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ORIGINAL PAPER

Synthesis of palladium-bidentate complex and its application in Sonogashira and Suzuki coupling reactions

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A new palladium-bidentate complex [m-$C_6H_4(CH_2ImMe)_2(PdCl_2)$] (*III*) was prepared in two steps. In the first step, [m-$C_6H_4(CH_2ImMeAgCl)_2$] (*II*) (Im = imidazole moiety) was obtained by reacting imidazolium salt [m-$C_6H_4(CH_2ImMe)_2$]Cl_2 (*I*) (prepared by quaternisation of *N*-methylimidazole with 1,3-bis(chloromethyl)benzene) and Ag_2O in CH_2Cl_2. In the next step, treatment of (*II*) with $Pd(CH_3CN)_2Cl_2$ afforded complex *III* which was evaluated for its catalytic activity for C—C bond-formation reactions by examining the coupling reaction of 3-iodoanisole with phenylacetylene in the Sonogashira reaction. In addition, 3-methoxybiphenyls were obtained with good to excellent yields by Suzuki coupling reactions of 3-iodoanisole with phenylboronic acids or phenylborates salts in the presence of this complex.

Keywords: palladium-bidentate complex, *N*-heterocyclic carbene (NHC), Sonogashira reaction, Suzuki coupling, imidazolium salt

Introduction

N-Heterocyclic carbenes are ligands with affordable and easy synthesis (Wanzlick & Schönherr, 1968). Their coordination to transition metals leads to complexes that are generally more stable than their phosphine analogues (Arduengo et al., 1991; Herrmann, 2002; Nair et al., 2004), and their use in catalysis over the last twenty years has demonstrated performances equal to or even higher than those of the phosphine complexes (Jafarpour & Nolan, 2000). In recent reports, chelating ligands were developed (Flahaut et al., 2006; Mata et al., 2007) allowing the formation of very active complexes by diverse catalytic reactions (Nandurkar et al., 2007; Negishi, 2003). More specifically, these reactions have been widely employed in the synthesis of natural products, and biologically active molecules and materials (Cornils & Herrmann, 2005; Yasuda, 2002).

Many papers are devoted to the properties of various forms of palladium (Pd) compounds and their applications in catalysis (Akiyama et al., 2009; Amini & Etemadi, 2013; Bakherad et al., 2009; Buchmeiser et al., 2001; Corma et al., 2005; Islam et al., 2010; Koukal et al., 2013; Nandurkar & Bhanage, 2008; Phan & Le, 2011; Reddy et al., 2006; Zhang et al., 2009). Particularly, palladium-catalysed coupling of an aryl halide with aryl boronic acid (Suzuki coupling) (Böhm et al., 2000; Inamoto et al., 2009; Kumar et al., 2009; Patil et al., 2009; Weskamp et al., 1999) or with a terminal alkyne (Sonogashira coupling) (Dash et al., 2009; Li & Hor, 2008; Ray et al., 2008) are recognised as the most successful methods of carbon–carbon bond formation (Stauffer et al., 2000).

As reported by Tudose et al. (2006), the precise architecture of Pd species plays a crucial role in designing highly efficient Pd catalyst systems and electronic properties can be tuned by vary-

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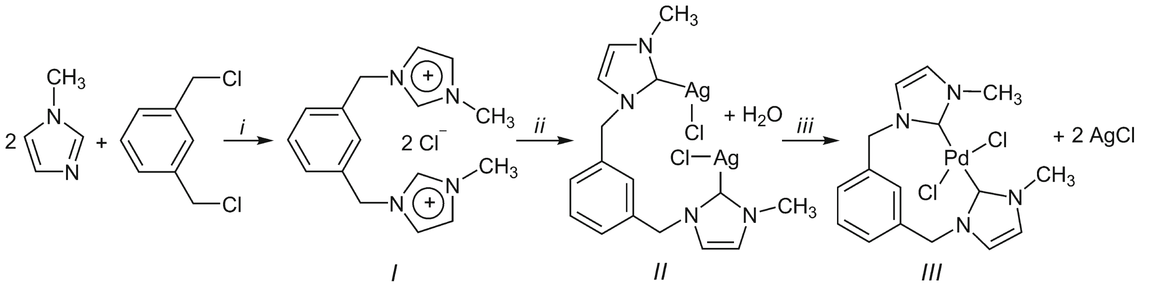


Fig. 1. Synthesis of precursors *I* and *II* and Pd-bidentate complex *III*. Reaction conditions: *i*) DMF, reflux; *ii*) Ag_2O; *iii*) $Pd(CH_3CN)_2Cl_2$; r.t., 30 min.

ing the organic ligands. The aim of the present study is to synthesise a new palladium-pincer complex (*III*), and to examine its application in cross-coupling reactions such as (*i*) Sonogashira reaction of 3-iodoanisole with phenylacetylene; (*ii*) Suzuki reaction of 3-iodoanisole with phenylboronic acids, and (*iii*) Suzuki reaction of 3-iodoanisole with phenylborate salts.

Experimental

All reactions and manipulations were performed under dry nitrogen atmosphere using a Radleys Carousel 12.

^1H (400 MHz) and ^{13}C (100.6 MHz) NMR spectra were recorded in dimethyl sulfoxide (DMSO-d_6) on a Bruker DRX 400 MHz spectrometer, using the DMSO-d_6 residual peak as the ^1H internal reference ($\delta = 2.5$), and the central peak of DMSO-d_6 at $\delta = 39.5$ as the ^{13}C reference. Chemical shifts (δ) are referenced to the signal of internal TMS. IR spectra (in KBr pellets) were recorded on a Perkin–Elmer Spectrum BX FTIR spectrophotometer.

Compounds *I*–*III* (Fig. 1) were prepared by slight modification of procedures already described (Arnold & Pearson, 2007; Chen et al., 2002; Danopoulos et al., 2003; Lin & Vasam, 2007) as follows: a mixture of 1,3-bis(chloromethyl)benzene (*m*-xylylene dichloride) (2.27 g, 10 mmol) and *N*-methylimidazole (4.26 g, 40 mmol) was heated in DMF at 80 °C for 6 h. The solvent was evaporated under reduced pressure and the product was washed with diethyl ether (100 mL) to give *I* as a white hygroscopic solid. According to the literature methods (Chen et al., 2002), compound *I* was added to a suspension of Ag_2O (in the mole ratio of 1 : 1) in dichloromethane at ambient temperature and the mixture was stirred overnight. The black Ag_2O solid disappeared and the silver-carbene complex *II* was isolated (91 % yield) after the evaporation of the solvent. Treatment of the silver-carbene complex *II* with $Pd(CH_3CN)_2Cl_2$ afforded the corresponding palladium-bidentate complex, $[m\text{-}C_6H_4(CH_2ImMe)_2(PdCl_2)]$ (*III*), in a 71 % yield as an air stable cream-coloured solid.

General procedure for Sonogashira cross-coupling reaction

A solution of 3-iodoanisole (1 mmol) and phenylacetylene (1.2 mmol) in DMF/H_2O (10 mL, $\varphi_r = 4 : 1$) was added to the mixture of Et_3N (2 mmol), CuI (2.0 mmol) (or no CuI), and $[C_6H_4(CH_2ImMe)_2(PdCl_2)]$ (0.5 mole %) and the reaction mixture was heated at 80 °C for 6 h. The product was extracted with diethyl ether (5 × 50 mL), the combined extracts were dried with $MgSO_4$, filtered and the solvent was removed under diminished pressure to give a crude product which was purified by column chromatography on silica gel using hexane/ethyl acetate ($\varphi_r = 1 : 3$) as the eluent to afford the desired product. The product was identified by NMR and FTIR spectroscopy. Spectral data of 1-methoxy-3-(2-phenylethynyl)benzene (*VI*) are in accord with those already reported (Giraud et al., 2008; Yang et al., 2007).

General procedure for Suzuki cross-coupling reaction

A mixture of 3-iodoanisole (1 mmol), phenylboronic acid (1.2 mmol), $[C_6H_4(CH_2ImMe)_2(PdCl_2)]$ (0.5 mol %), and *tert*-BuOK (2 mmol) in DMF (10 mL), was stirred at 80 °C for 8 h. The reaction mixture was then cooled to ambient temperature and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel) using hexane/ethyl acetate ($\varphi_r = 1 : 1$) as the eluent to afford the desired product. Spectral data of 1-methoxy-3-(4-methoxyphenyl)benzene (*VIIIa*) and 1-(4-chlorophenyl)-3-methoxybenzene (*VIIIb*) were reported previously (Cella et al., 2006; Lu et al., 2010).

Results and discussion

The ^1H NMR spectrum of *I* showed a singlet at $\delta = 8.28$ corresponding to the NCHN of the imidazolium moiety protons and a multiplet in the range of $\delta = 7.46–7.39$ for the NCHCHN protons. For complexes *II* and *III*, the signals of the imidazolium pro-

Table 1. Spectral data of the compounds prepared

Compound	Physical and spectral data
I	IR, $\tilde{\nu}$/cm^{-1}: 3004, 2869, 1564, 1455,1078, 755 ^{1}H NMR (DMSO-d_6), δ: 8.28 (s, 2H, NCHN), 7.46–7.39 (m, 4H, NCHCHN), 7.19–7.07 (m, 4H, C_6H_4), 4.07 (s, 4H, CH_2), 3.99 (s, 6H, 2 × CH_3) ^{13}C NMR (DMSO-d_6), δ: 147.9, 133.9, 128.3, 127.5, 123.4, 120.6, 53.1, 34.3
II	IR, $\tilde{\nu}$/cm^{-1}: 3122, 2861, 1565,1460, 1238, 749 ^{1}H NMR (DMSO-d_6), δ: 7.05–7.03 (d, 2H, NCH), 6.58–6.52 (m, 4H,C_6H_4), 6.01 (d, 2H, NCH), 5.03 (s, 4H, CH_2), 3.42 (s, 6H, 2 × CH_3) ^{13}C NMR (DMSO-d_6), δ: 164.1, 160.6, 159.4, 137.8, 134.2, 123.5, 122.6, 50.9, 37.3
III	IR, $\tilde{\nu}$/cm^{-1}: 3121, 2923, 2335, 1548, 1237, 749 ^{1}H MR (DMSO-d_6), δ: 7.15–7.08 (d, 2H, NCH), 6.73–6.69 (m, 4H, C_6H_4), 6.23 (d, 2H, NCH), 4.99 (s, 4H, CH_2), 3.60 (s, 6H, 2 × CH_3) ^{13}C NMR (DMSO-d_6), δ: 168.2, 161.1, 156.1, 145.2, 139.3, 126.5, 121.9, 51.2, 371
VIIIa	Yield = 90 %, colourless solid IR, $\tilde{\nu}$/cm^{-1}: 2957, 2833, 1582, 1472, 1284, 1227, 1060, 821, 763, 679 ^{1}H NMR (DMSO-d_6), δ: 7.34 (m, 1H, 2 × CHC$\underline{H}$CH), 7.28 (m, 1H, CHC$\underline{H}$CH), 7.07 (m, 1H, C$\underline{H}$CCH), 7.05 (m, 1H, C$\underline{H}$CCH), 6.93 (m, 2H, C$\underline{H}$CCH), 6.91 (m, 1H, C$\underline{H}$CHC), 3.83 (s, 6H, 2 × CH_3) ^{13}C NMR (DMSO-d_6), δ: 158.18, 134.55, 129.87, 129.08, 113.78, 113.02, 111.11, 105.32, 103.09, 93.76, 51.55
VIIIc	Yield = 84 %, colourless solid IR, $\tilde{\nu}$/cm^{-1}: 2969, 1468, 1292, 1213, 1053, 817, 773, 690 ^{1}H NMR (DMSO-d_6), δ: 7.59 (m, 1H, CHC$\underline{H}$CH), 7.47 (m, 1H, CHC$\underline{H}$CH), 7.29 (m, 1H, CHC$\underline{H}$CH), 7.26 (m, 1H, CHC$\underline{H}$CH), 7.23 (m, 1H, CHC$\underline{H}$CH), 7.02 (m, 1H, CC$\underline{H}$CH), 6.98 (m, 1H, CC$\underline{H}$C), 6.90 (m, 1H, CC$\underline{H}$CH), 3.86 (s, 3H, CH_3) ^{13}C NMR (DMSO-d_6), δ: 160.14, 131.92, 131.65, 130.77, 129.84, 128.36, 128.32, 123.01, 116.33, 114.97, 113.77, 55.42
VIIId	Yield = 86 %; colourless solid IR, $\tilde{\nu}$/cm^{-1}: 2945,2839, 1470, 1268, 1256, 1208, 1029, 819, 761 ^{1}H NMR (DMSO-d_6), δ: 7.18 (m, 2H, CHC$\underline{H}$CH), 7.12 (m, 2H, CHC$\underline{H}$CH), 7.03 (m, 2H, CC$\underline{H}$CH), 6.93 (m, 1H, CC$\underline{H}$C), 6.90 (m, 2H, CC$\underline{H}$CH), 3.83 (s, 3H, CH_3) ^{13}C NMR (DMSO-d_6), δ: 159.73, 135.28, 131.15, 129.84, 129.31, 128.36, 128.30, 111.79, 55.31
VIIIe	Yield = 89 %; colourless solid IR, $\tilde{\nu}$/cm^{-1}: 2936, 2832, 1462, 1295, 1223, 1039, 803, 783, 686 ^{1}H NMR (DMSO-d_6), δ: 7.98 (m, 2H, 2 × CHC$\underline{H}$CH), 7.95 (m, 1H, CHC$\underline{H}$CH), 7.54 (m, 1H, CHC$\underline{H}$CH), 7.50 (m, 1H, CHC$\underline{H}$CH), 7.46 (m, 2H, 2 × CHC$\underline{H}$CH), 7.43 (m, 1H, CHC$\underline{H}$CH), 7.03 (m, 1H, CC$\underline{H}$CH), 7.01 (m, 1H, CC$\underline{H}$C), 6.99 (m, 1H, CC$\underline{H}$CH), 3.80 (s, 3H, CH_3) ^{13}C NMR (DMSO-d_6), δ: 160.14, 145.02, 141.94, 141.34, 130.77, 129.85, 129.83, 127.07, 124.76, 124.12, 119.44, 113.59, 112.03, 55.89.

tons NCHCHN appeared as two doublets at δ = 7.05–7.03 and a multiplet in the range of δ = 7.15–7.08, respectively. These are typical values reported previously (Baker et al., 2005; Chen & Matsumoto, 2002; Heckenroth et al., 2006) for imidazolium salts. For *I*, *II*, and *III*, the resonances of the methylene protons of the bridge were observed as singlets at δ = 4.07, 5.03, and 4.99, respectively. On the other hand, the resonances of the aromatic phenyl groups in *I*, *II*, and *III* were observed as multiplets at δ = 7.07–7.19, δ = 6.58–6.52, and δ = 6.73–6.69, respectively. Qualitatively, the ^{1}H NMR spectral data of *III* are very similar to those of *II*.

The ^{13}C NMR spectrum of *I* also showed signals at δ = 120.6 for the C-3 atom of the imidazolium moiety, and signals at δ = 123.4, δ = 127.5, δ = 128.3, and δ = 133.9 for the C-4, C-5, C-6, and C-7 atoms of the phenyl group. Carbene formation is indicated by the signal of the C-8 atom of the NCN group appearing at δ = 146.9 in *I*, whereas the coordinating carbene carbons can be observed at δ = 164.1 and δ = 168.2 for *II* and *III*, respectively, suggesting the formation of the C—AgCl and Pd—C bonds (for details, Table 1).

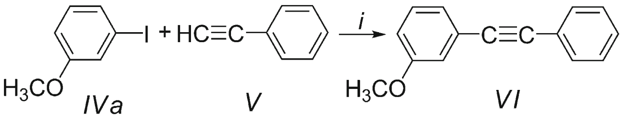


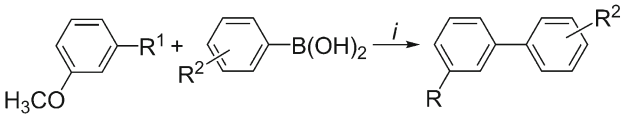
Fig. 2. Sonogashira reaction of 3-iodoanisole with phenylacetylene catalysed by Pd-bidentate complex *III*. Reaction conditions: *i*) 3-iodoanisole (1.0 mmol), phenylacetylene (1.2 mmol), catalyst (0.5 mole % Pd), Et_3N (2.0 mmol), DMF/H_2O or H_2O (10 mL), 80 °C, 6 h (unoptimised time) in the presence (1.0 mmol) or absence of CuI.

To evaluate the catalytic activity, the Pd-bidentate complex *III* in the Sonogashira coupling reaction of 3-iodoanisole (*IVa*) with phenylacetylene (*V*) was first examined. When copper iodide (CuI) was used as a co-catalyst and triethylamine as the base, *V* was coupled smoothly with *IVa* affording the desired product, 1-methoxy-3-(2-phenylethynyl)benzene (*VI*), in a good yield (79 %). However, for analogous reaction

Table 2. Suzuki coupling reaction using Pd-bidentate complex *III* in DMF^a and DMF/H_2O^b

Entry	Haloarene	Boronic acid	Product	Yield/%	Reference
1	*IVa*	*VIIa*	*VIIIa*	92	Lu et al. (2010)
2	*IVa*	*VIIb*	*VIIIb*	76	Cella et al. (2006)
3	*IVa*	*VIIc*	*VIIIc*	84	Beadle et al. (1984)
4	*IVa*	*VIId*	*VIIId*	95	Molander and Biolatto (2003)
5	*IVb*	*VIId*	*VIIId*	25	Molander and Biolatto (2003)
6	*IVc*	*VIId*	*VIIId*	0	Molander and Biolatto (2003)
7	*IVa*	*VIIe*	*VIIIe*	82	Cella et al. (2006)
8	*IVd*	*VIId*	*VIIIf*	86	Arentsen et al. (2005)
9	*IVe*	*VIId*	*VIIIg*	90	Hoshino et al. (1997)
10	*IVf*	*VIId*	*VIIIh*	95	Molander and Iannazzo (2011)
11	*IVa*	*VIIf*	*VIIId*	86	Molander and Biolatto (2003)
12	*IVa*	*VIIg*	*VIIIa*	90	Lu et al. (2010)

a) Reaction conditions for entries 1–10: haloarene (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (0.5 mole % Pd), *tert*-BuOK (2.0 mmol), DMF (10 mL), 80 °C, 8 h (unoptimised time); *b*) for entries 11 and 12: 3-iodoanisole (*IVa*) (1.2 mmol), phenylborate salt (*VIIf* or *VIIg*) (1.8 mmol), catalyst (0.5 mole % Pd), 80 °C, DMF/H_2O, 8 h (unoptimised time); *IVd* = methyl 4-iodobenzoate; *IVe* = 4-iodoacetophenone; *IVf* = 1-iodo-4-(trifluoromethyl)benzene; *VIIe* = 1-naphthylboronic acid; *VIIf* = sodium tetraphenylborate; *VIIg* = potassium (4-methoxyphenyl)trifluoroborate; *VIIIe* = 1-(3-methoxyphenyl)naphthalene.



IVa–IVf *VIIa–VIIe* *VIIIa–VIIIh*

IVa $R^1 = I$
IVb $R^1 = Br$
IVc $R^1 = Cl$
IVd see Table 2
IVe see Table 2
IVf see Table 2
VIIa $R^2 = 4\text{-}OCH_3$
VIIb $R^2 = 4\text{-}Cl$
VIIc $R^2 = 3\text{-}Cl$
VIId $R^2 = H$
VIIe see Table 2
VIIf see Table 2
VIIg see Table 2
VIIIa $R = OCH_3$, $R^2 = 4\text{-}OCH_3$
VIIIb $R = OCH_3$, $R^2 = 4\text{-}Cl$
VIIIc $R = OCH_3$, $R^2 = 3\text{-}Cl$
VIIId $R = OCH_3$, $R^2 = H$
VIIIe see Table 2
VIIIf $R = COOCH_3$, $R^2 = H$
VIIIg $R = COCH_3$, $R^2 = H$
VIIIh $R = CF_3$, $R^2 = H$

Fig. 3. Suzuki coupling reaction of 3-haloanisole with various phenylboronic acids catalysed by Pd-bidentate complex *III*. Reaction conditions: *i*) see Table 2.

but in the absence of CuI, an unexpected decrease in the yield (56 %) was observed. The effect of the charged group has been fully elucidated by Yang et al. (2007). Catalytic activity of the structurally similar Pd complex (NHC)Pd was reported considering the Sonogashira reaction of terminal alkynes. When CuI was used as a co-catalyst, complex *III* showed similar activity and the monocarbene system gave consistently higher yields of the desired product than the chelating derivatives. However, when the reaction was performed in water and in the absence of CuI, the obtained similar complex without *N*-heterocyclic carbene showed almost no activity in the same reaction (Giraud et al., 2008).

Catalytic activity of the Pd-bidentate complex *III* in the Suzuki cross-coupling reaction was also investigated. In this respect, the reaction conditions were optimised for the coupling of 3-iodoanisole (*IVa*) and some other haloarenes (*IVb–IVf*, Fig. 3) with various phenylboronic acids using potassium *tert*-butoxide as a strong base and dimethylformamide as a solvent. The coupling products were obtained in good yields (Table 2).

The yields of coupling products (Table 2) with iodoarenes (entries 1–4, 7–10) were generally good but yield was low in case of bromobenzene (entry 5) and no reaction was observed when using chlorobenzene (entry 6). These results are in good agreement with published data (Böhm et al., 2000; Buchmeiser et al., 2001; Inamoto et al., 2009).

The mechanism incorporating similar catalytically active species has been the subject of much speculation. A recent work by Cella et al. (2006) on the Suzuki–Miyaura cross-coupling reactions of aryl tellurides with potassium aryltrifluoroborate salts in DMF using complex *III* (with NHC ligands) showed similar activity and recyclability as a similar complex in the reactions applying aryl bromide, but much higher activity when aryl chloride was applied.

As shown in Table 2, the Pd-bidentate complex *III* was successfully employed as an efficient catalyst in the Suzuki coupling reactions of 3-iodoanisole with sodium tetraphenylborate (entry 11) or potassium (4-methoxyphenyl)trifluoroborate (entry 12), affording the corresponding products in excellent yields.

Conclusions

In summary, a new Pd-bidentate complex was prepared and successfully employed as an efficient catalyst for the Sonogashira coupling reaction of 3-iodoanisole with phenylacetylene. From this reaction, in the presence of copper iodide as a co-catalyst, 1-methoxy-3-(2-phenylethynyl)benzene was obtained in a good yield (79 %). This complex was also successfully used as a catalyst for the Suzuki coupling reaction of 3-iodoanisole with phenylboronic acids as well as with phenylborate salts, producing 3-methoxybiphenyls in good to excellent yields.

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References

Akiyama, Y., Meng, X., Fujita, S., Chen, Y. C., Lu, N., Cheng, H., Zhao, F., & Arai, M. (2009). Carbon dioxide pressure induced heterogeneous and homogeneous Heck and Sonogashira coupling reactions using fluorinated palladium complex catalysts. *The Journal of Supercritical Fluids*, *51*, 209–216. DOI: 10.1016/j.supflu.2009.08.006.

Amini, M., & Etemadi, H. (2013). D-Glucosamine as an efficient and green additive for palladium-catalyzed Heck reaction. *Chemical Papers*, *67*, 759–763. DOI: 10.2478/s11696-013-0367-z.

Arduengo, A. J., III., Harlow, R. L., & Kline, M. (1991). A stable crystalline carbene. *Journal of the American Chemical Society*, *113*, 361–363. DOI: 10.1021/ja00001a054.

Arentsen, K., Caddick, S., & Cloke, F. G. N. (2005). On the efficiency of two-coordinate palladium(0) *N*-heterocyclic carbene complexes in amination and Suzuki–Miyaura reactions of aryl chlorides. *Tetrahedron*, *61*, 9710–9715. DOI: 10.1016/j.tet.2005.06.070.

Arnold, P. L., & Pearson, S. (2007). Abnormal *N*-heterocyclic carbenes. *Coordination Chemistry Reviews*, *251*, 596–609. DOI: 10.1016/j.ccr.2006.08.006.

Baker, M. V., Brayshaw, S. K., Skelton, B. W., White, A. H., & Williams, C. C. (2005). Synthesis and structure of N-heterocyclic carbene complexes of rhodium and iridium derived from an imidazolium-linked cyclophane. *Journal of Organometallic Chemistry*, *690*, 2312–2322. DOI: 10.1016/j.jorganchem.2005.02.042.

Bakherad, M., Keivanloo, A., Bahramian, B., & Mihanparast, S. (2009). A diphenylphosphinoethane-functionalized polystyrene resin-supported Pd(0) complex as an effective catalyst for copper-free Sonogashira coupling reactions under aerobic conditions. *Tetrahedron Letters*, *50*, 6418–6420. DOI: 10.1016/j.tetlet.2009.05.118.

Beadle, J. R., Korzeniowsky, S. H., Rosenberg, D. E., Garcia-Slanga, B. J., & Gokel, G. W. (1984). Phase-transfer-catalyzed Gomberg-Bachmann synthesis of unsymmetrical biarenes: a survey of catalysts and substrates. *The Journal of Organic Chemistry*, *49*, 1594–1603. DOI: 10.1021/jo00183a021.

Böhm, V. P. W., Gstöttmayr, C. W. K., Weskamp, T., & Herrmann, W. A. (2000). *N*-Heterocyclic carbenes: Part 26. *N*-Heterocyclic carbene complexes of palladium(0): synthesis and application in the Suzuki cross-coupling reaction. *Journal of Organometallic Chemistry*, *595*, 186–190. DOI: 10.1016/s0022-328x(99)00590-2.

Buchmeiser, M. R., Schareina, T., Kempe, R., & Wurst, K. (2001). Bis(pyrimidine)-based palladium catalysts: synthesis, X-ray structure and applications in Heck–, Suzuki–, Sonogashira–Hagihara couplings and amination reactions. *Journal of Organometallic Chemistry*, *634*, 39–46. DOI: 10.1016/s0022-328x(01)01083-x.

Cella, R., Cunha, R. L. O. R., Reis, A. E. S., Pimenta, D. C., Klitzke, C. F., & Stefani, H. A. (2006). Suzuki–Miyaura cross-coupling reactions of aryl tellurides with potassium aryltrifluoroborate salts. *The Journal of Organic Chemistry*, *71*, 244–250. DOI: 10.1021/jo052061r.

Chen, W., & Matsumoto, K. (2002). Synthesis and structural characterization of *N,N'*-dialkylimidazolium tetrachloroplatinate and monoaquatrichloroplatinate salts. *Bulletin of the Chemical Society of Japan*, *75*, 1561–1562. DOI: 10.1246/bcsj.75.1561.

Chen, W., Wu, B., & Matsumoto, K. (2002). Synthesis and crystal structure of N-heterocyclic carbene complex of silver. *Journal of Organometallic Chemistry*, *654*, 233–236. DOI: 10.1016/s0022-328x(02)01411-0.

Corma, A., García, H., & Leyva, A. (2005). Comparison between polyethylenglycol and imidazolium ionic liquids as solvents for developing a homogeneous and reusable palladium catalytic system for the Suzuki and Sonogashira coupling. *Tetrahedron*, *61*, 9848–9854. DOI: 10.1016/j.tet.2005.06.119.

Cornils, B., & Herrmann, W. A. (Eds.) (2005). Aqueous-phase organometallic catalysis: Concepts and applications (2nd ed.). Weinheim, Germany: Wiley-VCH. DOI: 10.1002/3527602488.

Danopoulos, A. A., Tulloch, A. A. D., Winston, S., Eastham, G., & Hursthouse, M. B. (2003). Chelating and 'pincer' dicarbene complexes of palladium; synthesis and structural studies. *Dalton Transactions*, *2003*, 1009–1015. DOI: 10.1039/b209739g.

Dash, C., Shaikh, M. M., & Ghosh, P. (2009). Fluoride-free Hiyama and copper- and amine-free Sonogashira coupling in air in a mixed aqueous medium by a series of PEPPSI-themed precatalysts. *European Journal of Inorganic Chemistry*, *2009*, 1608–1618. DOI: 10.1002/ejic.200900115.

Flahaut, A., Baltaze, J. P., Roland, S., & Mangeney, P. (2006). Synthesis of chiral imino- and amino-imidazolium salts and of chelating amino-*N*-heterocyclic carbene palladium(II) complexes. *Journal of Organometallic Chemistry*, *691*, 3498–3508. DOI: 10.1016/j.jorganchem.2006.04.038.

Giraud, A., Provot, O., Hamzé, A., Brion, J. D., & Alami, M. (2008). One-pot hydrosilylation–protodesilylation of functionalized diarylalkynes: a highly selective access to *Z*-stilbenes. Application to the synthesis of combretastatin A-4. *Tetrahedron Letters*, *49*, 1107–1110. DOI: 10.1016/j.tetlet.2007.12.057.

Heckenroth, M., Neels, A., Stoeckli-Evans, H., & Albrecht, M. (2006). Synthesis and structural analysis of palladium biscarbene complexes derived from bisimidazolium ligand precursors. *Inorganica Chimica Acta*, *359*, 1929–1938. DOI: 10.1016/j.ica.2005.10.045.

Herrmann, W. A. (2002). N-Heterocyclic carbenes: A new concept in organometallic catalysis. *Angewandte Chemie International Edition*, *41*, 1290–1309. DOI: 10.1002/1521-3773(20020415)41:8<1290::AID-ANIE1290>3.0.CO;2-Y.

Hoshino, M., Degenkolb, P., & Curran, D. P. (1997). Palladium-catalyzed Stille couplings with fluorous tin reactants. *The Journal of Organic Chemistry*, *62*, 8341–8349. DOI: 10.1021/jo9709413.

Inamoto, K., Kuroda, J. I., Kwon, E., Hiroya, K., & Doi, T. (2009). Pincer-type bis(carbene)-derived complexes of nickel(II): Synthesis, structure, and catalytic activity. *Journal of Organometallic Chemistry*, *694*, 389–396. DOI: 10.1016/j.jorganchem.2008.11.003.

Islam, S. M., Mondal, P., Roy, A. S., Mondal, S., & Hossain, D. (2010). Heterogeneous Suzuki and copper-free Sonogashira cross-coupling reactions catalyzed by a reusable palladium(II) complex in water medium. *Tetrahedron Letters*, *51*, 2067–2070. DOI: 10.1016/j.tetlet.2010.02.079.

Jafarpour, L., & Nolan, S. P. (2000). Transition-metal systems bearing a nucleophilic carbene ancillary ligand: from thermochemistry to catalysis. *Advances in Organometallic Chemistry*, *46*, 181–222. DOI: 10.1016/s0065-3055(00)46004-1.

Koukal, P., Dvořáková, H., Dvořák, D., & Tobrman, T. (2013). Palladium-catalysed Claisen rearrangement of 6-allyloxypurines. *Chemical Papers*, *67*, 3–8. DOI: DOI: 10.2478/s11696-012-0239-y.

Kumar, S., Shaikh, M. M., & Ghosh, P. (2009). Palladium complexes of amido-functionalized N-heterocyclic carbenes as effective precatalysts for the Suzuki–Miyaura C–C cross-coupling reactions of aryl bromides and iodides. *Journal of Organometallic Chemistry*, *694*, 4162–4169. DOI: 10.1016/j.jorganchem.2009.09.011.

Li, F., & Hor, T. S. A. (2008). Benzimidazolium-pyrazole-palladium(II) complexes: New and efficient catalysts for Suzuki, Heck and Sonogashira reactions. *Advanced Synthesis & Catalysis*, *350*, 2391–2400. DOI: 10.1002/adsc.200800356.

Lin, I. J. B., & Vasam, C. S. (2007). Preparation and application of N-heterocyclic carbene complexes of Ag(I). *Coordination Chemistry Reviews*, *251*, 642–670. DOI: 10.1016/j.ccr.2006.09.004.

Lu, J. M., Ma, H., Li, S. S., Ma, D., & Shao, L. X. (2010). 2,2′-Diamino-6,6′-dimethylbiphenyl as an efficient ligand in the palladium-catalyzed Suzuki–Miyaura and Mizoroki–Heck reactions. *Tetrahedron*, *66*, 5185–5189. DOI: 10.1016/j.tet.2010.04.099.

Mata, J. A., Poyatos, M., & Peris, E. (2007). Structural and catalytic properties of chelating bis- and tris-*N*-heterocyclic carbenes. *Coordination Chemistry Reviews*, *251*, 841–859. DOI: 10.1016/j.ccr.2006.06.008.

Molander, G. A., & Biolatto, B. (2003). Palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of potassium aryl- and heteroaryltrifluoroborates. *The Journal of Organic Chemistry*, *68*, 4302–4314. DOI: 10.1021/jo0342368.

Molander, G. A., & Iannazzo, L. (2011). Palladium-catalyzed Hiyama cross-coupling of aryltrifluorosilanes with aryl and heteroaryl chlorides. *The Journal of Organic Chemistry*, *76*, 9182–9187. DOI: 10.1021/jo201840n.

Nair, V., Bindu, S., & Sreekumar, V. (2004). N-Heterocyclic carbenes: Reagents, not just ligands! *Angewandte Chemie International Edition*, *43*, 5130–5135. DOI: 10.1002/anie.200301714.

Nandurkar, N. S., Bhanushali, M. J., Bhor, M. D., & Bhanage, B. M. (2007). N-Arylation of aliphatic, aromatic and heteroaromatic amines catalyzed by copper bis(2,2,6,6-tetramethyl-3,5-heptanedionate). *Tetrahedron Letters*, *48*, 6573–6576. DOI: 10.1016/j.tetlet.2007.07.009.

Nandurkar, N. S., & Bhanage, B. M. (2008). Palladium bis(2,2,6,6-tetramethyl-3,5-heptanedionate) catalyzed Suzuki, Heck, Sonogashira, and cyanation reactions. *Tetrahedron*, *64*, 3655–3660. DOI: 10.1016/j.tet.2008.02.038.

Negishi, E. I. (Ed.) (2003). *Handbook of organopalladium chemistry for organic synthesis*. New York, NY, USA: Wiley. DOI: 10.1002/0471212466.

Patil, S. A., Weng, C. M., Huang, P. C., & Hong, F. E. (2009). Convenient and efficient Suzuki–Miyaura cross-coupling reactions catalyzed by palladium complexes containing *N*, *N*,*O*-tridentate ligands. *Tetrahedron*, *65*, 2889–2897. DOI: 10.1016/j.tet.2009.02.017.

Phan, N. T. S., & Le, H. V. (2011). Superparamagnetic nanoparticles-supported phosphine-free palladium catalyst for the Sonogashira coupling reaction. *Journal of Molecular Catalysis A: Chemical*, *334*, 130–138. DOI: 10.1016/j.molcata.2010.11.009.

Ray, L., Barman, S., Shaikh, M. M., & Ghosh, P. (2008). Highly convenient amine-free Sonogashira coupling in air in a polar mixed aqueous medium by *trans*- and *cis*-$[(\mathrm{NHC})_2\mathrm{PdX}_2]$ (X = Cl, Br) complexes of *N*/*O*-functionalized N-heterocyclic carbenes. *Chemistry - A European Journal*, *14*, 6646–6655. DOI: 10.1002/chem.200800301.

Reddy, K. R., Kumar, N. S., Reddy, P. S., Sreedhar, B., & Kantam, M. L. (2006). Cellulose supported palladium(0) catalyst for Heck and Sonogashira coupling reactions. *Journal of Molecular Catalysis A: Chemical*, *252*, 12–16. DOI: 10.1016/j.molcata.2006.02.024.

Stauffer, S. R., Lee, S., Stambuli, J. P., Hauck, S. I., & Hartwig, J. F. (2000). High turnover number and rapid, room-temperature amination of chloroarenes using saturated carbene ligands. *Organic Letters*, *2*, 1423–1426. DOI: 10.1021/ol005751k.

Tudose, A., Maj, A., Sauvage, X., Delaude, L., Demonceau, A., & Noels, A. F. (2006). Synthesis of stilbenoids via the Suzuki–Miyaura reaction catalysed by palladium *N*-heterocyclic carbene complexes. *Journal of Molecular Catalysis A: Chemical*, *257*, 158–166. DOI: 10.1016/j.molcata.2006.04.064.

Wanzlick, H. W., & Schönherr, H. J. (1968). Direct synthesis of a mercury salt-carbene complex. *Angewandte Chemie International Edition in English*, *7*, 141–142. DOI: 10.1002/anie.196801412.

Weskamp, T., Böhm, V. P. W., & Herrmann, W. A. (1999). Combining *N*-heterocyclic carbenes and phosphines: improved palladium(II) catalysts for aryl coupling reactions. *Journal of Organometallic Chemistry*, *585*, 348–352. DOI: 10.1016/s0022-328x(99)00237-5.

Yang, F., Cui, X., Li, Y., Zhang, J., Ren, G., & Wu, Y. (2007). Cyclopalladated ferrocenylimines: efficient catalysts for homocoupling and Sonogashira reaction of terminal alkynes. *Tetrahedron*, *63*, 1963–1969. DOI: 10.1016/j.tet.2006.12.064.

Yasuda, N. (2002). Application of cross-coupling reactions in Merck. *Journal of Organometallic Chemistry*, *653*, 279–287. DOI: 10.1016/s0022-328x(02)01263-9.

Zhang, B. S., Wang, C., Gong, J. F., & Song, M. P. (2009). Facile synthesis of achiral and chiral PCN pincer palladium(II) complexes and their application in the Suzuki and copper-free Sonogashira cross-coupling reactions. *Journal of Organometallic Chemistry*, *694*, 2555–2561. DOI: 10.1016/j.jorganchem.2009.04.002.