ChemPubSoc Europe

DOI: 10.1002/ejic.201501031

EurJIC European Journal of Inorganic Chemistry

Full Paper

Mesoionic Carbenes

Palladium Complexes Bearing Mesoionic Carbene Ligands: Applications in α-Arylation, α-Methylation and Suzuki–Miyaura Coupling Reactions

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Abstract: Complexes of mesoionic carbene (MIC) ligands are gaining immense popularity in organometallic chemistry and homogeneous catalysis. We present here a series of palladium(II) complexes that are comprised of MIC donor ligands, and we demonstrate their applications in α-arylation, α-methylation, and Suzuki–Miyaura coupling reactions. All the complexes have been structurally characterized by X-ray crystallographic analysis. These palladium(II) complexes are potent pre-catalysts and they deliver good to excellent yields for both α-arylation and Suzuki–Miyaura coupling reactions. A palladium(II) complex bearing two MIC units in a *trans* fashion is used for chemoselective Suzuki–Miyaura coupling reaction. This complex delivers lower yields in α-arylation reactions compared with PEPPSI-type complexes, however, it gives an α-methylated product when the reaction is conducted in *N*,*N*-dimethylformamide. Mercury poisoning experiments suggest that the Suzuki–Miyaura coupling reaction likely proceeds via Pd nanoparticles. However, the α-arylation reaction proceeds homogeneously, as shown by the negative mercury poison test. The present results thus open up new avenues for MIC ligands in catalytic α-arylation and α-methylation reactions.

Introduction

N-Heterocyclic carbenes (NHCs) have made an impressive impact in a number of fields such as organometallic chemistry,[1] homogeneous catalysis,[2] biologically active complexes,[3] redox-active molecular material chemistry[4] and, very recently, in metallosupramolecular chemistry.[5] Although the majority of these ligands are based on classical NHC donors (imidazol-2-ylidenes or 1,2,4-triazol-5-ylidenes),[6] their mesoionic carbene (MIC) counterparts 1,2,3-triazol-5-ylidenes have received a lot of attention in the last few years.[7] 1,2,3-Triazol-5-ylidenes have been postulated as being even better ligands in catalysis because of their superior donor ability compared with their classical *N*-heterocyclic carbene (NHC) counterparts of the imidazole-2-ylidene type.[7a] A number of important reactions have been catalyzed by transition-metal complexes bearing 1,2,3-triazol-5-ylidenes with the catalytic transfer hydrogenation,[8] oxidation reactions,[9] hydroarylation of alkynes,[10] cross-coupling reactions,[11] click reactions,[12] and cyclization reactions[13] constituting prominent examples. Furthermore, such complexes have recently been used in photophysical applications.[14] In addition, substituted 1,2,3-triazoles can easily be synthesized by the 1,3-dipolar cycloaddition reaction of an azide to an alkyne (click reaction).[15] Alkylation of the triazoles results in the formation of the corresponding 1,2,3-triazolium salts, which are the precursors for the 1,2,3-triazol-5-ylidenes.

We present here the synthesis of PEPPSI-type palladium(II) 1,2,3-triazol-5-ylidene complexes and $Pd(MIC)_2X_2$ (X = halide) type complexes along with their applications in α-arylation, α-methylation, and Suzuki–Miyaura cross coupling reactions. All the complexes have been characterized by ^1H, $^{13}C\{^1H\}$, 2D correlation NMR spectroscopy, mass spectrometry, and also by X-ray crystallography.

Results and Discussion

Synthesis and Characterization of Complexes

The triazolium salts (*R*)-**1** and (*S*)-**1** were prepared from the corresponding triazoles by using methyl iodide as methylating agent under heating conditions by using a reported procedure.[16] The reaction of the triazolium salt (*R*)-**1** with $PdCl_2$ and K_2CO_3 in pyridine or with the corresponding chloro-substituted pyridines resulted in the formation of PEPPSI-type palladium(II) complexes (*R*)-[**2**], (*R*)-[**3**] and (*R*)-[**4**] (Scheme 1).

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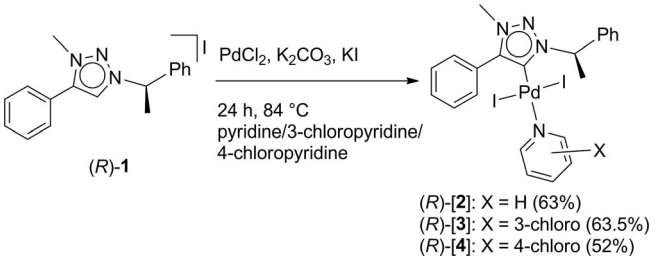
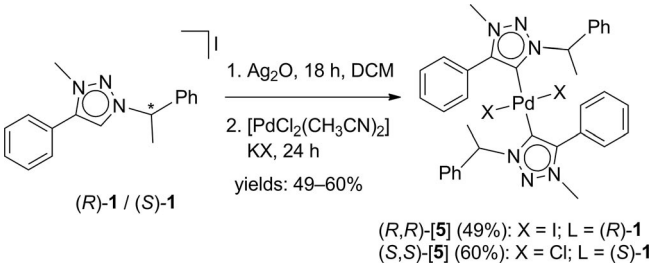
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201501031.



Scheme 1. Preparation of complexes (*R*)-[**2**], (*R*)-[**3**] and (*R*)-[**4**].

The triazolium salts as well as the palladium(II) complexes were isolated in pure enantiomeric forms. All the complexes were obtained in reasonable yields of 52–63.5 %, they were well soluble in chlorinated solvents such as dichloromethane and chloroform and they were all stable towards both air and moisture. The formation of these complexes was easily monitored by ^{1}H NMR spectroscopy, which showed the disappearance of the triazolium C–H proton signal (δ = 9.20 ppm)[16] for the triazolium salt (*R*)-**1** in the ^{1}H NMR spectrum of each complex. The resonance of the pyridine protons appeared at δ = 8.90–8.94, 7.64–7.68, and 7.23–7.26 ppm in the ^{1}H NMR spectrum of complex (*R*)-[**2**]. However, four (δ = 8.94, 8.85, 7.63–7.67, and 7.20 ppm) and two resonances (δ = 8.87 and 7.25–7.26 ppm) attributed to the pyridine protons, appeared in the ^{1}H NMR spectra of complexes (*R*)-[**3**] and (*R*)-[**4**], respectively. Upon complex formation, the resonance for the α-hydrogen atoms of the pyridine ring {(*R*)-[**2**]: δ = 8.90–8.94 ppm} was observed to be more downfield shifted compared with their corresponding resonance in free pyridine (δ = 8.62 ppm).[17] The ^{13}C{^{1}H} NMR spectrum of all complexes (*R*)-[**2**], (*R*)-[**3**], and (*R*)-[**4**] showed the characteristic resonance for the carbene carbon atoms at δ = 133.6, 128.77, and 128.76 ppm, which are not significantly shifted from the C5 resonance of the precursor triazolium salt (*R*)-**1** (δ = 129.3 ppm).[16] The ESI mass spectra (positive ions) of these complexes show peaks at *m/z* 495.9510 (calcd. for [(*R*)-[**2**]-I-Py]$^+$ 495.9509), 495.9508 (calcd. for [(*R*)-[**3**]-I-(3-Cl-Py)]$^+$ 495.9509) and 495.9507 (calcd. for [(*R*)-[**4**]-I-(4-Cl-Py)]$^+$ 495.9509) for complexes (*R*)-[**2**], (*R*)-[**3**] and (*R*)-[**4**], respectively.

The reaction of the triazolium salts (*R*)-**1** or (*S*)-**1** with Ag_2O, followed by the addition of $[PdCl_2(CH_3CN)_2]$ in dichloromethane, resulted in the formation of the mononuclear palladium(II) complexes (*R*,*R*)-[**5**] or (*S*,*S*)-[**5**] in good yields (49 and 60 %; Scheme 2). Both complexes were isolated in enantiomeric pure forms. The solubility and stability of these complexes are similar to the others discussed above.



Scheme 2. Preparation of complexes (*R*,*R*)-[**5**] and (*S*,*S*)-[**5**].

The formation of these complexes was confirmed by ^{1}H, ^{13}C{^{1}H} NMR spectroscopy, mass spectrometry and X-ray crystallography. The ^{1}H NMR spectra of both complexes (*R*,*R*)-[**5**], and (*S*,*S*)-[**5**] show the disappearance of the triazolium C–H proton signals, which was observed at δ = 9.20 ppm[16] for the original triazolium salts (*R*)-**1** and (*S*)-**1**, respectively. Two sets of signals appeared in both ^{1}H and ^{13}C{^{1}H} NMR spectra of complex (*R*,*R*)-[**5**]. This might be due to the presence of two different geometrical isomers, depending on the two different relative orientations of the carbene moieties around the palladium(II) center. At room temperature, the ratio of the two isomers as measured from the ^{1}H NMR spectrum was 1:0.2. Heating of a sample of (*R*,*R*)-[**5**] changed this ratio to 1:0.4 (Figure S11). Additional heating for 2 hours did not have any further influence on the ratio of the two isomers. Furthermore, the addition of excess KI to the reaction mixture also did not have any influence on the isomer ratio. The complex (*S*,*S*)-[**5**] shows the presence of mainly one isomer in solution. The resonance for the characteristic carbene carbon atoms appeared at δ = 128.3, 128.8 {(*R*,*R*)-[**5**]} and 127.5 {(*S*,*S*)-[**5**]} ppm, which are not significantly shifted from the original triazolium C5 resonance (δ = 129.3 ppm). However, a downfield shifted resonance was observed at δ = 144.3 and 144.6 ppm for complex (*R*,*R*)-[**5**] and δ = 143.8 ppm for complex (*S*,*S*)-[**5**], attributed to the C_{Trz} atom connected to the aryl ring. These resonances fall in the range reported for the palladium complexes bearing MIC donor ligands.[18] The formation of these complexes was supported by the ESI mass spectrometric analysis (positive ions), which showed peaks at *m/z* 759.0943 (calcd. for [(*R*,*R*)-[**5**]-I]$^+$ 759.0937), and 669.1575 (calcd. for [(*S*,*S*)-[**5**]-Cl]$^+$ 669.1570) as strongest signals.

X-ray Crystal Structures of Complexes

Single crystals that were suitable for X-ray diffraction study were obtained for all the complexes by slow diffusion of pentane into a saturated dichloromethane/acetonitrile solution of each complex at ambient temperature. Molecular structure analysis with these crystals confirmed the formation of palladium(II) PEPPSI-type complexes (*R*)-[**2**], (*R*)-[**3**], and (*R*)-[**4**] along with the complexes of Pd(MIC)$_2$-type {(*R*,*R*)-[**5**] and (*S*,*S*)-[**5**]; Figure 1}, respectively.

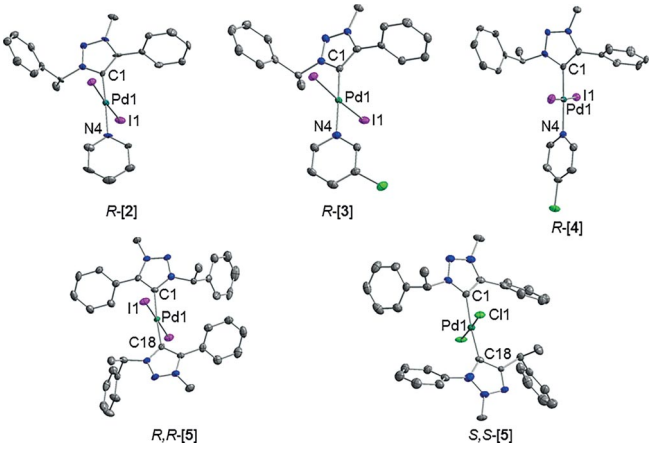


Figure 1. ORTEP plots of complexes (*R*)-[**2**], (*R*)-[**3**], (*R*)-[**4**], (*R*,*R*)-[**5**] and (*S*,*S*)-[**5**]. Ellipsoids are drawn at 50 % probability. Solvent molecules have been omitted for clarity.

The coordination geometry around the palladium(II) center in all complexes was distorted square planar, and the MIC and pyridine or another MIC donors were coordinated to the palladium center in a *trans*-fashion with the remaining coordination sites around the palladium center occupied by either iodide or chloride donors. The C_{MIC}–Pd–N_{Py} bond angles are in the range of 176.23(18)–177.05(14)°. The C_{MIC}–Pd–C_{MIC} bond angles in complexes (*R*,*R*)-[**5**] and (*S*,*S*)-[**5**] measure 174.4(3) and 174.5(2)°, respectively. These values, like the Pd–C_{MIC} bond lengths [1.949(8)–2.032(5) Å], fall in the range previously described for palladium(II) MIC complexes of similar type.[11c,11e] However, the Pd–C_{MIC} bond lengths for PEPPSI-type complexes is slightly longer in chloro-substituted pyridine complexes (*R*)-[**3**] [1.957(3) Å] and (*R*)-[**4**] [1.979(5) Å] compared with the value in complex (*R*)-[**2**] [1.949(8) Å]. The Pd–C_{MIC} bond lengths in Pd(MIC)$_2$X$_2$-type complexes [2.007(6)–2.032(5) Å] are longer than those in PEPPSI-type complexes [1.949(8)–1.979(5) Å].

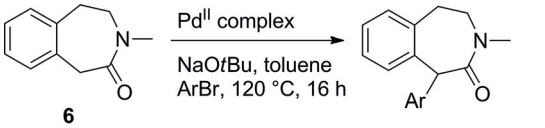
Suzuki–Miyaura Cross-Coupling and α-Arylation Reactions Using Pd^{II} Complexes

Organic transformations that are brought about through metal-catalyzed C–C bond-formation reactions have been widely studied as mild catalytic methods.[11,19] Consequently, a large number of synthetic transformations have been successfully catalyzed by complexes possessing monodentate NHCs with palladium-catalyzed Heck[20] or Suzuki coupling[21] reactions and the ruthenium-catalyzed olefin metathesis[22] constituting prominent examples. It has also been seen that the palladium-catalyzed intermolecular coupling reactions offer a mild and easy way to synthesize α-aryl ketones and α-aryl esters.[23] However, α-arylation of amides is comparatively difficult and requires a stronger base than required for ketones and esters to generate the enolate.[24,25] Although there are a handful of examples of intramolecular α-arylation of amides,[24] the intermolecular α-arylation of amides is less common[25] and has rarely been explored with palladium(II) NHC complexes until recently.[18b]

All the PEPPSI-type complexes (*R*)-[**2**], (*R*)-[**3**], and (*R*)-[**4**], along with the Pd(MIC)$_2$X$_2$-type palladium(II) complex (*R*,*R*)-[**5**] have been tested as catalysts for both the α-arylation and Suzuki–Miyaura cross-coupling reactions. The α-arylation reactions were typically carried out in toluene in the presence of NaO*t*Bu (2.5 equiv.) as a base, and the reactions were performed with 5.0 mol-% catalyst loading at 120 °C for 16 h.

On performing the reactions with substrate **6** and 4-bromotoluene, the complex (*R*)-[**2**] delivered the highest isolated yield (85 %) of compound **7b** among the complexes; the lowest isolated yield (16 %) was shown by the Pd(MIC)$_2$X$_2$-type complex (*R*,*R*)-[**5**]. The complexes (*R*)-[**3**] and (*R*)-[**4**], under the same reaction conditions and with the same substrates, delivered compound **7b** with 70 and 52 % yield, respectively (Table 1). The PEPPSI-type complexes (*R*)-[**2**], (*R*)-[**3**], and (*R*)-[**4**] were more active precatalysts for the α-arylation reaction compared with the Pd(MIC)$_2$X$_2$-type of complex (*R*,*R*)-[**5**]. The most active precatalyst (*R*)-[**2**] has also been tested for α-arylation reaction using other aryl halides such as 4-bromobenzene and 4-bromoanisole; however, similar conversion into α-arylated product (**7a**: 76 %; **7c**: 72 %) was observed for both aryl halides. The active palladium catalyst was unaffected by the addition of excess Hg^0 to the reaction mixture and led to similar yield for the α-arylation product. The reaction thus likely proceeds through a homogeneous pathway.

Table 1. α-Arylation reaction using Pd^{II} complexes.[a]



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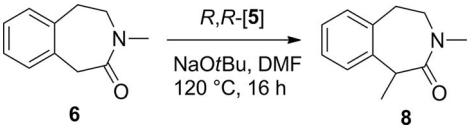
7a: Ar = Ph
7b: Ar = (4-Me)Ph
7c: Ar = (4-OMe)Ph

Entry	ArBr	Catalyst	Isolated yield [%]
1	4-bromotoluene	(*R*)-[**2**]	85
2	4-bromotoluene	(*R*)-[**3**]	70
3	4-bromotoluene	(*R*)-[**4**]	52
4	4-bromotoluene	(*R*,*R*)-[**5**]	16
5	4-bromobenzene	(*R*)-[**2**]	76
6	4-bromoanisole	(*R*)-[**2**]	72

[a] Reactions conditions: catalyst (5.0 mol-%), NaO*t*Bu (2.5 equiv.), toluene, 120 °C, 16 h.

Surprisingly, an α-methylation product was observed with precatalyst (*R*,*R*)-[**5**], when the same reaction was carried out in *N*,*N*-dimethylformamide (DMF)/dioxane mixture and in the absence of an aryl halide (Scheme 3). The product **8** was obtained in 50 % yield. Given that DMF was used as solvent system for the reactions, DMF is likely acting as a methyl donor in these cases. Performing the reaction under identical conditions but in the absence of the precatalyst (*R*,*R*)-[**5**] did not lead to any product formation, thus establishing the vital role of the precatalyst for this reaction. No α-methylation product was observed on performing this reaction in either dioxane or toluene under identical conditions but in the absence of DMF. The reaction in a DMF–toluene mixture did lead to the α-methylation product, albeit in a much lower yield compared with that obtained upon reaction in the DMF/dioxane mixture mentioned above. A similar observation was also reported for palladium-catalyzed α-arylation reactions with Cu^I as co-catalyst in DMF/dioxane.[25a] In addition, a trace amount of *N*-methylformamide (NMF) was also detected in the reaction mixture by HPLC analysis.[25a] In our case, no additional Cu^I source is required for this reaction. Despite the use of enantiopure ligands, and their metal complexes, we did not observe any enantiomeric excess in the products formed through either α-arylation or α-alkylation of amides. These results show that the incorporation of just one chiral center in the ligand with relatively sterically unhindered groups is not enough to transfer chirality in the types of catalysis tested here.

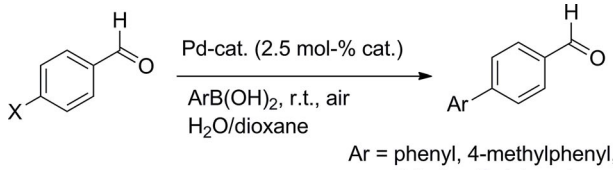


6 **8**

Scheme 3. α-Methylation reaction using complex (*R*,*R*)-[**5**].

Both the PEPPSI-type and $Pd(MIC)_2X_2$-type complexes were used as precatalysts for the Suzuki–Miyaura cross-coupling reactions. All these complexes show good conversion (Table 2) into the biaryl aldehyde products when the reaction was started with 4-Cl/Br-benzaldehyde and phenylboronic acid or substituted phenylboronic acid. The reaction with 4-bromobenzaldehyde occurred at room temperature. However, the use of 4-chlorobenzaldehyde as substrate required elevated temperature and longer reaction times for completion (Table 2). The PEPPSI-type complexes were more active precatalysts (99 % conv. in 3 h) compared with the $Pd(MIC)_2X_2$-type complex (75 % conv. in 3 h) (*R*,*R*)-[**5**].

Table 2. Suzuki–Miyaura cross-coupling reaction.[a,b]

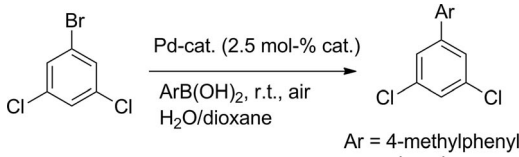


Entry	Ar	X	Catalyst	Time (h)	Conv. [%]
1[a]	Ph	Br	(*R*)-[**2**]	3	99
2[a]	Ph	Br	(*R*)-[**3**]	3	99
3[a]	Ph	Br	(*R*)-[**4**]	3	99
4[a]	Ph	Br	(*R*,*R*)-[**5**]	3	75
5[a]	Ph	Br	(*R*,*R*)-[**5**]	6	99
6[a]	4-MeC_6H_4	Br	(*R*,*R*)-[**5**]	6	99
7[a]	3,5-$Me_2C_6H_3$	Br	(*R*,*R*)-[**5**]	6	99
8[b]	4-MeC_6H_4	Cl	(*R*,*R*)-[**5**]	6	78
9[b]	4-MeC_6H_4	Cl	(*R*,*R*)-[**5**]	10	99
10[b]	3,5-$Me_2C_6H_3$	Cl	(*R*,*R*)-[**5**]	6	90
11[b]	3,5-$Me_2C_6H_3$	Cl	(*R*,*R*)-[**5**]	10	99

[a] Reactions conditions: aldehyde (1.0 equiv.), catalyst (2.5 mol-%), boronic acid (1.2 equiv.), K_2CO_3 (2.5 equiv.), H_2O/dioxane (3:2 v/v), room temperature. [b] Temperature: 60 °C.

The complex (*R*,*R*)-[**5**] was also successfully used for the chemoselective Suzuki–Miyaura cross-coupling reaction with 1-bromo-3,5-dichlorobenzene as substrate. The reaction of 1-bromo-3,5-dichlorobenzene with either phenylboronic acid or (4-methylphenyl)boronic acid at room temperature gave quantitative conversion into the biaryl aldehyde products (Table 3). No other higher substituted aldehyde products were obtained during the reaction under these reaction conditions (Table 3).

Table 3. Chemoselective Suzuki–Miyaura cross-coupling reaction.[a]



Entry	Ar	X	Catalyst	Conversion [%] after 6 h
1[a]	Ph	Br	(*R*,*R*)-[**5**]	99
2[a]	4-MeC_6H_4	Br	(*R*,*R*)-[**5**]	99

[a] Reactions conditions: aldehyde (1.0 equiv.), catalyst (2.5 mol-%), boronic acid (1.2 equiv.), K_2CO_3 (2.5 equiv.), H_2O/dioxane (3:2 v/v), room temperature.

We have also performed the mercury poison test for the Suzuki–Miyaura cross-coupling reaction under the described conditions. For these reactions no further conversion into the coupling biaryl aldehyde product was observed after Hg^0 addition. As an example, addition of mercury after 1 h (80 %) conversion using catalyst (*R*)-[**4**] inhibited further catalytic coupling and no biaryl aldehyde product (phenylboronic acid and 4-bromobenzaldehyde as substrates) was formed during the subsequent 3 h time. This observation suggests that Pd^0 nanoparticles (NP) are the active catalyst in Suzuki–Miyaura cross-coupling reactions under the described reaction conditions.[11c] It should, however, be noted that the presence of the MIC ligands are necessary for the generation of such Pd^0 NP; the catalysis does not work in the presence of only palladium(II) salts.

Conclusions

Two different types of chiral Pd^{II} complexes [PEPPSI-type and $Pd(MIC)_2X_2$-type] with MIC ligands have been synthesized starting from the chiral triazolium ligand precursors (*R*)-**1** or (*S*)-**1**. All the complexes have been tested as active precatalysts for both Suzuki–Miyaura cross-coupling reaction and α-arylation of amides. The PEPPSI-type complexes (*R*)-[**2**], (*R*)-[**3**], and (*R*)-[**4**] are more active catalysts compared with the $Pd(MIC)_2X_2$-type complex (*R*,*R*)-[**5**] in both catalytic transformations. In the α-arylation of amides, the complex (*R*)-[**2**] shows better catalytic activity compared with both complexes (*R*)-[**3**] and (*R*)-[**4**]. Complex (*R*)-[**3**], with 3-chloropyridine, shows better activity compared with complex (*R*)-[**4**], bearing 4-chloropyridine as co-ligand. In addition, α-methylated benzazepinone product **8** was obtained with moderate yield (50 % isolated yield) when the reaction was carried out in DMF/dioxane mixture in the absence of aryl halide under similar reaction conditions. DMF is suspected to be acting as methyl donor in this reaction. A chemoselective Suzuki–Miyaura cross-coupling reaction has also been carried out using complex (*R*,*R*)-[**5**] with 1-bromo-3,5-dichlorobenzene and phenylboronic acid as substrates. At room temperature, only the biphenyl product was formed through the C–Br bond activation and no formation of other products was observed under the described reaction conditions. The PEPPSI-type complexes are active precatalysts for the Suzuki–Miyaura cross-coupling reaction for both bromo-benzaldehyde and chlorobenzaldehyde substrates. Mercury poison tests show the heterogeneous nature of the Suzuki–Miyaura cross-coupling reaction, and Pd-NPs are likely to be the real active catalyst. However, the palladium catalyst was unaffected by the addition of mercury in case of α-arylation of amides, possibly showing the homogeneous nature of these reactions. No enantioselective catalysis was observed with the described chiral complexes, which might be the due to insufficient steric protection and/or a more flexible nature of the chiral site of the complexes. It will be intriguing to use either a larger or a rigid steric platform on the chiral site of the complex and hence make these complexes effective for enantioselective catalysis. Although no enantioselective catalysis could be realized with these complexes, they are nevertheless potent precatalysts for cross-coupling reactions under mild conditions, and for intermolecular α-arylation

and α-methylation of amides. The precedence of such intermolecular α-arylation and α-methylation of amides is limited. Further research in our laboratory will be directed towards making these potent catalysts function in an enantioselective fashion.

Experimental Section

General Procedures: All reactions were carried out under a nitrogen atmosphere either by using standard Schlenk techniques or in a glove box. Glassware was oven-dried at 100 °C. Solvents were distilled by standard procedures prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker AVANCE 500, a JEOL ECS 400, or a JEOL ECP 500 spectrometer. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz and only given for ^{1}H,^{1}H couplings unless mentioned otherwise. Mass spectra were obtained with an Agilent 6210 ESI-TOF MS. The triazolium salts (*R*)-**1** and (*S*)-**1**[16] were synthesized as described previously. K_2CO_3, Ag_2O, KI, NaCl, and $Pd(OAc)_2$ were purchased from commercial sources and were used as received without further purification.

General Procedure for the Synthesis of Chiral PEPPSI Complexes: To a mixture of triazolium salt (*R*)-**1** (1.0 equiv.), $PdCl_2$ (1.1 equiv.), K_2CO_3 (2.0 equiv.), and KI (excess) was added pyridine/3-chloropyridine/4-chloropyridine hydrochloride (5 mL; in case of 4-chloropyridine hydrochloride CH_3CN was used as solvent and 3.0 equiv K_2CO_3 was used). The mixture was stirred for 24 h at 84 °C. After removal of pyridine in vacuo, the residue was extracted with dichloromethane and passed through a short pad of Celite to obtain a clear solution. The solvents were removed under reduced pressure and the resulting solid was packed onto a silica gel column. Elution with dichloromethane gave the desired products.

Compound (*R*)-[2]: The general procedure was applied starting from triazolium salt (*R*)-**1** (0.174 g, 0.446 mmol), $PdCl_2$ (0.080 g, 0.451 mmol), K_2CO_3 (0.123 g, 0.890 mmol), and KI (excess), yield 0.198 g (0.282 mmol, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94–8.90 (m, 2 H, H_{Py}), 7.92–7.89 (m, 2 H, H_{Ar}), 7.85–7.82 (m, 2 H, H_{Ar}), 7.68–7.64 (m, 1 H, H_{Py}), 7.57–7.48 (m, 3 H, H_{Ar}), 7.43–7.37 (m, 3 H, H_{Ar}), 7.26–7.23 (m, 2 H, H_{Py}), 6.90 [q, ^3J = 7.2 Hz, 1 H, N-C*H*(CH_3)], 3.91 (s, 3 H, N-CH_3), 2.14 (t, ^3J = 7.2 Hz, 3 H, N-CH-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 154.0 (C_{Py}), 143.4 (C_{trz}-Ar), 138.2 (C_{Ar}-C_{trz}), 137.4 (C_{Py}), 133.6 (C_{trz}-Pd), 130.6 (C_{Ar}-H), 130.0 (C_{Ar}-H), 128.8 (C_{Ar}-H), 128.73 (C_{Ar}-H), 128.71 [C_{Ar}-CH(CH_3)], 128.6 (C_{Ar}-H), 124.9 (C_{Ar}-H), 124.4 (C_{Py}), 65.3 [N-*C*H(CH_3)], 37.8 (N-CH_3), 20.9 (N-CH-*C*H$_3$) ppm. HRMS (ESI, positive ions): *m/z* calcd. for [(*R*)-[**2**]-I-Py]$^+$ 495.9509; found 495.9510.

Compound (*R*)-[3]: Prepared by using the same synthetic procedure described for (*R*)-[**2**], yield 0.208 g (0.283 mmol, 63.5 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.94 (t, ^4J = 1.8 Hz, 1 H, H_{Py}), 8.85 (dt, ^3J = 5.4, ^4J = 1.8 Hz, 1 H, H_{Py}), 7.89–7.86 (m, 2 H, H_{Ar}), 7.82–7.80 (m, 2 H, H_{Ar}), 7.67–7.63 (m, 1 H, H_{Py}), 7.58–7.48 (m, 3 H, H_{Ar}), 7.43–7.35 (m, 3 H, H_{Ar}), 7.20 (dd, ^3J = 5.4 Hz, 1 H, H_{Py}), 6.85 [q, ^3J = 7.1 Hz, 1 H, N-C*H*(CH_3)], 3.90 (m, 3 H, N-CH_3), 2.12 (m, 3 H, N-CH-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 152.9 (C_{Py}), 151.9 (C_{Py}), 143.3 (C_{trz}-Ar), 138.4 [C_{Ar}-CH(CH_3)], 137.5 (C_{Py}), 132.2 (C_{Ar}-C_{trz}), 130.6 (C_{Ar}-H), 130.1 (C_{Ar}-H), 128.82 (C_{Ar}-H), 128.80 (C_{Ar}-H), 128.77 (C_{trz}-Pd), 128.6 (C_{Ar}-H), 127.4 (C_{Ar}-H), 124.6 (C_{Py}), 65.4 [N-*C*H(CH_3)], 37.8 (N-CH_3), 20.9 (N-CH-*C*H$_3$) ppm. HRMS (ESI, positive ions): *m/z* calcd. for [(*R*)-[**3**]-I-(3-Cl-Py)]$^+$ 495.9509; found 495.9508.

Compound (*R*)-[4]: Prepared by using the synthetic procedure described for (*R*)-[**2**]. 4-Chloropyridine hydrochloride and CH_3CN were used instead of pyridine, yield 0.172 g (0.233 mmol, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (dd, ^3J = 5.0, ^4J = 1.4 Hz, 2 H, H_{Py}), 7.89–7.86 (m, 2 H, H_{Ar}), 7.82–7.81 (m, 2 H, H_{Ar}), 7.57–7.49 (m, 3 H, H_{Ar}), 7.43–7.33 (m, 3 H, H_{Ar}), 7.26–7.25 (m, 2 H, H_{Py}), 6.86 [q, ^3J = 6.9 Hz, 1 H, N-C*H*(CH_3)], 3.89 (s, 3 H, N-CH_3), 2.13 (d, ^3J = 6.9 Hz, 3 H, N-CH-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 154.7 (C_{Py}), 146.0 (C_{Py}), 143.4 (C_{trz}-Ar), 138.4 [C_{Ar}-CH(CH_3)], 132.6 (C_{Ar}-C_{trz}), 130.6 (C_{Ar}-H), 130.0 (C_{Ar}-H), 128.81 (C_{Ar}-H), 128.77 (C_{Ar}-H), 128.76 (C_{trz}-Pd), 128.6 (C_{Ar}-H), 127.5 (C_{Ar}-H), 124.9 (C_{Py}), 65.3 [N-*C*H(CH_3)], 37.8 (N-CH_3), 20.9 (N-CH-*C*H$_3$) ppm. HRMS (ESI, positive ions): *m/z* calcd. for [(*R*)-[**4**]-I-(4-Cl-Py)]$^+$ 495.9509; found 495.9507.

Compound (*R,R*)-[5]: To a mixture of triazolium salt (*R*)-**1** (0.126 g, 0.322 mmol) and Ag_2O (0.080 g, 0.346 mmol) was added dichloromethane (10 mL), and the resulting suspension was stirred at ambient temperature for 18 h under the exclusion of light. To the reaction mixture were then added [$Pd(Cl)_2(CH_3CN)_2$] (0.042 g, 0.162 mmol) and KI (excess). The reaction mixture was stirred for 24 h at ambient temperature then filtered through a pad of Celite to obtain a clear solution. The solvent was removed and the solution was concentrated to 2 mL and diethyl ether was added to the solution to produce a yellow precipitate. The solid was washed with diethyl ether and dried in vacuo, yield 0.070 g (0.079 mmol, 49 %).

Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.95 (m, 4 H, H_{Ar}), 7.64–7.61 (m, 4 H, H_{Ar}), 7.45–7.40 (m, 5 H, H_{Ar}), 7.32–7.29 (m, 7 H, H_{Ar}), 6.59 [q, ^3J = 7.5 Hz, 2 H, N-C*H*(CH_3)], 3.89 (s, 6 H, N-CH_3), 2.01 (d, ^3J = 7.5 Hz, 6 H, N-CH-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 144.3 (C_{trz}-Ar), 138.8 [C_{Ar}-CH(CH_3)], 130.6 (C_{Ar}-H), 128.91 (C_{Ar}-H), 128.8 (C_{trz}-Pd), 128.6 (C_{Ar}-H), 128.4 (C_{Ar}-H), 128.4 (C_{Ar}-C_{trz}), 128.38 (C_{Ar}-H), 64.5 [N-*C*H(CH_3)], 37.3 (N-CH_3), 21.0 (N-CH-*C*H$_3$) ppm.

Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.75 (m, 3 H, H_{Ar}), 7.72–7.69 (m, 3 H, H_{Ar}), 7.38–7.35 (m, 14 H, H_{Ar}), 6.92 [q, ^3J = 7.0 Hz, 2 H, N-C*H*(CH_3)], 3.85 (s, 6 H, N-CH_3), 2.07 (d, ^3J = 7.0 Hz, 6 H, N-CH-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 144.6 (C_{trz}-Ar), 139.3 [C_{Ar}-CH(CH_3)], 130.4 (C_{Ar}-H), 129.3 (C_{Ar}-H), 128.9 (C_{Ar}-H), 128.8 (C_{Ar}-H), 128.6 (C_{Ar}-H), 128.42 (C_{Ar}-H), 128.42 (C_{Ar}-C_{trz}), 128.3 (C_{trz}-Pd), 64.6 [N-*C*H(CH_3)], 37.4 (N-CH_3), 20.9 (N-CH-*C*H$_3$) ppm. HRMS (ESI, positive ions): *m/z* calcd. for [(*R,R*)-[**5**]-I]$^+$ 759.0937; found 759.0943.

Compound (*S,S*)-[5]: Prepared by following the procedure described for (*R,R*)-[**5**] from triazolium salt (*S*)-**1** (0.126 g, 0.322 mmol) and Ag_2O (0.080 g, 0.346 mmol) for the first step and [$Pd(Cl)_2(CH_3CN)_2$] (0.042 g, 0.162 mmol) and KCl (excess) for the second step. Exclusively one isomeric complex of compound (*S,S*)-[**5**] was obtained as a yellow solid, yield 0.068 g (0.097 mmol, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.88 (m, 4 H, H_{Ar}), 7.59–7.54 (m, 6 H, H_{Ar}), 7.53–7.51 (m, 4 H, H_{Ar}), 7.44–7.41 (m, 4 H, H_{Ar}), 7.36–7.33 (m, 2 H, H_{Ar}), 6.71 [q, ^3J = 6.4 Hz, 2 H, N-C*H*(CH_3)], 4.13 (s, 6 H, N-CH_3), 2.0 (d, ^3J = 6.4 Hz, 6 H, N-CH-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 143.8 (C_{trz}-Ar), 140.7 [C_{Ar}-CH(CH_3)], 130.58 (C_{Ar}-H), 130.57 (C_{Ar}-H), 129.3 (C_{Ar}-H), 129.2 (C_{Ar}-H), 128.6 (C_{Ar}-H), 127.5 (C_{Ar}-H), 127.5 (C_{trz}-Pd), 126.5 (C_{Ar}-C_{trz}), 64.8 [N-*C*H(CH_3)], 37.9 (N-CH_3), 21.6 (N-CH-*C*H$_3$) ppm. HRMS (ESI, positive ions): *m/z* calcd. for [*S,S*-[**5**]-Cl]$^+$ 669.1570; found 669.1575.

General Procedure for Suzuki–Miyaura Coupling Reactions: To a mixture of aryl halide (0.1 mmol), boronic acid (0.15 mmol), palladium(II) complexes (*R*)-[**2**], (*R*)-[**3**], *R*-[**4**], or (*R,R*)-[**5**] (0.0025 mmol, 2.5 mol-%) and K_2CO_3 (2.5 equiv., 0.25 mmol) was added 1,4-dioxane (2 mL) and water (3 mL). The resulting suspension was stirred at the mentioned temperature. Water was added to the reaction

mixture (10 mL) and the biphasic solution was extracted with dichloromethane (15 × 2 mL). The organic part was dried with Na_2SO_4 and the solvent was removed under vacuum at room temperature to give the crude mixture, yields were determined by ^1H NMR spectroscopic analysis and were based on the integrals of the aldehyde protons.

General Procedure for α-Arylation of Amides: An oven-dried sealed tube equipped with a stir bar was charged with **6** (0.57 mmol) and the corresponding aryl halide (0.637 mmol) under a nitrogen atmosphere. This was followed by addition of Pd catalyst (5 mol-%), corresponding base (1.4 mmol) and anhydrous toluene (10.0 mL) by using a syringe. The reaction vessel was sealed and the reaction mixture was stirred at 120 °C for 16 h then cooled to room temperature. The reaction was quenched with H_2O (15 mL) and extracted with ethyl acetate. The organic part was dried with $MgSO_4$ and the solvent was removed. The crude mixture was loaded onto a silica gel column and eluted with hexane/ethyl acetate (100:20 v:v).

X-ray Crystallography: Single crystals suitable for X-ray diffraction studies were obtained for the complexes (*R*)-[**2**]·CH_2Cl_2, (*R*)-[**3**]·CH_2Cl_2, (*R*)-[**4**], (*R*,*R*)-[**5**]·CH_2Cl_2, and (*S*,*S*)-[**5**]·CH_3CN by slow diffusion of pentane into a concentrated dichloromethane/acetonitrile solution of the corresponding complexes at room temperature. X-ray diffraction data were collected at T = 140 K with a Bruker Smart AXS diffractometer equipped with a rotating anode using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were collected by using the standard "phi-omega scan techniques". The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97, refining on F^2.[26] Crystallographic details are given in Table S1. CCDC 1412898 {for (*R*)-[**2**]·CH_2Cl_2}, 1412895 {for (*R*)-[**3**]·CH_2Cl_2}, 1412899 {for (*R*)-[**4**]}, 1412896 {for (*R*,*R*)-[**5**]·CH_2Cl_2}, and 1412897 {for (*S*,*S*)-[**5**]·CH_3CN} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

The Fonds der Chemischen Industrie (FCI) and the Freie Universität Berlin are kindly acknowledged for financial support. The ERASMUS-MUNDUS program is acknowledged for providing a post-doctoral fellowship to A. V.

Keywords: Carbene ligands · Palladium · Cross-coupling · Arylation · Methylation

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Received: September 9, 2015
Published Online: December 7, 2015