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Pd-*N*-Heterocyclic carbene catalysed Suzuki-Miyaura coupling reactions in aqueous medium

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Dedicated to Prof. Kenneth K. Laali on the occasion of his 65th anniversary

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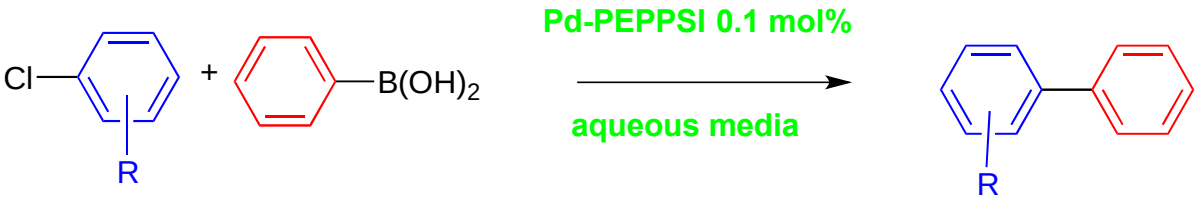
Abstract

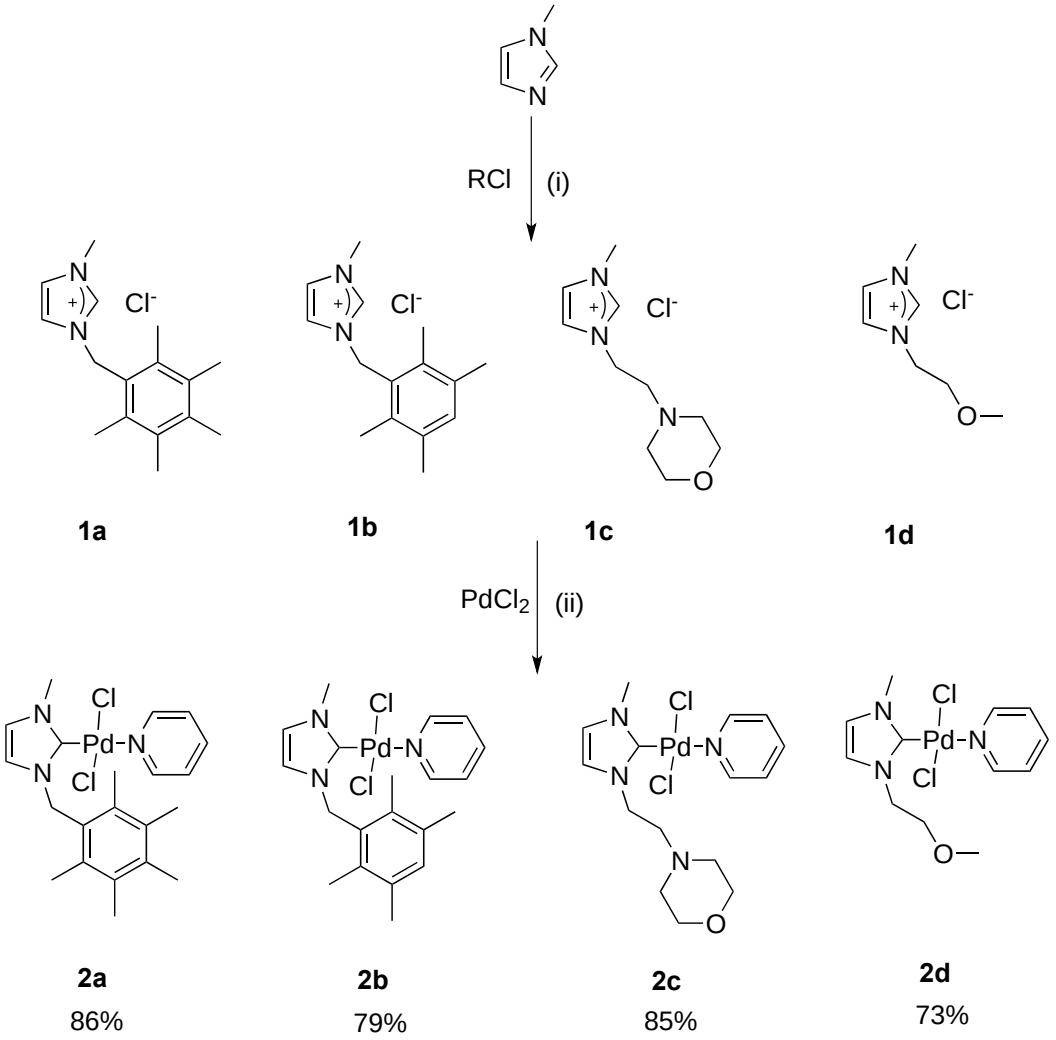
A new series of methyl substituted imidazole-based *N*-heterocyclic carbene (NHC) palladium complexes ($PdCl_2(L^1)NHC(L^1$ =pyridine) is reported. Structural definitions of Pd-PEPPSI complexes were determined by NMR spectroscopy, elemental analysis and LC-MS spectroscopy techniques. To evolve a more efficient catalytic system for electronically different aryl chloride substrates on the Suzuki cross-coupling reaction, complexes were used as pre-catalyst. Activity of palladium(II)-NHC complexes screened under mild reaction conditions in aqueous media. With this catalytic system, the reaction proceeded in moderate or good yields with low catalyst loading (0.1 mol%).



Keywords: Suzuki-Miyaura cross-coupling reaction, *N*-heterocyclic carbene, Pd-PEPPSI complex, C-C bond formation

Introduction

The development of *N*-heterocyclic carbenes (NHC) and their different metal complexes has provided a new approach in homogeneous catalysis.[1] With these developments, numerous metal-NHC complexes with the inclusion of Ag,[2] Ru,[3] Ir,[4] Rh,[5] and Pd [6] have been prepared. Although there are numerous metal complexes of NHCs, Pd-NHC complexes have particular importance due to their robustness regarding air, moisture and high temperature. The basis of this interest lies in strong σ-donor and weak π-acceptor ability and the ease of adjusting the steric effects of NHC by nitrogen atoms. Complexes bearing sterically bulky and electron-rich ligands show enhanced catalytic activity in oxidative addition and reductive elimination reactions, which are key steps of many catalytic reactions using homogeneous catalysts.[7-9] These unique features make these compounds indispensable strong ligands for transition metals and homogeneous catalytic systems.[10-14] Organ at al. synthesized different types of palladium *N*-heterocyclic carbene PEPPSI complexes (PEPSSI=**P**yridine-**E**nhanced **P**re-catalyst **P**reparation **S**tabilization (and) **I**nitiation) in 2006.[15] Then, couple studies were reported by Doucet, Matt and Cavell groups.[16-18] Following these studies, PEPPSI complexes have been extensively studied, and it has been reported that these complexes exhibit very good catalytic and biological activity.[19-26]



Scheme 1. Synthesis method of un-symmetrical imidazole based-NHC precursors and their Pd-PEPPSI complexes: (i) THF, reflux; (ii) K_2CO_3, pyridine, 80 °C.

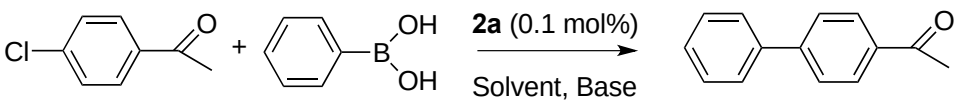
The Suzuki coupling reaction is one of the most preferred reactions for C-C bond formation reactions due to the mild reaction conditions. Capretta et al. reported the first NHC-based Suzuki protocol.[27] Recently, important advanced studies in the field of well-defined and air-stable palladium-NHC complex-catalyzed Suzuki-Miyaura reactions were published by Glorius,[28] Beller,[29] Herrmann,[30] Nolan,[31] Organ,[32] and others.[11,33-38] However, most of these catalytic systems are need to optimise due to the requirement for hazardous solvents, harsh reaction conditions and high catalyst loading. Catalytic systems that use water as the solvent are inherently safer processes, and offer significant advantages.[39] For example, the poor solubility of Suzuki products in water is one of the advantages of this type system because of simplify separation of the desired products from the reaction medium. Considering these important points, to demonstrate the usefulness of electron-rich imidazol based palladium complexes **2a-d**, we investigated the catalytic performance of the compounds as co-catalysts in Suzuki-Miyaura coupling reactions in aqueous media.

Result and Discussion

The imidazole-based NHC precursors **1a-d** were synthesized according to the literature (Scheme 1) and the spectroscopic data of **1a-d** were consistent with the corresponding literature.[40,41] Pd-PEPPSI complexes **2a-d** were synthesized using Organ's method (Scheme 1), i.e. the reaction of NHCs **1a-d** with $PdCl_2$ in pyridine at 80 ^oC in the presence of K_2CO_3, to provide the NHC palladium complexes **2a-d** in 86%, 79%, 85%, 73% respectively. The $^{13}C\{^1H\}$ NMR spectra provide information on complex formation, for example an increasing downfield shift of the N*C*N carbon from **1a-d** to **2a-d**; i.e. the $^{13}C\{^1H\}$ N-C-N shifts of **1a-d** and **2a-d** were 137.5 and 152.5 ppm, 137.2 and 151.3 ppm, 137.3 and 161.2 ppm, and 137.7 and 151.2 ppm, respectively**.**

In the first instance, to find the optimum conditions for the Suzuki coupling reaction, an extensive screening of the reaction conditions was carried out using common mineral bases with different solvent variations under standard conditions. To assess the influence of the solvent, we used 4-chloroacetophenone as the substrate and K_2CO_3 as the base (**2a:**1 mol%, 4-chloroacetophenone (1 mmol), $PhB(OH)_2$ (1.5 mmol), 80 ^oC, 3h). In all cases, the reactions were heated for 3h at 80 ^oC. After several reactions, the results showed that this catalytic system is effective with all solvents and bases, but the best one is K_2CO_3-DMF/H_2O. The optimum yield was obtained with the most polar solvents in an equal ratio of DMF/H_2O. The results are summarized in Table 1, entries 1-12. These optimum results were attributed to water due to its high polarity and the good solubility of the base in water. Solubility of the base is important to generate water-soluble aryl boronate derivatives.[42] The use of pure DMF, H_2O, *i*-PrOH or 1,4-dioxane afforded lower yields than the use of a mixture of DMF and water in equal proportions.

Table 1. The effect of solvent and base on yield in the Suzuki coupling reaction[a]



Entry	Solvent	Base(eq)	Yield [%]
1	Dioxane(6 mL)	Na_2CO_3 (2)	60
2	Dioxane (6 mL)	K_2CO_3 (2)	75
3	Dioxane(6 mL)	Cs_2CO_3 (2)	30
4	*i*-PrOH	Na_2CO_3 (2)	50
5	*i*-PrOH	K_2CO_3 (2)	52

Table 1. Continued

Entry	Solvent	Base(eq)	Yield [%]
6	*i*-PrOH	Cs_2CO_3 (2)	33
7	DMF (6 mL)	K_2CO_3 (2)	69
8	DMF/H_2O (4/2 mL)	K_2CO_3 (2)	74
9	DMF/H_2O (3/3 mL)	K_2CO_3 (2)	98
10	DMF/H_2O (2/4 mL)	K_2CO_3 (2)	88
11	H_2O (6 mL)	K_2CO_3 (2)	10
12	DMF/H_2O (3/3 mL)	Na_2CO_3 (2)	70
13	DMF/H_2O (3/3 mL)	Cs_2CO_3 (2)	45

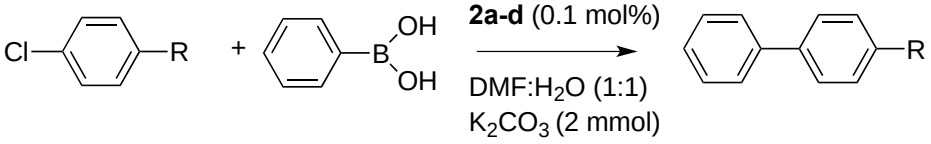
[a] Reaction conditions: **2a** (0.1 mol%), 4-chloroacetophenone (1 mmol), $Ph(OH)_2$ (1.5 mmol), 80 ^oC, 3 h.

This catalytic system led to the investigation of cheap and abundant sodium and potassium carbonate bases that have poor solubility, except in water. All carbonate bases resulted in sufficient conversions, but potassium carbonate demonstrated significantly better performance (Table 1, entry 9, 10).

Catalytic data are available in the literature for the Suzuki coupling reaction catalyzed by Pd-NHC derived complexes in a variety of different conditions.[43-45] Therefore, it is hard to make a comparison of palladium catalysts, but we can make a provisional comparison with the Organ system ((Pd-PEPPSI**:** 2 mol %, chloroanisole (1 mmol), $PhBF_3K$ (1.0 mmol), 60^oC, 24h, MeOH) in the Suzuki-Miyaura reaction.[15]

A series of activated and non-activated aryl chloride substrates with phenylboronic acid was used under the optimized conditions described above (Table 2). The results show that complexes **2a-d** were sufficiently active catalysts in the Suzuki coupling reaction, similar to Organ's catalyst under similar reaction conditions. When catalytic activity of **2a-d** was compared in the Suzuki coupling reaction, complex **2a** gave the best results, in almost each case with different substrates except in the case of chlorobenzene. We attributed these performance differences to the electron richness of **2a**. It is known that electron rich Pd-complexes undergo oxidative additions more readily. Also, the steric effect of the catalyst facilitates the reductive elimination of the product from the active catalyst. The general opinion on this issue is that, the steric and electronic properties need to be equipoise to create a highly active catalyst system.[28, 43, 46,47]

Table 2. The Suzuki coupling reaction of aryl chlorides[a]



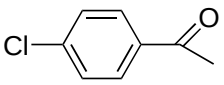
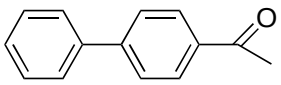
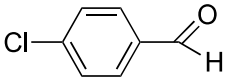
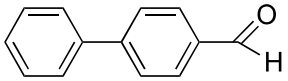
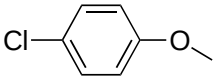
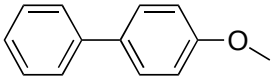
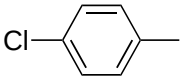
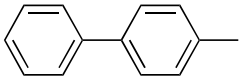
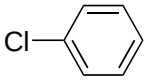
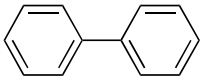
Entry	Aryl chloride	Product	Pd-NHC	Yield [%]
1			-	1
2			**2a**	94
3			**2b**	86
4			**2c**	92
5			**2d**	90

Table 2. Continued

Entry	Aryl chloride	Product	Pd-NHC	Yield [%]
6			-	3
7			**2a**	98
8			**2b**	94
9			**2c**	89
10			**2d**	84
11			-	0
12			**2a**	85
13			**2b**	79
14			**2c**	71
15			**2d**	69
16			-	1
17			**2a**	82
18			**2b**	75
19			**2c**	69
20			**2d**	72
21			-	2
22			**2a**	94
23			**2b**	98
24			**2c**	80
25			**2d**	88

[a] Reaction conditions: 1.0 mmol of *p*-R–C_6H_4Cl, 1.5 mmol of phenylboronic acid, 2 mmol K_2CO_3, 0.1 mol% Pd-NHC (**2a-d)**, water (3 ml)–DMF (3 ml), 80 ^oC, 3 h.

The efficiency of our catalytic system is better than the literature[48-50] within the meaning of the catalyst loading and aryl chloride substrates.

Conclusions

Herein, we reported synthesize and define highly active, easy to produce and environmentally friendly new Pd-PEPPSI complexes. Due to the structure of the Pd-PEPPSI complexes, the carbene remains electron-rich upon coordination to palladium, which makes the palladium-carbon bond strong and stable. This outstanding property of Pd-PEPPSI complexes creates advantages over other complexes in catalytic cross-coupling reactions. The catalytic activity of **2a-d** was moderate and encouraged us to synthesize additional Pd complexes that are electronically and structurally different previously reported Pd-PEPPSI complexes.

Experimental Section

General. Unless stated otherwise, all procedures were carried out under a normal air atmosphere. Chemicals and solvents were purchased from Sigma Aldrich Co. (Dorset, UK) and used without any purification. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 400 operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$. Coupling constants (*J* values) are given in Hertz. NMR multiplicities are abbreviated as follows: s= singlet, d= doublet, t= triplet, m= multiplet, bs= broad singlet. Melting points were detected by Stuart automatic melting point apparatus (SMP-40).

General preparation of 1-methyl-3-alkylimidazolium salts

These known compounds were synthesized *according to literature* [40] and characterized by m.p, ^{1}H and ^{13}C NMR and micro analyses.

1-methyl-3-(2,3,4,5,6-penthamethylbenzyl)imidazolium chloride (1a). This known compound was synthesized *according to literature.*[40]

1-methyl-3-(2,3, 5,6-tetramethylbenzyl)imidazolium chloride (1b). This known compound was synthesized *according to literature.*[40]

1-methyl-3-(2-morpholinoethyl)imidazolium chloride (1c). Yield: 90%. m.p: 132-133 ^{o}C. ^{1}H NMR (399.9 MHz, DMSO-d_6,25 ^{o}C): δ=9.24 [s, 1H, NC***H***N], 7.79 [s, 1H, NC***H***CHN], 7.72 [s, 1H, NCHC***H***N], 4.31 [t, *J=8* Hz, 2H, C***H₂***$CH_2N(CH_2CH_2)_2O$], 3.89 [s, 3H, NC***H₃***], 3.55 [t, *J=4* Hz, 4H $CH_2CH_2N(CH_2C$***H₂***$)_2O$] 2.68 [t, *J=8* Hz, 2H, CH_2C***H₂***$N(CH_2CH_2)_2O$], 2.42 [t, *J=4* Hz, 4H $CH_2CH_2N(C$***H₂***$CH_2)_2O$]. ^{13}C NMR (100 MHz, DMSO-d_6,25 ^{o}C): δ=137.3, 123.6, 123.2, 67.5, 57.3, 53.3, 46.0, 36.2.

1-methyl-3-(2-methoxyethyl)imidazolium chloride (1d). This known compound was synthesized *according to literature.*[40]

Preparation of the NHC-palladium-pyridine (PEPPSI) complexes 2a-d

In air, a pressure tube was charged with $PdCl_2$ (180 mg, 1 mmol), **1a-d** (1.1 mmol), K_2CO_3 (700 mg, 5 mmol) and 3 mL of pyridine. The reaction mixture was heated with vigorous stirring for 17 h at 80 ^{o}C then cooled to room temperature and diluted with dichloromethane (DCM). A short silica column was used for purification. All volatiles were evaporated. The yellow solid residue was washed with hexane (2x10 mL) and diethyl ether (2x10 mL). The crystalline yellow solid was used in the Suzuki reaction as obtained.

Dichloro[1-methyl-3-(2,3,4,5,6-penthamethylbenzyl)imidazol-2-ylidene]pyridine palladium(II) (2a). Yield: 86%. m.p: 225.1 ^{o}C. ^{1}H NMR (399.9 MHz, DMSO-d_6, 25 ^{o}C): δ= 2.17 [s, 6H, $CH_2C_6(C$***H₃***$)_5$-2,3,4,5,6], 2.19 s, 6H, $CH_2C_6(C$***H₃***$)_5$-2,3,4,5,6], 2.22 [s, 3H, $CH_2C_6(C$***H₃***$)_5$-2,3,4,5,6], 4.02 [s, 3H, NCH_3], 5.63 [s, 2H, C***H***$_2C_6(CH_3)_5$-2,3,4,5,6], 6.36 [s, 1H, NC***H***CHN], 7.28 [s, 1H, NC***H***CHN], 7.56, 7.99 and 8.92 [m, 5H, NC_5***H₅***]. ^{13}C NMR (100 MHz, DMSO, 25 ^{o}C): δ= 17.0, 17.1, 17.4, 38.2, 50.4, 120.4, 123.9, 125.4, 127.7, 133.1, 134.0, 135.9, 139.1, 147.0, 151.9, 152.5 Anal. Calcd. for $C_{21}H_{27}Cl_2N_3Pd$: C,50.57; H, 5.46; N, 8.42 Found: C, 50.68; H, 5.60, N, 8.63. LC-MS (ESI): *m/z* 427.7 [M-2Cl].

Dichloro[1-methyl-3-(2,3,5,6-tetramethylbenzyl)imidazol-2-ylidene]pyridine palladium(II) (2b). Yield: 79%. m.p: 202.5 ^{o}C. ^{1}H NMR (399.9 MHz, $CDCl_3$, 25 ^{o}C): δ= 2.25 and 2.28 [s, 12H, $CH_2C_6H(C$***H₃***$)_4$-2,3,5,6], 4.20 [s, 3H, NCH_3], 5.88 [s, 2H, $CH_2C_6H(C$***H₃***$)_4$-2,3,5,6], 6.33 and 6.79 [s, 2H, NC***H***C***H***N], 7.06 [s, 1H, CH_2C_6***H***$(CH_3)_4$-2,3,5,6], 7.40 [m, 2H, NC_5***H₅***], 7.81 [m, 1H, NC_5***H₅***], 9.08 [m, 2H, NC_5***H₅***]. ^{13}C NMR (100 MHz, DMSO, 25 ^{o}C): δ= 15.9, 20.5, 38.0, 49.7, 120.2, 122.2, 123.7, 124.5, 130.2, 132.5, 134.4, 134.7, 135.9, 138.0, 148.5, 149.9, 151.3 Anal. Calcd for $C_{20}H_{25}Cl_2N_3Pd$: C,49.55; H, 5.20; N, 8.67 Found: C, 49.59; H, 5.28, N, 8.78. LC-MS (ESI): *m/z* 411.3 [M-2Cl+2H^{-}].

Dichloro[1-methyl-3-(2-morpholinoethyl)imidazol-2-ylidene]pyridine palladium(II) (2c). Yield: 85%. m.p: 185.3 ^{o}C. ^{1}H NMR (399.9 MHz, DMSO-d_6, 25 ^{o}C): δ= 2.51 [bs, 8H, $CH_2CH_2(N(C\boldsymbol{H_2}CH_2)_2O]$, 2.97 [t, *J*=6.4 Hz, 2H, $CH_2C\boldsymbol{H_2}(N(CH_2CH_2)_2O]$, 3.56 [t, *J*=4.4 Hz, 4H, $CH_2CH_2(N(CH_2C\boldsymbol{H_2})_2O]$, 4.03 [s, $NC\boldsymbol{H_3}$], 4.54 [t, *J*=6.4 Hz, 2H, $C\boldsymbol{H_2}CH_2(N(CH_2CH_2)_2O]$, 7.37 and 7.40 [s, 2H, NC***H***C***H***N], 7.57 [m, 2H, $NC_5\boldsymbol{H_5}$], 8.01 [m, 1H, $NC_5\boldsymbol{H_5}$], 8.82 [m, 2H, $NC_5\boldsymbol{H_5}$]. ^{13}C NMR (100 MHz, DMSO, 25 ^{o}C): δ=44.3, 52.0, 57.2, 65.9, 109.6, 120.2, 122.5, 133.7, 137.5, 150.1, 161.2. Anal. Calcd. for $C_{15}H_{22}Cl_2N_4OPd$: C, 39.89, H, 4.91, N, 12.40. Found: C, 39.98; H, 5.02; N, 12.66. LC-MS (ESI): *m/z* 450.12 [MH^-].

Dichloro[1-methyl-3-(2-methoxyethyl)imidazol-2-ylidene]pyridine palladium(II) (2d). Yield: 73%. m.p: 176.9 ^{o}C. ^{1}H NMR (399.9 MHz, $CDCl_3$, 25 ^{o}C): δ= 3.38 [s, 3H, $CH_2CH_2(OC\boldsymbol{H_3})$], 3.98 [t, *J*= 5.2 Hz, 2H, $CH_2C\boldsymbol{H_2}(OCH_3)$], 4.17 [s, 3H, NCH_3], 4.76 [t, *J*=5.2 Hz, 2H, $C\boldsymbol{H_2}CH_2(OCH_3)$], 6.9 and 7.11 [s, 2H, NC***H***C***H***N], 7.38, 7.80 and 9.00 [m, 5H, $NC_5\boldsymbol{H_5}$]. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ= 37.9, 50.9, 59.0, 71.9, 122.6, 123.4, 124.5, 151.2. Anal. Calcd. for $C_{12}H_{17}Cl_2N_3OPd$: C, 36.34; H, 4.32; N, 10.59. Found: C, 36.44; H, 4.45; N, 10.78. LC-MS (ESI): *m/z* 653.3 [2M-4Cl+$2H^+$].

General procedure for Suzuki Cross-Coupling reaction

In air, **2a-d** (0.1 mol%, aryl chloride (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and 3 mL of a mixture of water and DMF (1:1) were added to a small round-bottom flask and the mixture was heated at 80 ^{o}C for an appropriate period of time. The reaction mixture was cooled to room temperature and 10 mL of water was added to the reaction mixture and extracted with Et_2O. The organic phase was dried with $MgSO_4$ and filtrated by short chromatography on silica gel column. Then volatiles were removed under reduced pressure and yield distribution was determined by GC using undecane as internal standard. The yields are based on corresponding aryl chlorides. All catalytic reactions were duplicated. All coupling products obtained via Suzuki-Miyaura coupling reaction are previously reported compounds, and were identified by comparison of our data with that available in the literature.

Acknowledgements

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References

1. Gonzalez, S. D.; Marion, N.; Nolan, S. P. *Chem. Rev*. **2009**, *109*, 3612. http://dx.doi.org/10.1021/cr900074m
2. Fremont, P. D.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonal, C. L. B.; Clyburne, C. D. Abernethy, J. A. C.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301. https://dx.doi.org/10.1021/om050735i
3. Şahin, Z.; Gürbüz, N.; Özdemir, İ.; Şahin, O.; Büyükgüngör, O.; Achard, M.; Bruneau, C. *Organometallics*, **2015**, *34*, 2296. https://dx.doi.org/10.1021/om501066n
4. Raible, B.; Gierz, V.; Kunz, D. *Organometallics,* **2015**, *34*, 2018. https://dx.doi.org/10.1021/acs.organomet.5b00267

5. Palacios, L.; Giuseppe, A. D.; Castarlenas, R.; Lahoz, F. J.; Perez, J. J. T.; Oro, L. A. *Dalton. Trans*., **2015**, *44*, 5777.
https://dx.doi.org/10.1039/c5dt00182j
6. M. S.; Viciu, R. F.; Germaneau, and S. P. Nolan, *Org Lett*. **2002**, *4*, 4053.
https://dx.doi.org/10.1021/ol026745m
7. Boubakri, L.; Yaşar, S.; Dorcet, V.; Roisnel, T.; Bruneau, C.; Hamdi, N,; Özdemir, İ. *New. J. Chem.* **2017**, *41*, 5105.
https://dx.doi.org/10.1039/c7nj00488e
8. Littke, A. F.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.
http://dx.doi.org/10.1002/1521-3773(20021115)41:22<4176::AID-ANIE4176>3.0.CO;2-U
9. Hartwig, J. F. *Synlett* **2006**, 1283.
https://dx.doi.org/10.1055/s-2006-939728
10. Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
http://dx.doi.org/10.1002/1521-3773(20020415)41:8<1290::AID-ANIE1290>3.0.CO;2-Y
11. Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440.
https://dx.doi.org/10.1021/ar800020y
12. Herrmann, W. A.; Öfele, K.; Preysing, D. V.; Schneider, K. S. *J. Organomet. Chem.* **2003**, *687*, 229.
https://doi.org/10.1016/j.jorganchem.2003.07.028
13. González, S. D.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874.
https://doi.org/10.1016/j.ccr.2006.10.004
14. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev*. **2000**, *100*, 39.
https://dx.doi.org/10.1021/cr940472u
15. Brien, C. C. O.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J.* **2006**, *12*, 4743.
https://dx.doi.org/10.1002/chem.200600251
16. Karaca, E. Ö.; Gürbüz, N.; Özdemir, İ.; Doucet, H.; Şahin, O.; Büyükgüngör, O.; Çetinkaya, B. *Organometallics* **2015**, *34*, 2487.
https://dx.doi.org/10.1021/om501201r
17. Teci, M.; Brenner, E.; Matt, D.; Toupet, L. *Eur. J. Inorg. Chem*, **2013**, 2841.
http://dx.doi.org/10.1002/ejic.201300087
18. Dunsford, J. J.; Cavell, K. J. *Organometallics* **2014**, *33*, 2902.
https://dx.doi.org/10.1021/om5003107
19. Kaloğlu, M; Özdemir, İ.; Dorcet, V.; Bruneau, C.; Doucet, H. *Eur. J. Inorg. Chem*, **2017**, 1382
https://dx.doi.org/10.1002/ejic.201601452
20. Benhamou, L.; Besnard, C.; Kündig, P.E. *Organometallics*, **2014**, *33*, 260.
https://dx.doi.org/10.1021/om4009982
21. Osinska, M.; Gniewek, A.; Trzeciak, A. M. *J. Mol. Cat. A:Chemical*, **2016**, *418-419*, 9.
https://doi.org/10.1016/j.molcata.2016.03.022
22. Luconi, L.; Gafurov, Z.; Rossin, A.; Tuci, G.; Sinyashin, O.; Yakhvarov, D.; Giambastiani, G. *Inorg. Chem. Acta.* 2018, *470*, 100.
23. http://dx.doi.org/10.1016/j.ica.2017.03.026
Boubakri, L.; Mansour, L.; Harrath, A. H.; Özdemir, İ.; Yaşar, S.; Hamdi, *J. Coord. Chem.*, **2018**, *71*,183.
https://dx.doi.org/10.1080/00958972.2018.1430791

24. Sevaa,L.; Hwang, W.-S.; Sabiah, S. *J. Mol. Cat. A:Chemical*, **2016**, *418-419*, 125. http://dx.doi.org/10.1016/j.molcata.2016.03.032
25. Akkoç, S.; Gök, Y.; İlhan, Ö.İ.; Kayser, V. *Beilstein J. Org. Chem.* **2016,** *12,* 81. http://dx.doi.org/10.3762/bjoc.12.9
26. Boubakri, L.; Chakchouk-Mtibaa, A.; Hallouma, B.; Mansour, L. ; Mellouli, L.; Özdemir, İ.; Yaşar, S.; Hamdi, N. *Molecules* **2017**, *22*(3), 420. http://dx.doi.org/10.3390/molecules22030420
27. Brenstrum, T.; Gerristma, D. A.; Adjabeng, G. M.; Frampton, C. S.; Britten, J.; Robertson, A. J.; Nulty, J. M.; Capretta, A. *J. Org. Chem.* **2004**, *69*, 7635. https://dx.doi.org/10.1021/jo048875+
28. Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195. https://dx.doi.org/10.1021/ja045349r
29. Harkal, S.; Rataboul, F.; Zapf, A.; Fuhrmann, C.; Riermeier, T.; Monsees, A.; Beller, M. *Adv. Synth. Catal*. **2004**, *346*, 1742. https://dx.doi.org/10.1002/adsc.200404213
30. Schneider, S. K.; Roembke, P.; Julius, G. R.; Raubenheimer, H. G.; Herrmann, W. A. *Adv. Synth. Catal.* **2006**, *348*,1862. https://dx.doi.org/10.1002/adsc.200606009
31. Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804. https://dx.doi.org/10.1021/jo990554o
32. Kantchev, E. A. B.; Brien, C. J. O.; Organ, M. G. *Angew. Chem.* **2007**, *119*, 2824.
33. Rajabi, F.; Thiel, W. R. *Adv. Synth. Catal.,* **2014**, *356*, 1873. http://dx.doi.org/10.1002/adsc.201300841
34. Kantchev, E. A. B.; Brien, J. O.; Organ, M. G. *Angew. Chem. Int. Ed*., **2007**, *46*, 2768. http://dx.doi.org/10.1002/anie.200601663
35. Sydnes, M.O.; *Catalysts*, **2017**, *7(1)*, 35. http://dx.doi.org/10.3390/catal7010035
36. Katia, M.; Manzoli, M.; Gaudino, E. C.; Cravatto, G. *Catalysts,* **2017**, *7(4)*, 98. http://dx.doi.org/10.3390/catal7040098
37. Zapf, A.; Beller, M. *Chem. Commun.* **2005**, 431. http://dx.doi.org/10.1039/B410937F
38. Selvakumar, K.; Zapf, A.; Beller, M. *Org. Lett.* **2002**, *4*, 3031. https://dx.doi.org/10.1021/ol020103h
39. Schmidt, B.; Riemer, M. *J. Org. Chem.* **2013**, *78*, 8660. https://dx.doi.org/10.1021/jo401398n
40. Yaşar, S.; Karaca, E. Ö.; Şahin, Ç.; Özdemir, İ.; Şahin, O.; Büyükgüngör, O. *J. Organomet. Chem.* **2015**, *790,* 1. https://doi.org/10.1016/j.jorganchem.2015.04.012
41. Yaşar, S.; Çekirdek, S.; Özdemir, İ. *J. Coord. Chem.* **2014**, *67*, 1236. https://doi.org/10.1080/00958972.2014.911291
42. Akkoç, M.; İmik, F.; Yaşar, S.; Dorcet, V.; Roisnel, T.; Bruneau, C.; Özdemir, İ. *Chemistry Select* **2017**, *2*, 5729. http://dx.doi.org/10.1002/slct.201701354

43. Diebolt, O.; Braunstein, P.; Nolan, S. P.; Cazin, C. S. J. *Chem. Commun.* **2008**, 3190. http://dx.doi.org/10.1039/B804695F
44. Tang, Y.-Q.; Lu, J.-M.; Shao, L. -X. *J. Organomet. Chem.* **2011**, *696*, 3741. https://doi.org/10.1016/j.jorganchem.2011.08.042
45. Karimi, B.; Akhavan, P. F. *Chem. Commun.* **2011**, *47*, 7686. http://dx.doi.org/10.1039/C1CC00017A
46. Lebel, H.; Janes, M. J.; Charette, A. B.; Nolan, S. P. J. *Am. Chem. Soc.* **2004**, *126*, 5046. https://dx.doi.org/10.1021/ja049759r
47. Singh, R.; Viciu, M. S.; Kramareva, N.; Navarro, O.; Nolan, S. P. *Org. Lett.* **2005**, *7*, 1829. https://dx.doi.org/10.1021/ol050472o
48. Osinska, M.; Gniewek, A.; Trzeciak, A. M. *J. Mol. Catal. A Chem.* **2016**, *9*, 418. https://doi.org/10.1016/j.molcata.2016.03.022
49. Sureshbabu, B.; Ramkumar, V.; Sankararaman, S. *J. Org. Chem.* **2015**, *232*, 799. https://doi.org/10.1016/j.jorganchem.2015.10.002
50. Shen, A.; Ni, C.; Cao, Y. C.; Zhou, H.; Song, G. -H.; Ye, X. -F. *Tetrahedron Lett.* **2014**, *55*, 3278. https://doi.org/10.1016/j.tetlet.2014.04.044

