EurJIC European Journal of Inorganic Chemistry
ChemPubSoc Europe
FULL PAPER

DOI:10.1002/ejic.201301339

Structural Characterization, Solution Dynamics, and Reactivity of Palladium Complexes with Benzimidazolin-2-ylidene N-Heterocyclic Carbene Ligands

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Keywords: Carbene ligands / Structure elucidation / Palladium / Click chemistry / Cross coupling

Mononuclear and halide-bridged dinuclear palladium(II) complexes with symmetrically (**1** and **3**) and nonsymmetrically (**2**, **4**–**6**) substituted benzimidazolin-2-ylidene N-heterocyclic carbene ligands were synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystallography. The mononuclear complexes exist as a mixture of *cis* and *trans* isomers, and the identity of these was ascertained by NMR spectroscopy and structural characterization. The dinuclear complexes **4**–**6** with nonsymmetrically substituted benzimidazolin-2-ylidene ligands form rotamers (*cis*/*anti*, *cis*/*syn*, *trans*/*anti*, and *trans*/*syn*) at room temperature, which can be transformed to a single rotamer at higher temperatures as evidenced by ^{1}H NMR spectroscopy. Crystal structure analyses of representative examples show that the Pd^{II} centers are bound in a distorted square-planar environment by halides and carbene C ligands, and the carbene ligands are perpendicular to the Pd–halide plane. All of the complexes were tested for their efficiency as (pre)catalysts in the Suzuki–Miyaura cross-coupling reaction, as well as in hydrodehalogenation reactions, and they show good activity. The Suzuki–Miyaura coupling reactions can be performed under air and in water as an environmentally benign solvent. The most active catalyst for the Suzuki–Miyaura coupling was also used in a sequence together with a "click reaction" to synthesize valuable sterically demanding tripodal triazole ligands.

Introduction

N-Heterocyclic carbenes (NHCs) have established themselves as a privileged class of ligands in organometallic chemistry.[1] The reasons for this are the relatively easy tuning of the steric and electronic properties of these ligands by simple variation of the substituents at the nitrogen atoms. Such a tunable nature is extremely useful when these compounds are used as ligands in homogeneous catalysis.[2] Thus, metal complexes of NHCs have been one of the most extensively studied classes of homogeneous catalysts in recent decades.[1] Although NHCs based on imidazolin-2-ylidenes have certainly been the most popular class of such ligands,[3] particularly since the seminal isolation and characterization by Arduengo et al. of such compounds,[3c] the ones based on benzimidazolin-2-ylidenes have been investigated by several groups in recent years (Figure 1).[4] The introduction of a six-membered aromatic ring to the imidazolin-2-ylidene backbone changes the properties of the ligands and their metal complexes drastically.[4] Metal complexes of NHC ligands continue to be a lively research field,[1] and new concepts such as abnormal carbenes[5] and the redox-active nature of NHCs[6] continually add to its flavor.

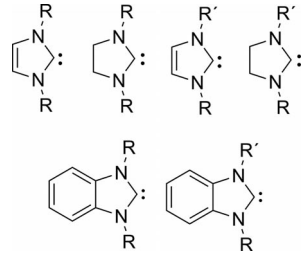

Figure 1. Selected examples of NHC ligands.

We have recently reported Cu^{I} complexes of substituted benzimidazolin-2-ylidenes and have shown these to be efficient catalysts for the click-type cycloaddition reactions between alkynes and azides.[7] Furthermore, we have also reported on Pd^{II} complexes of substituted benzimidazolin-2-ylidenes and have proven that these classes of ligands are redox-noninnocent.[6e] During the course of those studies, we became interested in comparing the properties of Pd^{II} complexes of symmetrically and nonsymmetrically substituted benzimidazolin-2-ylidenes in terms of their structures, dynamics, and NMR characteristics. Pd^{II} complexes of

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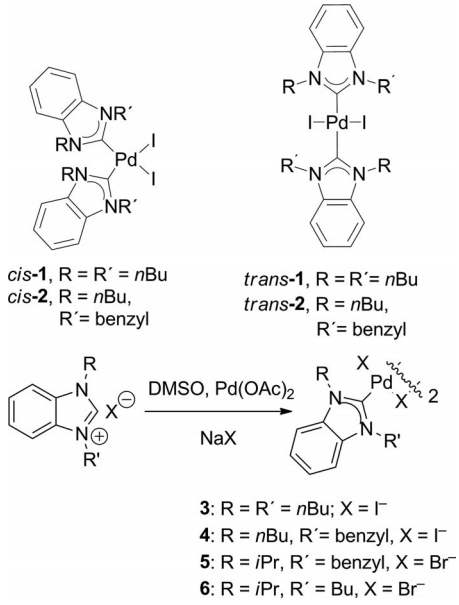
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201301339.

symmetrically substituted benzimidazolin-2-ylidenes have been extensively studied by Huynh et al. in recent years.[4g,4i] Furthermore, we were interested in the catalytic properties of such complexes in cross-coupling reactions with a special focus on post-functionalization of certain tripodal ligands that can be synthesized by the Cu^{I}-catalyzed click reactions.[8] In the following, we present the synthesis and characterization of *cis*-diiodo-bis(1,3-di-*n*-butylbenzimidazolin-2-ylidene)palladium(II) (*cis*-**1**), *trans*-diiodo-bis(1,3-di-*n*-butylbenzimidazolin-2-ylidene)palladium(II) (*trans*-**1**), and di-μ-iodo-bis(1,3-di-*n*-butylbenzimidazolin-2-ylidene)diiododipalladium(II) (**3**) with symmetrically substituted benzimidazolin-2-ylidenes as well as *cis*-diiodo-bis(1-benzyl-3-*n*-butylbenzimidazolin-2-ylidene)palladium(II) (*cis*-**2**), *trans*-diiodo-bis(1-benzyl-3-*n*-butylbenzimidazolin-2-ylidene)palladium(II) (*trans*-**2**), di-μ-iodo-bis(1-benzyl-3-*n*-butylbenzimidazolin-2-ylidene)diiododipalladium(II) (**4**), di-μ-bromo-bis(1-benzyl-3-isopropylbenzimidazolin-2-ylidene)dibromodipalladium(II) (**5**), and di-μ-bromo-bis(1-butyl-3-isopropylbenzimidazolin-2-ylidene)dibromodipalladium(II) (**6**) with nonsymmetrically substituted benzimidazolin-2-ylidenes. The dynamic behavior of such complexes in solution with respect to the existence of *cis*/*trans* isomers and rotamers was investigated by NMR spectroscopy. The identity of the isomers was determined by using structural characterization by single-crystal X-ray diffraction. The complexes were tested for their activity in the Suzuki–Miyaura cross-coupling and hydrodehalogenation reactions. The cross-coupling reactions were performed in air with water as an environmentally benign solvent. The best catalyst of this series was used for multiple C–C bond-formation reactions to generate a new kind of tripodal ligand.



Scheme 1. Mononuclear complexes presented in this work (top) and the synthesis of dinuclear complexes (bottom).

Results and Discussion

Synthesis and NMR Spectroscopy

The symmetrically substituted benzimidazolin-2-ylidenes were synthesized by one-pot alkylations of benzimidazole, and the nonsymmetric ones were synthesized by stepwise syntheses of benzimidazoles with two different alkyl halides by following reported procedures.[4a–4c]

The Pd^{II} complexes were synthesized by reacting $Pd(OAc)_2$ and the corresponding benzimidazolium salts in dimethyl sulfoxide (DMSO) or tetrahydrofuran (THF). Such reactions resulted in the mononuclear complexes **1** and **2**. The addition of sodium halides to the reaction mixture led to the formation of the halide-bridged dinuclear complexes **3**–**6** (Scheme 1).

The complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analyses, and in select cases by mass spectrometry.

For the mononuclear complexes *cis*-**1** and *trans*-**1** with the symmetrically substituted benzimidazolin-2-ylidene ligand, the initial product formed directly after synthesis was isomer-pure *cis*-**1** as evidenced by ^{1}H NMR spectroscopy. The binding of the carbene C atom to the Pd^{II} center was proved by the absence of the low-field-shifted C–H proton, which is characteristic of the benzimidazolium salt. Additionally, the carbene C atom was observed at δ = 179.8 ppm in the ^{13}C NMR spectrum of *cis*-**1**. The ^{1}H NMR spectrum of *cis*-**1** shows a clearly resolved triplet for the methyl protons of the *n*-butyl groups at δ = 1.06 ppm. Similarly, the CH_2 protons (NCH_2) of the *n*-butyl groups appear as a clear triplet at δ = 4.97 ppm (Figures 2 and S1, top). The other two CH_2 protons of the *n*-butyl groups appear as multiplets at δ = 2.49–2.32 and 1.70 ppm. The chemical shifts of the protons and the multiplicities rule out any kind of additional interactions between the protons of the *n*-butyl substituents and the Pd^{II} center in the *cis* complex *cis*-**1** (Figures 2 and S1, see Exp. Section). The identity of *cis*-**1** as the *cis*-isomer was eventually established by structure determination through single-crystal X-ray diffraction (see below).

When *cis*-**1** was left in *N*,*N*-dimethylformamide (DMF) at ambient temperature for 10 months, a quantitative conversion of *cis*-**1** to *trans*-**1** was observed. Heating a mixture of *cis*-**1** to force a faster conversion to *trans*-**1** was not successful. Structure determination through single-crystal X-ray diffraction established the identity of *trans*-**1** as the *trans* isomer (vide infra). In comparison with that of *cis*-**1**, the ^{1}H NMR spectrum of the *trans*-**1** is markedly different (Figures 2 and S1, bottom). The signal of the $NCH_2CH_2CH_2CH_3$ protons of the *n*-butyl groups is split into two and appears as multiplets at δ = 4.69–4.81 and 5.11–5.23 ppm. Similarly, the signals of the $NCH_2CH_2CH_2CH_3$ protons of the *n*-butyl group are also split into two signals, which appear as multiplets at δ = 2.04–2.26 and 2.28–2.51 ppm (Figure 2 and S1, bottom). The splitting of these signals, and their appearance as multiplets points to the inequivalence of the respective protons, which could be a result of their interaction with the Pd^{II}

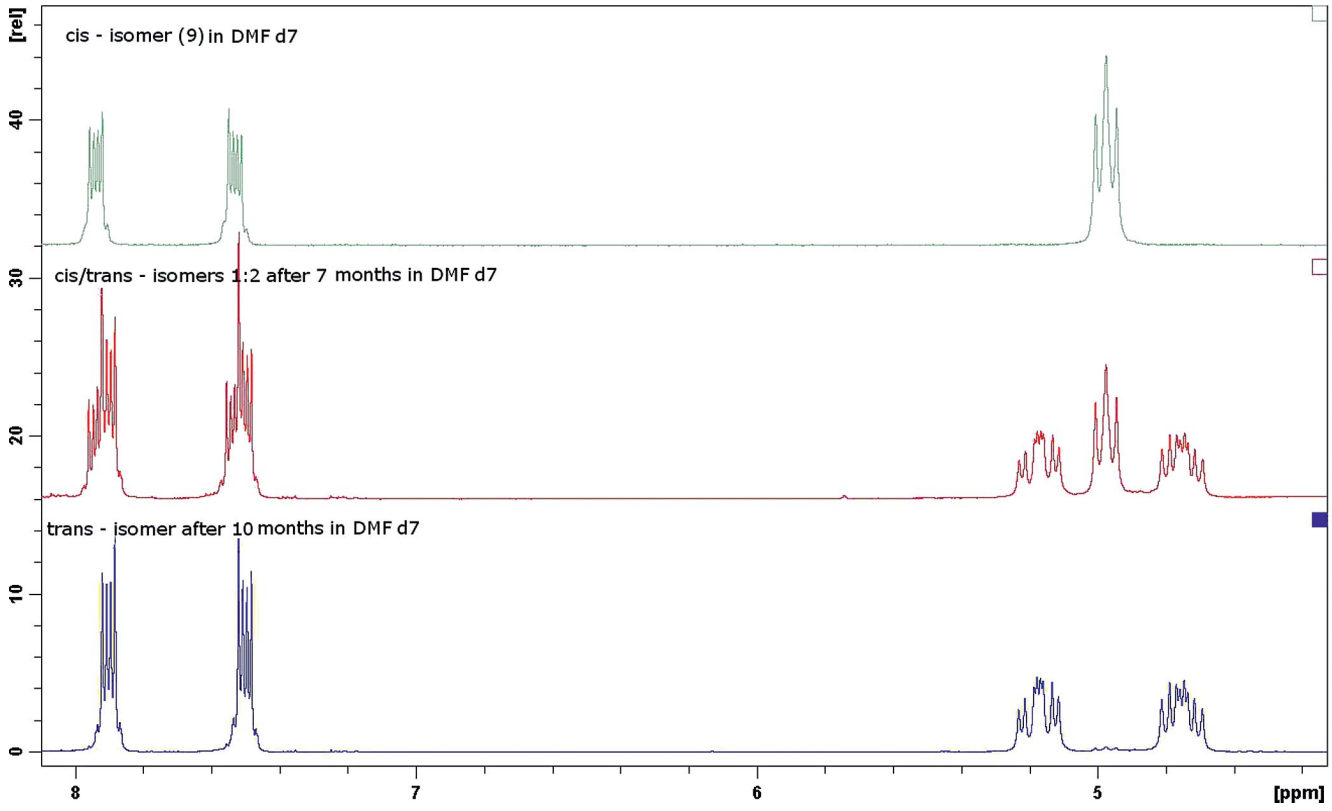


Figure 2. ^{1}H NMR spectra of *cis*-**1** (top) and *trans*-**1** (bottom) in deuterated DMF at 295 K. The central spectrum shows a mixture of *cis*-**1** and *trans*-**1**.

center. Additionally, the large downfield shift of the NCH_2 protons of the *n*-butyl substituents from the benzimidazolium salt to the Pd^{II} complex is also an indication of such interactions. Similar interactions have recently been observed for d^8 metal complexes with benzimidazolylidene ligands.[4c,4i] However, in those cases, only drastic changes in the chemical shift were reported, not changes in the multiplicities of the signals in the ^{1}H NMR spectra. These interactions have been labeled as "anagostic" interactions.[4c,4i] However, halide···H interactions are also possible, as has been reported for Pd^{II} complexes with chelating imidazole-2-ylidene ligands.[3d] The signals corresponding to the rest of the protons of the *n*-butyl groups and those of the phenyl backbone of the benzimidazolylidene ring have similar patterns for both *cis*-**1** and *trans*-**1** (Figures 2 and S1). The ^{13}C NMR signal of the carbene C atom for *trans*-**1** appears at δ = 176.1 ppm.

The synthesis of the mononuclear complex with a nonsymmetrically substituted benzimidazolylidene ligand delivered a mixture of *cis*-**2** and *trans*-**2** in a ratio of 1:1 (Scheme 1, see Exp. Section). The ^{13}C NMR signal corresponding to the carbene C atom in these complexes is observed at δ = 181 ppm. The interactions between the substituents on the nitrogen atoms and the Pd^{II} center as observed in the ^{1}H NMR spectrum of *trans*-**1** were not detected in the spectra of *cis*-**2** or *trans*-**2**. The identity of the *trans* isomer was determined by a single-crystal X-ray diffraction study of *trans*-**2** (see below). The ^{1}H NMR spectrum of the isolated single crystals helped us to identify the signals of the respective isomers (Figure S2).

For the halide-bridged dipalladium complex with the symmetrically substituted (*n*-butyl, **3**) ligand, an isomer-pure product was obtained after purification. The identity of this product as the *trans* isomer was established through structure determination. In contrast to the synthesis **3**, the synthesis of the dinuclear complexes **4**–**6** with the nonsymmetrically substituted benzimidazolylidene ligands delivered mixtures of various isomers, as indicated by ^{1}H NMR spectroscopy (Exp. Section and Figure S3). For example, the ^{1}H NMR spectra of **5** and **6** show huge downfield shifts of the *i*Pr CH proton (ca. 1 ppm shift with respect to the signals of the free benzimidazolium salts). The dinuclear natures of **4**–**6** were confirmed by mass spectrometry experiments. For each of these complexes, a peak corresponding to $[M - halide]^+$ was observed in their mass spectrum. Dinuclear complexes with such nonsymmetrically substituted ligands can exist as mixtures of various isomers (*cis*/*trans*, *syn*/*anti*, and various combinations of these).[9] The ^{1}H NMR spectra of these complexes displayed relatively broad signals at room temperature (a representative spectrum is shown in Figure S3 for **4**). The broadness of these peaks is an indication of dynamic phenomena in solution, which can be attributed to the interconversion between the various isomers mentioned above. Progressive heating of the ^{1}H NMR samples of these complexes in $[D_6]$DMSO resulted in the narrowing of the signals, and the final conversion to one

isomer at 363 K. In keeping with literature reports on the isomer stability for such complexes, and in view of steric arguments, we tentatively assign the isomer formed at 363 K to the *trans*/*anti* form.[5i,9] The ^{13}C NMR signals for the carbene C atoms were observed at δ = 156.9 and 159.6 ppm for **4** and **5,** respectively. For **6**, the signal for the carbene C atom was unfortunately not resolved.

Crystal Structures

Single crystals suitable for X-ray diffraction studies were grown for *cis*-**1**, *trans*-**1**, *trans*-**2**, and **3** (see Exp. Section). The crystallographic details are provided in Table S1. Complexes *cis*-**1** and **3** crystallize in the triclinic $P\bar{1}$ space group, and *trans*-**1** and *trans*-**2** crystallize in the monoclinic $P2_1/n$ space group. The quality of the structural data for *cis*-**1** is not good enough for a discussion of individual bond lengths (Figure S4). Attempts to improve the quality of the crystals were unsuccessful. However, the connectivity of the atoms within the molecule is clearly seen, and the *cis* form of the mononuclear complex *cis*-**1** can be unequivocally established from this structure (Figure S4).

The Pd^{II} centers in all of the complexes are in distorted square-planar environments and are coordinated by the carbene C atom and the iodo ligands. The structures of the mononuclear complexes *trans*-**1** and *trans*-**2** clearly establish these as the *trans* and *trans*/*anti* isomer, respectively (Figure 3). Complex *trans*-**2**, which contains a nonsymmetrically substituted benzimidazolylidene ligand, preferentially crystallizes from a mixture of *cis*- and *trans*-**2**. In *trans*-**2**, the benzimidazolylidene ligands are *trans* to each other, and the substituents on the nitrogen atoms are *anti* to each other. Such an observation has been made for related Ni^{II} complexes.[4c] The dinuclear complex **3** contains two *cis* iodo ligands and one *trans* to the benzimidazolylidene ligands (Figure 3).

The C–C and C–N bond lengths within the imidazolylidene rings are in the range expected for a delocalized system

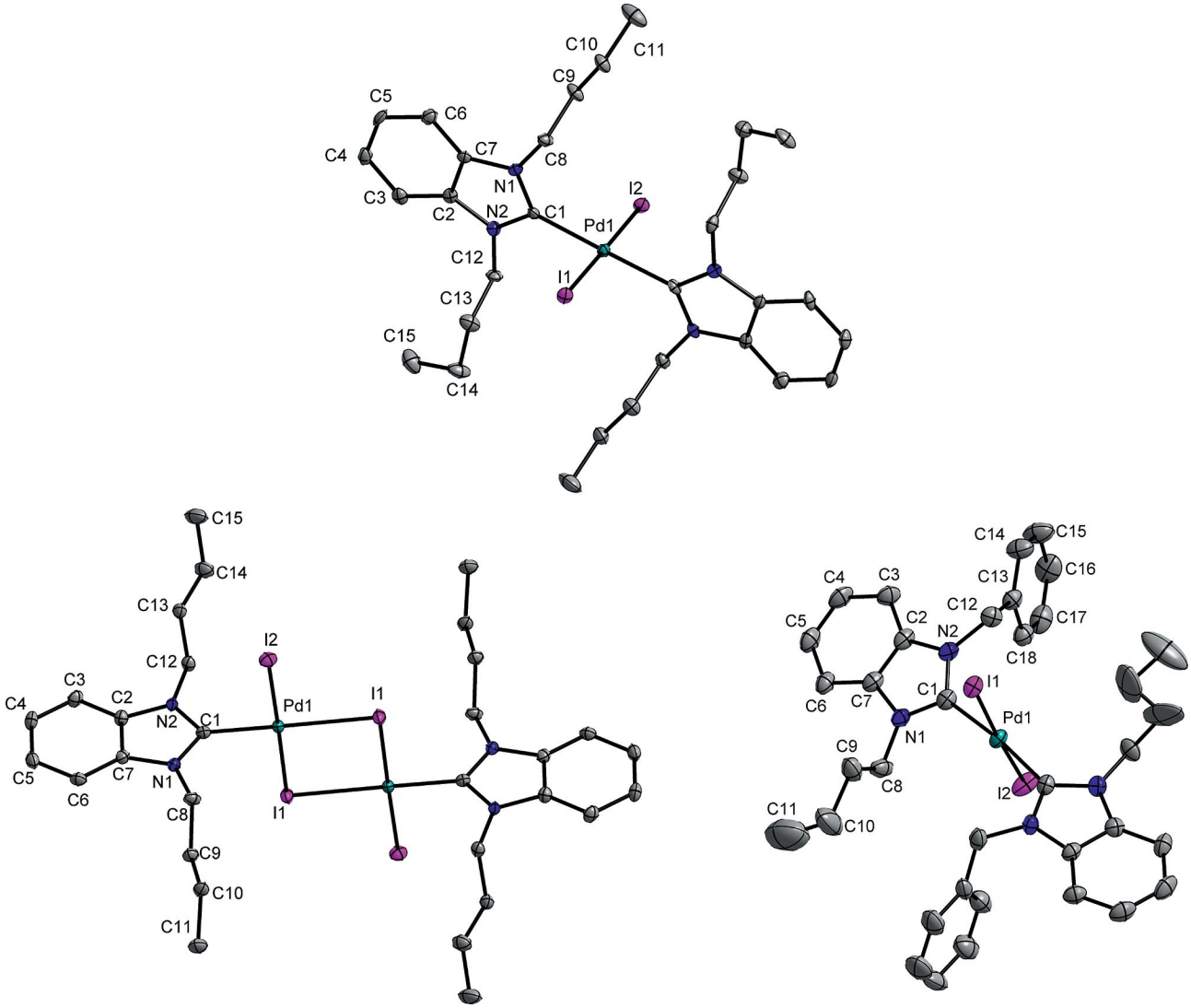


Figure 3. ORTEP plots of *trans*-**1** (top), *trans*-**2** (bottom right), and **3** (bottom left). Ellipsoids are drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

(Table 1).[4] The Pd–C(carbene) distances in the mononuclear complexes *trans*-**1** and *trans*-**2** are in the expected range, as are the Pd–I distances.[4i] The Pd–C(carbene) distance of 1.968(3) Å for the dinuclear complex **3** is shorter than the Pd–C(carbene) distances of 2.015(5) and 2.009(5) Å, respectively, for the *trans* mononuclear complexes *trans*-**1** and *trans*-**2**. This observation is related to the superior *trans* influence of the benzimidazolylidene ligands as compared to that of the iodo ligands. In *trans*-**1** and *trans*-**2**, the benzimidazolylidene ligands are *trans* to each other and, hence, mutually weaken their bonds to the Pd^{II} center. The Pd–I(bridging) bond that is *trans* to the carbene C atom is longer than the Pd–I bond in **3**. In all three complexes, the benzimidazolylidene rings are almost perpendicular to the plane containing the Pd and iodo ligands with dihedral angles of 80.5(1) and 80.8(1), 89.9(1), 78.8(2) and 74.0(1)°, respectively, for *trans*-**1**, **3**, and *trans*-**2**. The dihedral angles between the two benzimidazolylidene planes are 2.0(2) and 27.0(2)°, respectively, for *trans*-**1** and *trans*-**2**.

Table 1. Selected bond lengths [Å] and angles [°] for *trans*-**1**, *trans*-**2**, and **3**.

	trans-**1**	*trans*-**2**	**3**
Pd–C1A	2.028(6)	–	–
Pd–C1	2.015(5)	2.009(5)	1.968(3)
Pd–I1	2.606(1)	2.612(1)	2.664(1) or 2.609(1)
Pd–I2	2.599(1)	2.593(1)	2.590(1)
C1–N1	1.355(7)	1.346(6)	1.355(4)
C1–N2	1.355(7)	1.355(6)	1.353(4)
N1–C8	1.459(7)	1.468(7)	1.459(4)
N2–C12	1.466(6)	1.466(6)	1.460(4)
N1–C7	1.390(7)	1.393(6)	1.401(4)
N2–C2	1.382(6)	1.388(6)	1.399(4)
C2–C7	1.386(8)	1.394(7)	1.390(5)
N1–C1–N2	105.9(5)	106.0(4)	107.6(3)

The C–H groups from the alkyl substituents on the nitrogen atoms of the ligands possess relatively short distances to the Pd^{II} centers (Figures 4, S5, and S6). The relevant distances and angles are shown in Table 2. Such short distances are usually an indication of weak interactions between the C–H groups and the Pd^{II} centers. In recent literature, such interactions have been labeled as anagostic interactions.[4i] We would like to note that for the complex *trans*-**1**, such interactions seem to exist in solution as well, as seen from its ^1H NMR spectrum (Figure 2).

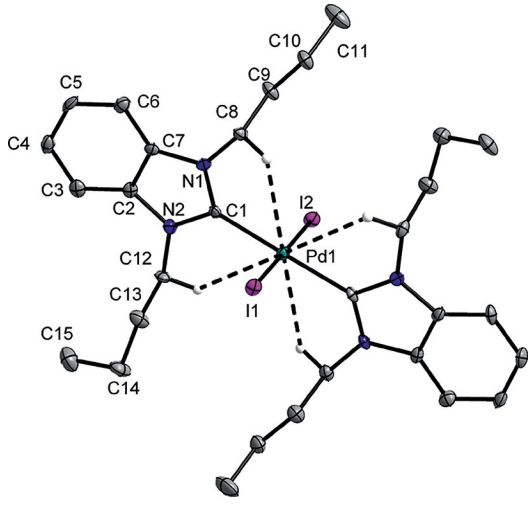


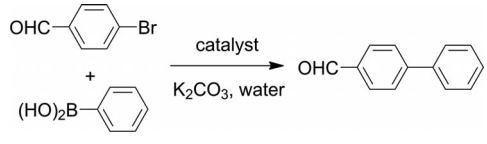
Figure 4. C–H···Pd^{II} interaction in the solid state for *trans*-**1**.

Table 2. C–H···Pd^{II} bond lengths [Å] and angles [°].

	trans-**1**	*trans*-**2**	**3**
Pd–H	2.9907(5)	2.7968(4)	2.8229(3)
Pd–H	2.9481(5)	2.8950(4)	2.9057(2)
Pd–H	2.9443(5)	2.9372(4)	
Pd–H	2.9405(5)	2.9754(4)	
C–H–Pd	111.6(3)	109.5(6)	114.6(2)
C–H–Pd	108.9(3)	117.6(4)	114.4(2)
C–H–Pd	110.9(3)	115.6(3)	
C–H–Pd	111.3(3)	116.8(3)	

Catalytic Cross-Coupling, Hydrodehalogenation, and Click Reactions

Pd^{II} complexes of NHC ligands are potent (pre)catalysts for the Suzuki–Miyaura[10] cross-coupling reaction between aryl halides and arylboronic acids.[11] Such reactions have also been catalyzed by Pd^{II} complexes of benzimidazolylidene ligands.[4i] Furthermore, in recent years, Pd–NHC complexes have been shown to be extremely effective catalysts for the hydrodehalogenation of haloarenes.[2b] In the backdrop of these literature reports, we were interested in testing the efficiency of the complexes reported here as (pre)catalysts for both these transformations. Inspired by our recent success in performing the Suzuki–Miyaura cross-coupling reaction with abnormal carbene complexes of Pd^{II} in water,[5i] we were interested in probing if the complexes presented here would also act as (pre)catalysts in water. All of the complexes were tested for their activity in the formation of the biphenyl compound shown in Scheme 2 with 0.5 mol-% catalyst loading. At room temperature, the mononuclear complex *cis*-**1** with the symmetrically substituted benzimidazolylidene ligand and its dinuclear counterpart **3** were least active (Table 3). However, at 90 °C, both of these complexes delivered the desired product in more than 95% yield. All of the other complexes delivered the desired product in 80–95% yield at room temperature.



Scheme 2. Suzuki–Miyaura cross-coupling reaction with the conditions stated in Table 3.

Thus, from this limited screening, it appears that the complexes that contain nonsymmetrically substituted benzimidazolylidene ligands are the most potent (pre)catalysts for the Suzuki–Miyaura cross-coupling reaction under the conditions described here. Even though we are not in a po-

Table 3. Catalytic results for the reaction shown in Scheme 2.[a]

Catalyst	Temperature	Yield [%]
cis-**1**	r.t.	20
cis-**1**	90 °C	99
trans-**1**	r.t.	95
2 (*cis* + *trans*)	r.t.	95
3	r.t.	11
3	90 °C	98
4	r.t.	99
5	r.t.	90
6	r.t.	99

[a] Reactions were performed for 5 h in H_2O with 0.5 mol-% of the catalyst and analyzed by ^1H NMR spectroscopy.

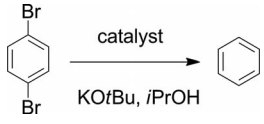
Table 4. Catalytic results for the reaction shown in Scheme 3.[a]

Catalyst	Temp. [°C]	Time [h]	Conv. [%]	Time [h]	Conv. [%]
cis-**1**	70	5	>99	–	–
trans-**1**	70	5	*	24	>99
2 (*cis* + *trans*)	70	5	15	24	>99
3	70	5	>99	–	–
4	70	5	95	24	>99
5	70	5	>99	–	–
6	70	5	>99	–	–

[a] Reactions were performed with 0.002 mol-% catalyst in 2-propanol. Reactions were stirred under argon for 5 or 24 h and analyzed by GC or HPLC; * conversion for the 5 h reaction was not measured.

sition to comment on the exact nature of the active catalyst, blind runs with Pd^{II}–acetate and $PdCl_2$ salts under identical conditions resulted in poor yields of the desired products, which emphasizes the need for the benzimidazolylidene ligands to form highly active catalytic species. On the basis of literature reports, it can be assumed that the complexes first undergo ligand dissociation and reduction prior to becoming catalytically active.[11] The formation of the biphenyl product from the Suzuki–Miyaura coupling was followed as a function of time with catalyst **4**. As can be seen from Figure S7, there is an initial induction period for this reaction, which is probably related to the initial formation of the catalytically active species through ligand dissociation and reduction of the Pd^{II} center. Approximately 80% conversion is achieved after 2 h. However, full conversion to the products requires a reaction time of 5 h.

All of the complexes were also tested for their activity in the hydrodehalogenation reaction of 1,4-dibromobenzene in 2-propanol in the presence of KO*t*Bu as a base (Scheme 3). As can be seen from Table 4, all of the complexes presented here are highly active catalysts for the hydrodehalogenation reaction, and most of them delivered quantitative product formation. It was possible to perform the hydrodehalogenation reaction with a catalyst loading of only 0.002 mol-%. As can be seen from the time versus conversion plot in Figure S8 with catalyst **6**, the amount of both bromobenzene and benzene increase initially at the expense of 1,4-dibromobenzene. Eventually, the amount of benzene increases at the expense of bromobenzene.

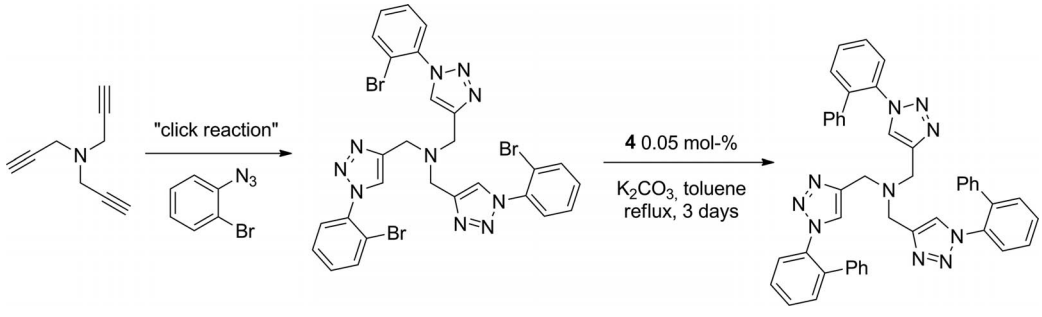


Scheme 3. Hydrodehalogenation reactions under the conditions stated in Table 4.

Finally, we were interested in using the complexes presented here as (pre)catalysts for the post-functionalization of click-based ligands to generate sterically bulky tripodal ligands. To do this, we first synthesized the tris(bromophenyl)-substituted tripodal ligand (Scheme 4) in reasonable yield by using a standard click protocol. We then used one of the most potent catalysts presented above (**4**) to perform post-functionalization of the bromo groups through a Suzuki–Miyaura cross-coupling reaction. To do this, the bromo-substituted tripodal triazole ligand was reacted with phenylboronic acid and K_2CO_3 in toluene under reflux. Complex **4** (0.05 mol-%) was used as a precatalyst for this reaction (Scheme 4 and Exp. Section). This reaction led to the formation of the desired tris(biphenyl)-substituted ligand in reasonable yield. Thus, in this reaction, three bromoaryl groups are converted into their biphenyl counterpart. Such biphenyl-substituted sterically bulky ligands can provide a useful platform for small molecule activation at transition metal centers.

Conclusions

We have presented here eight new Pd^{II} complexes by using one symmetrically substituted benzimidazol-2-ylidene ligand and three nonsymmetrically substituted benzimidazol-2-ylidene ligands. Four of these complexes have been characterized by single-crystal X-ray diffraction, and these



Scheme 4. Sequential click and Suzuki–Miyaura cross-coupling reactions for the generation of new bulky tripodal ligands.

studies establish the identity of *cis*-**1** as mononuclear, *trans*-**1** as mononuclear, *trans*-**2** as *anti*-mononuclear, and **3** as an iodo-bridged dinuclear complex. ^{1}H NMR spectroscopic studies on *trans*-**1** show that there are strong C–H···Pd^{II} interactions in solution. For the dinuclear complexes **4**–**6** with nonsymmetrically substituted benzimidazolylidene ligands, the formation of rotamers (*cis*/*anti*, *cis*/*syn*, *trans*/*anti*, and *trans*/*syn*) and their slow interconversion have been detected on the NMR timescale at room temperature. Complexes **4**–**6** converted to single isomers at higher temperatures, and these isomers have been tentatively assigned as the *trans*/*anti* isomers. All complexes presented here are active (pre)catalysts for the Suzuki–Miyaura cross-coupling reaction. Most complexes catalyzed these C–C bond-forming reactions at room temperature in water as an environmentally benign solvent. All of the complexes are also active catalysts for the hydrodehalogenation reaction of 1,4-dibromobenzene in 2-propanol with KO*t*Bu as base. Furthermore, one of the most potent catalysts was used in a sequential reaction together with the click method to generate a sterically bulky, tripodal ligand. In that reaction, the Pd^{II}–NHC catalysts presented here are capable of performing three C–C bond formation reactions. Metal complexes of such bulky tripodal ligands can display a variety of fascinating properties, as we have recently shown.[12] Further work in that direction is being pursued in our laboratories.

Experimental Section

General: All solvents were dried and distilled by using common techniques unless otherwise mentioned. All ligands used in this work[4a–4c] and 2-azidophenyl bromide[13] were synthesized by following literature procedures. ^{1}H and ^{13}C NMR spectra were recorded at 250.13 MHz with a Bruker AC250 instrument and at 500 MHz with a Bruker Avance500 instrument. Elemental analyses were performed by using a Perkin–Elmer 240 analyzer. Mass spectrometry measurements were performed by using an Agilent 6210 ESI-TOF instrument.

GC analysis was performed with a Varian Saturn 2100C GC instrument (column: Varian factory four capillary column VF-5ms, method: 35 to 280 °C at a heating rate of 10 K/min) with hexadecane as an internal standard.

***cis*/*trans*-Diiodo-bis(1,3-di-*n*-butylbenzimidazolin-2-ylidene)palladium(II) (*cis*-1 and *trans*-1):** The product was obtained by heating the corresponding benzimidazolium salt (72 mg, 0.2 mmol; 2 equiv.) with palladium(II) acetate (22 mg, 0.1 mmol; 1 equiv.) in DMSO (10 mL, c = 0.01 mol L^{-1}) at 90 °C for 12 h. The resultant suspension was cooled to ambient temperature and filtered, and the solid was washed with diethyl ether (20 mL). Upon drying in vacuo, the *cis* product was obtained as a yellow crystalline solid in a yield of 80% (73 mg, 0.09 mmol). ***cis*-1**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06 (t, J = 7.28 Hz, 12 H, CH_3), 1.54 (m, 8 H, CH_2), 2.11–2.30 (m, 8 H, CH_2), 4.71 (t, J = 7.94 Hz, 8 H, CH_2), 7.22–7.31 (m, 4 H, aryl-H), 7.35–7.43 (m, 4 H, aryl-H) ppm. ^{1}H NMR (250 MHz, [D$_7$]DMF): δ = 1.06 (t, J = 7.37 Hz, 12 H, CH_3), 1.70 (sext, J = 7.60 Hz, 8 H, CH_2), 2.32–2.49 (m, 8 H, CH_2), 4.97 (t, J = 7.77 Hz, 8 H, CH_2), 7.49–7.57 (m, 4 H, aryl-H), 7.89–7.99 (m, 4 H, aryl-H) ppm. ^{13}C NMR ($CDCl_3$, 60 MHz): δ = 13.9 (CH_3), 20.6 (CH_2), 31.1 (CH_2), 48.7 (CH_2), 110.3, 122.4, 135.0 (all aryl-C), 179.8 (carbene C) ppm.

After 10 months in DMF solution at ambient temperature, quantitative conversion of *cis*-**1** to *trans*-**2** occurred, as monitored by ^{1}H NMR spectroscopy. Heating of the solution unfortunately did not result in the enhancement of the rate of this reaction. ***trans*-1**: ^{1}H NMR (250 MHz, [D$_7$]DMF): δ = 1.17 (t, J = 7.33 Hz, 12 H, $NCH_2CH_2CH_2CH_3$), 1.72 (sext, J = 7.45 Hz, 8 H, $NCH_2CH_2CH_2CH_3$), 2.04–2.26 (m, 4 H, $NCH_2CHHCH_2CH_3$), 2.28–2.51 (m, 4 H, $NCH_2CHHCH_2CH_3$), 4.69–4.81 (m, 4 H, $NCHHCH_2CH_2CH_3$), 5.11–5.23 (m, 4 H, $NCHHCH_2CH_2CH_3$), 7.47–7.53 (m, 4 H, aryl-H), 7.86–7.94 (m, 4 H, aryl-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.0, 20.8, 30.4, 49.4, 111.1, 123.2, 134.4, 176.1 (carbene C) ppm. $C_{30}H_{44}I_2N_4Pd$ (820.07): calcd. C 43.89, H 5.40, N 6.82; found C 43.51, H 5.40, N 6.60.

***cis*/*trans*-Diiodo-bis(1-benzyl-3-*n*-butylbenzimidazolin-2-ylidene)palladium(II) (*cis*-2 and *trans*-2):** The corresponding benzimidazolium salt (79 mg, 0.2 mmol; 2 equiv.) was mixed with palladium(II) acetate (22 mg, 0.1 mmol; 1 equiv.) in THF (10 mL, c = 0.01 mol L^{-1}), and the mixture was stirred overnight. The reaction mixture was then diluted with dichloromethane (50 mL) and washed twice with water (100 mL). The organic layer was dried with sodium sulfate and filtered, and the solvents were evaporated. The remaining yellow solid was washed twice with diethyl ether (15 mL). The product was obtained as yellow crystals as a 1:1 (by ^{1}H NMR spectroscopy) *cis*/*trans* mixture in a yield of 92% (82 mg, 0.092 mmol). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.79 (t, J = 7.5 Hz, 6 H, CH_3), 1.06 (t, J = 7.5 Hz, 6 H, CH_3), 1.21–1.36 (m, 8 H, CH_2), 2.05–2.31 (m, 8 H, CH_2), 4.64 (t, J = 8 Hz, 4 H, CH_2, *trans*), 4.75 (t, J = 8 Hz, 4 H, CH_2, *cis*), 5.84 (s, 4 H, CH_2, *cis*), 6.03 (s, 4 H, CH_2, *trans*), 6.93–7.22 (m, 17 H, aryl-H), 7.28–7.44 (m, 15 H, aryl-H), 7.54–7.61 (m, 4 H, aryl-H) ppm. ^{13}C NMR (60 MHz, $CDCl_3$): δ = 13.89, 13.51 (CH_3-butyl), 20.6, 20.3 (CH_2-butyl), 31.2, 30.9 (CH_2-butyl), 48.9, 48.8 (CH_2-butyl), 53.8, 53.44 (CH_2-benzyl), 110.2, 110.3, 111.4, 111.5, 122.5, 122.5, 122.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.5, 128.7, 129.0, 134.7, 134.9, 135.1, 135.2, 135.2, 135.3 (all aryl-C), 181.0 (carbene C) ppm. $C_{36}H_{40}I_2N_4Pd$ (888.95): calcd. C 48.64, H 4.54, N 6.30; found C 47.81, H 4.45, N 6.20.

General Procedure for the Synthesis of the Dipalladium Complexes: All of the dipalladium complexes were synthesized by a general procedure as described below.

The corresponding benzimidazolium salt, palladium(II) acetate, and the corresponding sodium halide were dissolved in dimethyl sulfoxide in a capped flask. The reaction mixture was then heated to 90 °C overnight. After cooling, dichloromethane and water were added to the mixture, and the product was extracted. The aqueous phase was washed five times with dichloromethane. The combined organic layers were dried with sodium sulfate and filtered, and the solvent was evaporated. The solids were then dissolved in dichloromethane/hexane (1:1) to obtain the clean microcrystalline products after one night at –20 °C.

Di-μ-iodo-bis(1,3-di-*n*-butylbenzimidazolin-2-ylidene)diiododipalladium(II) (3): The product was obtained by following the general procedure with palladium(II) acetate (44 mg, 0.2 mmol;1 equiv.), the corresponding benzimidazolium salt (78 mg, 0.2 mmol; 1 equiv.), and sodium iodide (120 mg, 0.8 mmol; 4 equiv.) in DMSO (4 mL; c = 0.05 mol L^{-1}). The product was obtained as an orange solid in a yield of 84% (108 mg, 0.084 mmol). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13 (t, J = 7.31 Hz, 12 H, CH_3), 1.59 (m, 8 H, CH_2), 2.20 (m, 8 H, CH_2), 4.81 (t, J = 7.82 Hz, 8 H, CH_2), 7.50–7.57 (m, 4 H, aryl-H), 7.66–7.74 (m, 4 H, aryl-H) ppm. ^{13}C NMR ($CDCl_3$, 60 MHz): δ = 13.7 (CH_3), 20.2 (CH_2), 29.5 (CH_2), 49.1 (CH_2), 110.4, 123.0, 134.6 (all aryl-C) ppm; the carbene signal was not

detected. $C_{30}H_{44}I_4N_4Pd_2$·1.5hexane: calcd. 35.75, H 5.00, N 4.28; found C 35.81, H 4.72, N 4.15.

Di-μ-iodo-bis(1-benzyl-3-*n*-butylbenzimidazolin-2-ylidene)diiodo-dipalladium(II) (4): The product was obtained by following the general procedure with palladium(II) acetate (44 mg, 0.2 mmol;1 equiv.), the corresponding benzimidazolium salt (78 mg, 0.2 mmol; 1 equiv.), and sodium iodide (120 mg, 0.8 mol; 4 equiv.) in DMSO (4 mL; c = 0.05 mol L^{-1}). The product was obtained as a red solid in 99% yield (122 mg, 0.099 mmol). ^{1}H ([D$_6$]DMSO, 250 MHz, 363 K): δ = 1.03 (t, J = 7.5 Hz, 6 H, CH_3), 1.51 (sex, J = 7.5 Hz, 4 H, CH_2), 2.17 (p, J = 7.5 Hz, 4 H, CH_2), 4.68 (t, J = 7.75 Hz, 4 H, CH_2), 5.93 (s, 4 H, CH_2), 7.09–7.37 (m, 12 H, aryl-H), 7.55–7.68 (m, 6 H, aryl-H) ppm. ^{13}C NMR ([D$_6$]-DMSO, 60 MHz, 298 K): δ = 13.6 (CH_3), 19.5 (CH_2), 29.8 (CH_2), 48.5 (CH_2), 53.0 (CH_2), 111.1, 111.5, 123.0, 123.1, 125.2, 127.9, 128.1, 128.4, 128.8, 133.6, 134.4, 134.7 (all aryl-C), 156.9 (carbene C) ppm. $C_{36}H_{40}I_4N_4Pd_2$ (1249.16): calcd. C 34.61, H 3.23, N 4.49; found C 34.79, H 3.52, N 4.33. HRMS (ESI): calcd. for $C_{36}H_{40}N_4I_3Pd_2$ [**6** – I]$^+$ 1122.8461; found 1122.8566.

Di-μ-bromo-bis(1-benzyl-3-isopropylbenzimidazolin-2-ylidene)di-bromodipalladium(II) (5): The product was obtained by following the general procedure with palladium(II) acetate (44 mg, 0.2 mmol; 1 equiv.), the corresponding benzimidazolium salt (66 mg, 0.2 mmol; 1 equiv.), and sodium bromide (81 mg, 0.8 mmol; 4 equiv.) in DMSO (4 mL; c = 0.05 mol L^{-1}). The product was obtained as a yellow solid in 98% yield (102 mg, 0.098 mmol). ^{1}H NMR ([D$_6$]DMSO, 250 MHz, 363 K): δ = 1.76 (d, J = 7.0 Hz, 12 H, CH_3), 6.06–6.23 (m, 6 H, CH_2-benzyl and CH-isopropyl), 7.17–7.38 (m, 12 H, aryl-H), 7.59–7.63 (m, 4 H, aryl-H), 7.80–7.83 (m, 2 H, aryl-H) ppm. ^{13}C NMR ([D$_6$]DMSO, 60 MHz, 298 K): δ = 20.8 (CH_3), 52.9 (CH), 55.4 (CH_2), 112.7, 113.7, 124.1, 129.0, 129.4, 129.4, 132.7, 135.2, 135.9 (all aryl-C), 159.6 (carbene C) ppm. $C_{34}H_{36}Br_4N_4Pd_2$ (1033.10): calcd. C 39.53, H 3.51, N 5.42; found 39.56, H 3.68, N 5.30. HRMS (ESI): calcd. for $C_{34}H_{36}N_4Br_3Pd_2$ [**7** – Br]$^+$ 952.8543; found 952.8694.

Di-μ-bromo-bis(1-butyl-3-isopropylbenzimidazolin-2-ylidene)di-bromodipalladium(II) (6): The product was obtained by following the general procedure with palladium(II) acetate (44 mg, 0.2 mmol; 1 equiv.), the corresponding benzimidazolium salt (60 mg, 0.2 mmol; 1 equiv.), and sodium bromide (81 mg, 0.8 mmol; 4 equiv.) in DMSO (4 mL; c = 0.05 mol L^{-1}). The product was obtained as a yellow solid in 99% yield (96 mg, 0.099 mmol). ^{1}H (250 MHz, [D$_6$]DMSO, 363 K): δ = 1.02 (t, J = 7.5 Hz, 6 H, CH_3), 1.51 (sex, J = 7.5 Hz, 4 H, CH_2), 1.71 (d, J = 7.0 Hz, 12 H, CH_3), 2.13 (q, J = 7.5 Hz, 4 H, CH_2), 4.72 (t, J = 7.5 Hz, 4 H, CH_2), 6.08 (hept, J = 7.5 Hz, 2 H, CH), 7.30–7.36 (m, 4 H, aryl-H), 7.49–7.69 (m,2 H, aryl-H), 7.77–7.80 (m, 2 H, aryl-H) ppm. ^{13}C ([D$_6$]DMSO, 60 MHz, 298 K): δ = 13.6 (CH_3), 19.5 (CH_3), 19.9 (CH_2), 30.3 (CH_2), 47.5 (CH), 54.3 (CH_2), 111.2, 112.5, 122.9, 123.1, 131.3, 133.8, 134.8 (all aryl-C) ppm (carbene signal not detected). $C_{28}H_{40}Br_4N_4Pd_2$ (965.07): calcd. C 34.85, H 4.18, N 5.81; found C 35.05, H 4.29, N 5.84. HRMS (ESI): calcd. for $C_{28}H_{40}N_4Br_3Pd_2$ [**8** – Br]$^+$ 884.8856; found 884.8792.

Tris{[1-(2-bromophenyl)-1*H*-1,2,3-triazole-4-yl]methyl}amine: 2-Azidophenyl bromide (4.75 g, 24.0 mmol) and tripropargylamine (699 mg, 5.33 mmol) were dissolved in a mixture of CH_2Cl_2/H_2O/*tert*-butanol (25/25/50 mL). $CuSO_4$·5H_2O (200 mg, 0.8 mmol), sodium ascorbate (633 mg, 3.20 mmol), and tris(benzyltriazolylmethyl)amine (TBTA; 42.5 mg, 0.08 mmol) were added, and the solution was stirred for 5 d at 60 °C. The reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2 (3. 50 mL). The combined organic layers were washed several times with ethylenediaminetetraacetic acid (EDTA; 1%) dissolved in a concentrated ammonia solution (3× 50 mL) to remove traces of copper. Afterwards, the organic phase was washed with water (3× 50 mL) and dried with Na_2SO_4, and the solvent was evaporated. The product was purified by column chromatography over silica (DCM/MeOH 98:2) to yield a white solid (2.30 g, 60%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.03 (s, 6 H, NCH_2), 7.38 (t, $^3J_{H,H}$ = 7.9 Hz, 3 H, aromatic), 7.48 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, aromatic), 7.57 (d, $^3J_{H,H}$ = 7.8 Hz, 3 H, aryl-H), 7.76 (d, $^3J_{H,H}$ = 7.9 Hz, 3 H, aryl-H), 8.20 (s, 3 H, triazole-5-H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 47.5, 119.0, 126.1, 128.3, 128.6, 131.2, 134.0, 136.8, 143.9 ppm. $C_{27}H_{21}Br_3N_{10}$ (725.24): calcd. C 44.72, H 2.92, N 19.31; found C 44.62, H 2.93, 19.21. HRMS (ESI): calcd. for $C_{27}H_{22}Br_3N_{10}$ [M + H]$^+$ 722.9574; found 722.9564.

Tris{[1-(2-biphenyl)-1*H*-1,2,3-triazole-4-yl]methyl}amine: Tris{[1-(2-bromophenyl)-1*H*-1,2,3-triazole-4-yl]methyl}amine (116 mg, 0.16 mmol), phenylboronic acid (98 mg, 0.80 mmol), K_2CO_3 (132 mg, 0.96 mmol), and **4** (10 mg, 0.008 mmol) were dissolved in degassed toluene. The reaction mixture was heated to reflux for 3 d. The organic phase was extracted with water (3× 10 mL) and dried with Na_2SO_4. The solvent was evaporated, and the crude mixture was purified by column chromatography over silica (DCM/MeOH 95:5) to yield the product (75 mg, 65%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.32 (s, 6 H, NCH_2), 7.03–7.15 (m, 18 H, aryl-H), 7.49–7.63 (m, 12 H, aryl-H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 47.0, 125.7, 126.8, 128.0, 128.6, 128.7, 128.7, 130.0, 131.1, 135.4, 137.6, 137.6, 143.9 ppm. $C_{45}H_{36}N_{10}$·2MeOH (780.36): calcd. C 72.29, H 5.68, N 17.94; found C 71.69, H 5.39, 17.97. HRMS (ESI): calcd. for $C_{45}H_{37}N_{10}$ [M + H]$^+$ 717.3197; found 717.3202.

X-ray Crystallography: Single crystals of *cis*-**1**, *trans*-**1**, and *trans*-**2** were grown by layering concentrated dichloromethane solutions with *n*-hexane at 8 °C. Single crystals of **3** were obtained by slow diffusion of diethyl ether into a concentrated solution of dichloromethane at 8 °C. The crystal data were recorded with a Bruker Kappa ApexII duo diffractometer or a Kappa CCD Nonius instrument using "omega–phi" scan or "CCD scan" techniques. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97).[14] For complex *trans*-**2**, four protons belonging to the *n*-butyl substituents are heavily disordered and, hence, it was not possible to refine them.

CCDC-805490 (for **3**), -838652 (for *trans*-**2**), -838653 (for *cis*-**1**), and -838654 (for *trans*-**1**) 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.

Catalytic Experiments

Suzuki–Miyaura Cross-coupling Reactions: 0.5 mol-% of the catalyst, 4-bromobenzaldehyde (1 equiv., 0.1 mmol, 185 mg), phenylboronic acid (1.2 equiv., 1.2 mmol, 146 mg), and potassium carbonate (1.5 equiv., 1.5 mmol, 207 mg) were dissolved in water (3 mL), and the mixture was stirred for 5 h at room temperature (or 90 °C). Afterwards, the reaction mixture was diluted with water, and the organic compounds were extracted with dichloromethane (3 times). The combined organic layers were dried with sodium sulfate and filtered, and the solvents were evaporated. The conversions were determined by ^{1}H NMR spectroscopy. For time-dependent profiles of the reaction, small aliquots were taken and analyzed by ^{1}H NMR spectroscopy after a small workup (see above).

Hydrodehalogenation Reactions: 1,4-Dibrombenzene (1 equiv., 1 mmol, 236 mg), the catalyst (0.002 mol-%), and potassium *tert*-

butanolate (2.2 equiv., 2.2 mmol, 246 mg) were dissolved in 2-propanol (3 mL, c = 0.33 mol L^{-1}), and the mixture was stirred under an argon atmosphere for 24 h (or 5 h) at 70 °C. Afterwards, HPLC samples were taken, and the yields were determined by analytical HPLC analysis[2b] or GC analysis. For the time-dependent profiles of the reaction, small aliquots were taken and analyzed by GC.

Supporting Information (see footnote on the first page of this article): Table of crystallographic details; ^{1}H NMR spectra of *cis*-**1**, *trans*-**1**, and **4**; ORTEP plot of *cis*-**1**; and figure showing H bonding in **3** and *trans*-**2**.

Acknowledgments

The authors are indebted to the Baden-Württemberg-Stiftung for the financial support of this work. Dr. F. Lissner is kindly acknowledged for the measurements of the crystals of *cis*-**1** and **3**.

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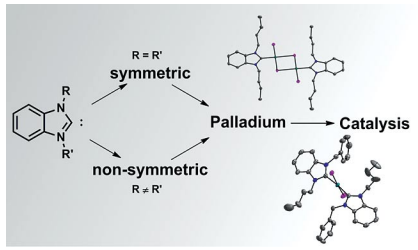
Received: October 15, 2013
Published Online: ■

EurJIC European Journal of Inorganic Chemistry

N-Heterocyclic Carbenes

Keywords: Carbene ligands / Structure elucidation / Palladium / Click chemistry / Cross coupling



Pd^{II} complexes with symmetrically and nonsymmetrically substituted benzimidazolylidene ligands are presented. The complexes exist as various isomers and rotamers in solution and exhibit C–H···Pd interactions in the solid state and in solution. All of the complexes are potent (pre)catalysts for the Suzuki–Miyaura cross-coupling reaction in water and the hydrodehalogenation reactions of haloarenes.

