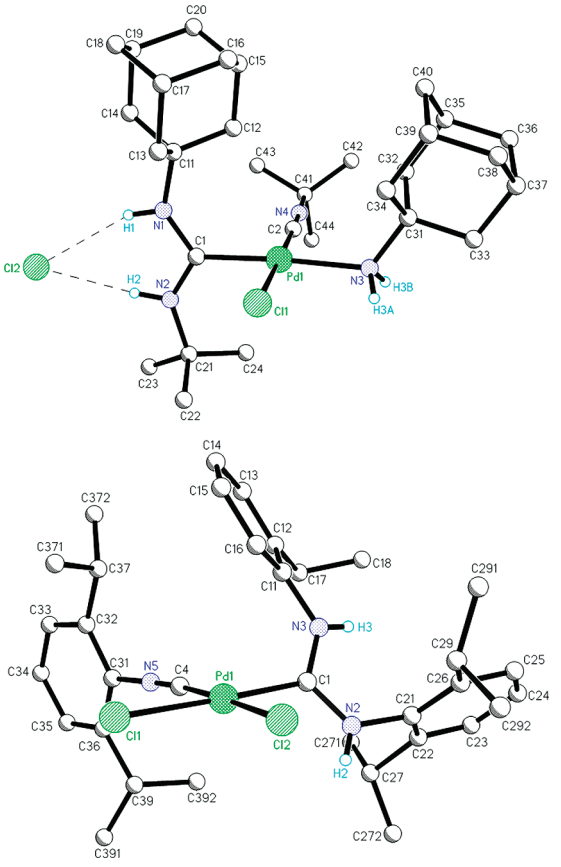


Figure 1. Solid-state molecular structures of compounds **8b** and **14**. Most hydrogen atoms are omitted for clarity.

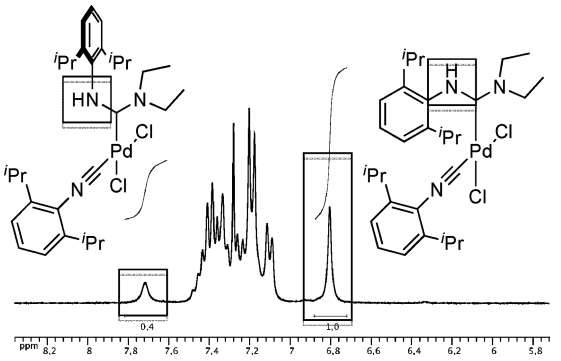
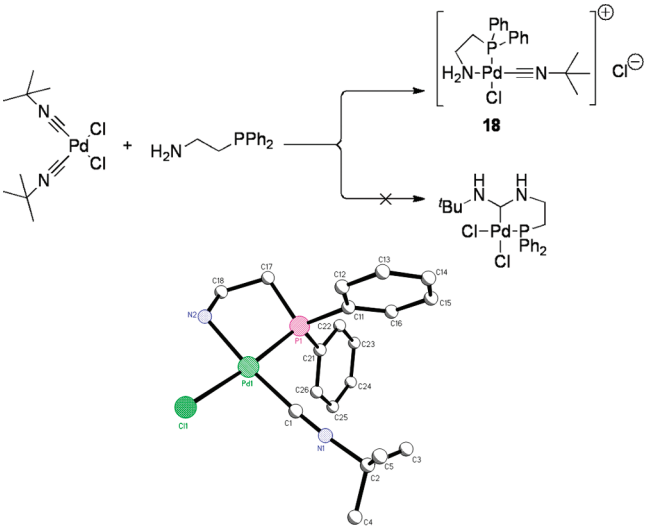


Figure 2. Aromatic region of the ^{1}H NMR spectrum of **11**.

nucleophilic substitution (Scheme 4b). For reasons of simplicity we did not use the free 2-(chloroethyl)amines, but the corresponding ammonium salts in the presence of triethylamine as base.

For the synthesis of NAC−Pd(II) complexes we used a number of different amines in order to demonstrate the high scope of this methodology. For this study we used two different bis(isonitrile)palladium(II) complexes bearing sterically very demanding groups R. As amines we introduced aliphatic as well as aromatic representatives. Table 1 summarizes the outcome of our experiments. Besides the use of less sterically demanding amines such as diethyl amine, pyrrolidine, or piperidine (entries 1, 2, 3, 7) we also managed to synthesize 1-adamantyl-substituted

Scheme 5. Synthesis of 18 and Solid-State Molecular Structure[a]



[a] All the hydrogen atoms and the chloride counterion are omitted for clarity.

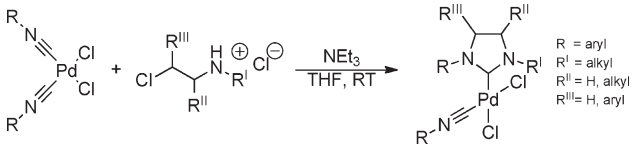
analogues **8** and **16** in good to moderate yields (entries 4, 12). In two other examples we used aniline derivatives as nucleophiles (entries 10, 11). Compound **9** was formed by the attack of an amine bearing a styryl group in the backbone (entry 5). The compound is perfectly stable and might find application in functionalized polymers, as the olefin moiety should serve as monomer in polymerization reactions.

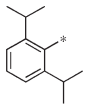
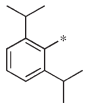
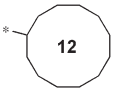
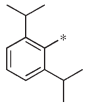
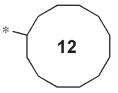
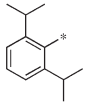
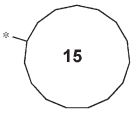
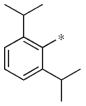
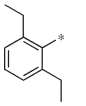
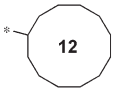
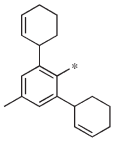
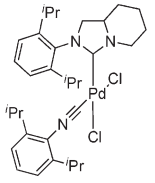
Compounds **10** and **13** were inspired by the impressive work of the Glorius group, which has shown that IBOX-carbenes are extremely good ligands for a number of different reactions, whereby the catalytic activity is characterized by the dynamic behavior of the adjacent aliphatic ring.[8] Two examples (entries 8 and 13) prove the applicability of this method to the formation of bimetallic compounds. The structure of complexe **14** was unambiguously proven by X-ray structure analysis (Figure 1).

The synthesis of **8** was repeated several times. In one case an excess of 1-adamantylamine was used, thus leading to the formation of a small amount of a certain byproduct, **8b**. Fortunately, we could grow single crystals suitable for X-ray analysis. On treatment of the initially formed complex with 1-adamantylamine, an internal complex was formed with the amine in *trans*-position to the carbene. A hydrogen-bonded chloride in the outer coordination sphere compensates the positive charge. The differing yields for the carbenes must be traced back to the workup process because the small precipitate was not always ideal. The addition of the amine to the isonitrile was quantitative in nearly all cases, as proven by the IR stretching frequencies of the reaction mixtures. The workup was accomplished by recrystallization of the crude products.

Due to the presence of partial double bonds in the carbene moiety, we observed the formation of rotamers. Taking the example of **11**, this fact can be exemplified impressively. Having a closer look at the aromatic region of the ^{1}H NMR spectrum, one can identify two different signals that must be assigned to the hydrogen atom on the nitrogen atom adjacent to the

Table 2. Synthesis of the NHC−Palladium Complexes 19−26



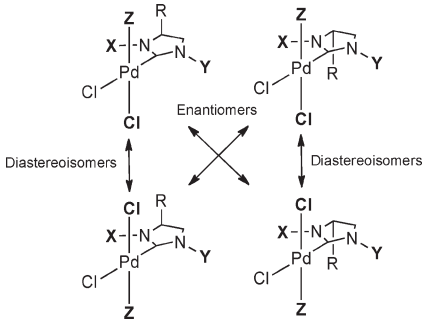
Entry	R	R^I	R^{II}	R^{III}	NHC-complex (yield)
1			H	Ph	**19** (78%)
2			H	H	**20** (63%)
3			H	Ph	**21** (67%)
4			H	Ph	**22** (55%)
5			H	H	**23** (76%)
6			H	Ph	**24** (86%)
7			H	H	**25** (52%)
8					**26** (54%)

carbene carbon. In this special case we found an isomeric ratio of 2.5:1.

In another experiment we tried to synthesize a bidentate NAC−Pd(II) complex.[18] In doing so, we obtained complex **18** (Scheme 5). Interestingly, only one isonitrile and one chloro ligand were replaced, forming a cationic complex.

As outlined above, we were also able to prepare NHC−Pd(II) compounds by a related procedure (Scheme 4). The synthesis of the 2-(chloroethyl)ammonium salts was accomplished according to standard procedures (see Supporting Information). The

Scheme 6. Formation of Diastereoisomers



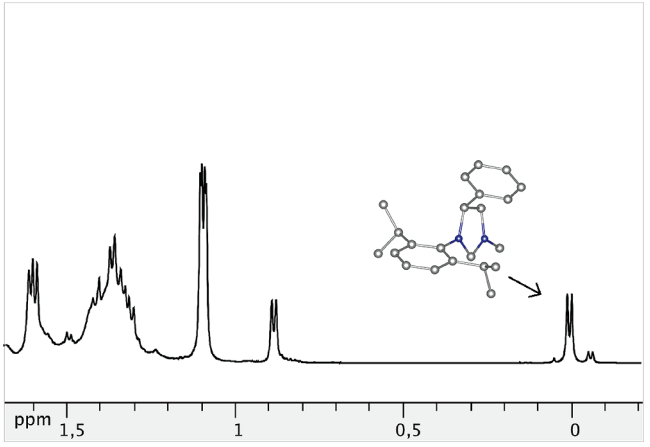
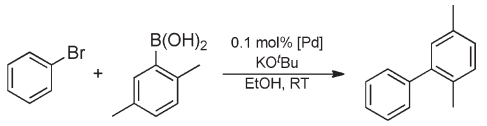


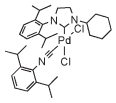
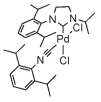
Figure 3. Aliphatic region of the ^{1}H NMR spectrum of **22**. Optimized structure of the simplified ligand (B3LYP, cc-PVDZ).

formation of the NHC−Pd(II) complexes was achieved in THF at room temperature. In this study we prepared a number of compounds bearing large aliphatic rings (Table 2, entries 2, 3, 4, and 6). The choice of these substituents was made on the basis of our earlier work. In catalytic studies we found cyclohexyl-substituted NHC−Pd(II) carbenes to be active catalysts for the activation of aryl chlorides in Suzuki−Miyaura cross-coupling reactions at room temperature in technical grade solvents. Although the yields were moderate, we were interested in the role these groups would play in further catalytic reactions. Thus we prepared a whole series of new NHC complexes of this type, varying the ring size (Table 2). The synthesis of these organometallic compounds succeeded without any problems, documenting the broad scope of our new method.[17] Our protocol allowed the incorporation of a chiral side group (entry 5) and of large aliphatic rings. So, we could synthesize a NHC containing a cyclopentadecyl unit for the first time. Moreover we prepared a NHC complex starting from **3** showing enormous steric demand (entry 7). The last entry in Table 2 shows a NHC with an annulated cyclohexyl ring. In 2008 Hahn and co-workers reported a synthesis delivering comparable Rh(I) complexes in a four-step synthesis, requiring reagents such as elemental sulfur and potassium.[19] The workup was simply accomplished by recrystallization or by precipitation from ethereal solution.

Our method also allowed the introduction of a phenyl group in the backbone of the NHC ligand. Due to the *cis*-configuration, these compounds form mixtures of diastereoisomers (Scheme 6).

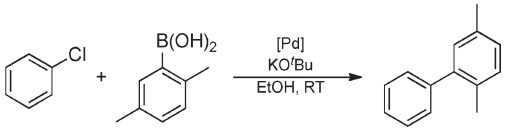
Table 3. [a]

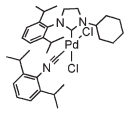
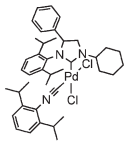


Entry	Catalyst	Mol% catalyst	Yield [%][a)]
1	**5**	0.1	48
2	**8**	0.1	46
3	**9**	0.1	23
4	**10**	0.1	50
5	**11**	0.1	60
6	**12**	0.1	61
7	**13**	0.1	35
8	**18**	0.1	n.a.
9		0.1	81[17]
10		0.1	79[17]
11		0.1	59[17]

[a] Average of two runs. Reaction conditions: 1.00 mmol of bromobenzene, 1.15 mmol of boronic acid, 1.00 mmol of KO^{t}Bu, 2.00 mL of EtOH, 12 h, RT. The yield was determined by GC, using dodecane as internal standard.

Table 4. Suzuki Cross-Coupling of Chlorobenzene and 2,5-Dimethylphenylboronic Acid by the New NHC−Palladium Complexes



Entry	Compound	Mol% catalyst	Yield [%][a)]
1		1.0	62[17]
2		1.0	64[17]
3	**19**	1.0	57
4	**20**	0.1	33
5	**20**	0.5	97
6	**20**	1.0	98
7	**21**	0.1	45
8	**22**	0.1	66
9	**23**	1.0	16
10	**25**	0.1	n.a.

[a] Average of two runs. Reaction conditions: 1.00 mmol of bromobenzene, 1.15 mmol of boronic acid, 1.00 mmol of KO^{t}Bu, 2.00 mL of EtOH, 12 h, RT. The yield was determined by GC, using dodecane as internal standard.

The phenyl group can be oriented in two different ways, pointing toward either the isonitrile or the chloro ligand, in which one direction is preferred. The isomeric ratios are in the range of 2:1 (**24**) and 6:1 (**22**).

Moreover, interesting electronic effects manifest in the ^{1}H NMR spectra of these compounds. The phenyl groups in the backbone are in short contact with the aliphatic groups of the aromatic moieties of the NHC−Pd(II) complexes. This orientation causes a shielding of these groups, and the corresponding signals are shifted toward higher field (Figure 3).

Some of the complexes synthesized were tested in Suzuki−Miyaura cross-coupling reactions using bromobenzene or chlorobenzene and 2,5-dimethylphenylboronic acid as coupling partner. The outcome of these experiments is listed in Tables 3 and 4. In this study we were interested only in structure −performance relationships of the catalysts. For this reason, we did not vary the reaction parameters. In order to have robust and user-friendly conditions, all reactions were performed at room temperature in technical grade solvent without prior degassing. In the case of NAC−Pd(II) complexes the compounds **11** and **12** delivered the highest yields (TON = 600 and 610, respectively). On the contrary, catalyst **9** showed only little reactivity (TON = 230). The cationic complex **18** was completely inactive. In comparison with the structurally related NHC−Pd(II) complexes (Table 3, entries 9, 10, 11) the yields were comparable (entry 11) or lower. However, we found the reactions to be extremely fast. For this reason we were interested in the kinetics of these transformations. In order to study the catalyses concerning the reaction time, we found ReactIR to be the best solution. However, we had to choose another combination of aryl bromide and boronic acid because our standard system was not suitable for this methodology. The combination of *p*-bromobenzaldehyde and 2-methoxyphenylboronic acid was appropriate for this task. Figure 4 shows the kinetics of the experiments using compounds **10** and **13** as well as **6** and **11** as catalysts. NAC **13** showed a TOF of 18 050 h^{-1} and a yield of 93%. Structurally related **10** showed a slightly smaller TOF (17 820 h^{-1}) and a comparable yield of 96%. Delivering comparable yields (**6**, 83%; **11**, 84%), the differences concerning the TOF of the reactions are quite remarkable (14 050 h^{-1}, **11**; 3700 h^{-1}, **6**).

In contrast to the NAC−Pd(II) complexes the NHC−Pd(II) analogues were also able to activate phenyl chloride at room temperature under these difficult conditions. Our experiments showed a clear dependence of the reaction outcome on the ring size of the adjacent aliphatic ring and the backbone substitution (Figure 6, Table 4). The catalysts bearing the six- and

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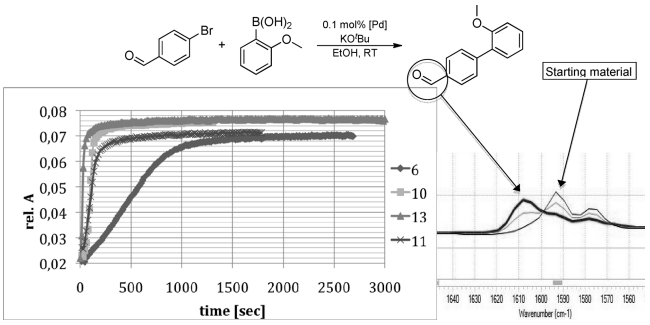

Figure 4. Time-course of the reactions and overlay of observed absorption bands of starting material and product.

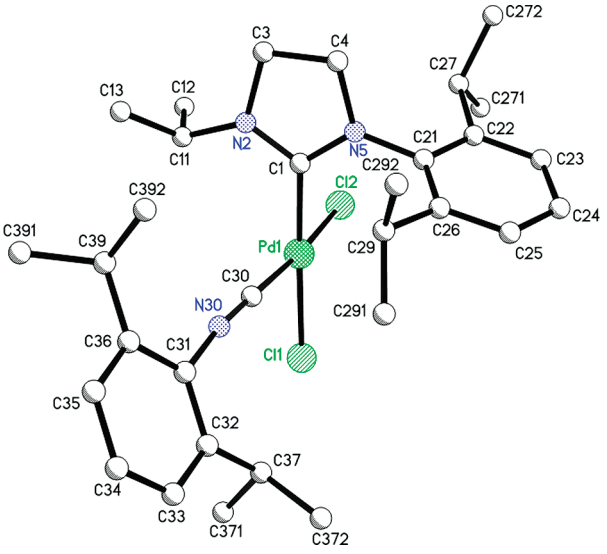

Figure 5. Solid-state molecular structure of NHC−Pd complex (Table 3, entry 10).

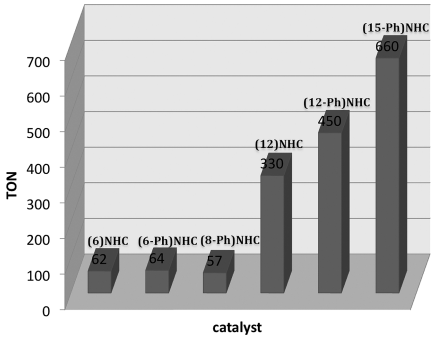

Figure 6. Relationship between ring size, backbone substitution, and TON (Table 4). The number in parentheses declares the ring size of the aliphatic ring. The abbreviation Ph indicates the presence of a phenyl group in the backbone of the catalyst.

eight-membered rings are in the same range. Doubling of the ring size (six- to 12-membered ring) improves the activity by 550%. Additional enlargement (12- to 15-membered ring) and incorporation of the phenyl group in the backbone further enhance the activity by 100%. Catalyst **25** showed no activity in this reaction, while a structurally related complex (entry 1) still delivered 40% yield. At the moment we have no explanation for this finding. However, this comparison clarifies that the catalytic activity is highly sensitive with regard to the geometric properties of the ligands and that parameters such as the percent buried volume do not always provide the right explanation.[20] In order to test the robustness of our catalysts, we performed a catalysis in rum (54 vol %) as solvent. Using 1 mol % of catalyst **22** we found 20% of coupling product starting from chlorobenzene.

CONCLUSION

We have synthesized new, highly stable NAC−Pd(II) and NHC−Pd(II) complexes by a very short and efficient route. The catalytic activity of the NHC compounds is much higher than that of the NAC analogues. This might originate from an improved stability and a longer catalyst lifetime. Nonetheless, we found high TOFs for the NAC−Pd(II) complexes of 18.050 h^{-1} and more.[21] Furthermore, we dicovered a dependence of the catalyst performance and the ring size of adjacent aliphatic rings. Paired with a phenyl-substituted backbone, large rings on the NHC lead to excellent results with high TONs for phenyl chloride at room temperature.[22] In our opinion this dependence is partially due to a hydrophobic effect caused by the unpolar aliphatic ring. Moreover, the phenyl group in the backbone exerts a steric effect on the isopropyl groups of the aromatic substituent of the NHC as proven by ^{1}H NMR spectroscopy (Figure 3). This might lead to enhanced rigidity of the aromatic side group, improving reductive elimination. The increasing ring size raises the degree of conformational freedom of this side group, thus facilitating oxidative addition. At the moment we are further exploring this ligand concept for other reactions and metals.

ASSOCIATED CONTENT

Supporting Information. Crystallographic information files (CIF) of compounds **4**, **8b**, **14**, and **18**, as well as characterization data of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: hashmi@hashmi.de.

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