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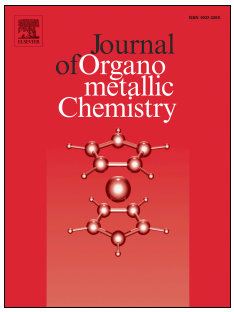

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Catalytic and Stoichiometric Reactions of Arylpalladium(II) Complexes Bearing a *trans*-Chelating Dinitrogen Ligand with Arylboronic Acids

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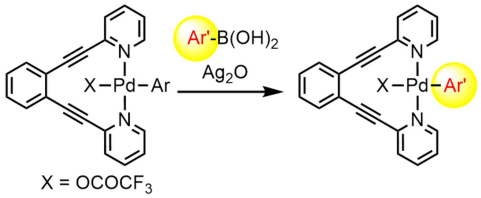
Keywords

Suzuki-Miyaura reaction • transmetalation • palladium complexes • trans-chelating ligand • arylboronic acids

Graphical abstract

The reaction of Ag_2O, $Ar'B(OH)_2$ and arylpalladium(II) complex, $PdAr(OCOCF_3)(bpeb)$ (bpeb = 1,2-bis(2-pyridylethylnyl)benzene) yields $PdAr'(OCOCF_3)(bpeb)$ via exchange of aryl ligands as well as biaryls and anisole.



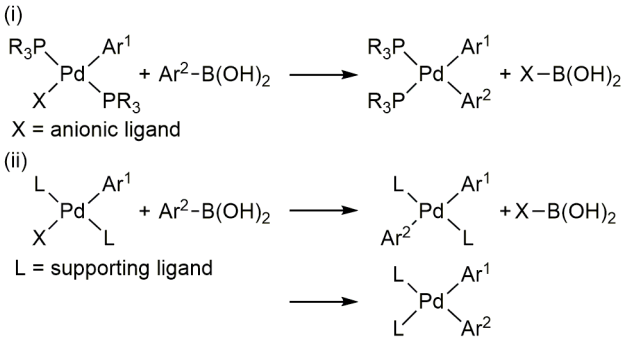
A**bstract**

Pd(II) complexes with 1,2-bis(2'-pyridylethylnyl)benzene (bpeb) ligand, $PdCl_2$(bpep) and $Pd(OAc)_2$(bpep), catalyze cross-coupling of arylboronic acids and aryl iodide, in spite of the *trans*-chelation of the ligand. Arylpalladium iodo and trifluoroacetate complexes with bpep ligand, Pd(C_6H_4X-4)(I)(bpep) (**3a-3h**, X = OMe, Me, H, COMe, CHO, COOEt, NO_2, F), Pd($C_6H_3F_2$-2,4)(I)(bpep) (**3i**), Pd(C_6H_4X-4)($OCOCF_3$)(bpep) (**4a-4e**, X = OMe, Me, H, COMe, CHO) and Pd(C_6F_5)($OCOCF_3$)(bpep) (**4j**), were obtained by ligand exchange of the Pd complexes having tmeda ligand (tmeda =*N*,*N*,*N*',*N*'-tetramethylethylenedi-amine). X-ray crystallographic results of arylpalladium(II) trifluoroacetate complex, Pd(C_6H_4OMe-4)($OCOCF_3$)(bpeb) (**4a**), and bis(trifluoroacetate)palladium(II) complex, Pd$(OCOCF_3)_2$(bpeb) (**5**) revealed the structures with two pyridyl groups of bpeb coordinated to Pd(II) in a *trans*-chelating bidentate mode. 2-Pyridyl hydrogens and an acetate oxygen of **5** are at close positions to each other (2.52 and 2.66 Å). The reaction of (4-MeC_6H_4)$B(OH)_2$ (**7b**) with Pd(C_6H_4OMe-4)($OCOCF_3$)(bpeb) (**4a**) in the presence of Ag_2O yields Pd(C_6H_4Me-4)($OCOCF_3$)(bpeb) (**4b**) via exchange of the aryl group between the palladium complex and arylboronic acid. The reaction of (4-CHOC_6H_4)$B(OH)_2$ (**7e**) yields not only Pd(C_6H_4CHO-4)($OCOCF_3$)(bpeb) (**4e**) but also biaryls, 4-MeOC_6H_4-C_6H_4Y-4 (Y = OMe (**8a**), CHO (**8e**)). Hammett plots of the reaction exchange suggest higher reactivity of the Pd complex with more electron-donating aryl ligand.

Introduction

Transmetalation of aryl ligand bonded to main group elements, such as Li, Mg, Si, Sn and B with late transition metal complexes is known as a key step of cross-coupling reactions [1]. The Pd-catalyzed coupling of arylboronic acids with aromatic halides, Suzuki-Miyaura reaction, provides unsymmetrical biaryls. The catalysis involves transmetalation of arylboronic acid, $ArB(OH)_2$, with $PdAr'X(L)$ (X = halogeno or pseudohalogeno ligand, L = supporting ligand), generated by oxidative addition reaction of aryl halides, Ar^1X and $Pd(0)L_n$, to yield diaryl palladium intermediate, $PdAr^1Ar^2(L_2)$, which undergoes reductive elimination of the product [2]. Recently, many research groups reported the mechanism of Suzuki-Miyaura reaction and transmetalation of the arylboronic acid, which is related to the catalysis [3-10]. Nishikata et al. showed a monoaryl Pd(II) intermediate having a cis-chelating diphosphine ligand, $Ph_2PCH_2CH_2PPh_2$ (dppe), obtained via transmetalation of $PhB(OH)_2$ or $PhSi(OMe)_3$ with $[Pd(dppe)(PhCN)_2](BF_4)_2$ in the presence of PPh_3.[11] Transmetalation of organometallic compounds of Li and Mg provides not only the coupling products but organotransition metal complexes under mild conditions. It is considered to involve the simple four-membered cyclic intermediate having the alkyl ligand that bridges boron and the transition metal. Arylboronic acid also undergoes smooth transmetalation with the Pd complex having a halogeno ligand. The reaction, however, was revealed to involve aryl boronate and/or the Pd intermediate with a Pd–OH bond. The bimetallic intermediates of the reaction has a bridging OH ligand or a more complicated structure based on the experimental results and theoretical calculations.

Scheme 1(i) shows a typical reaction of the arylboronic acid with arylpalladium complexes having two monophosphine ligands. Addition of the arylboronic acid to the arylpalladium halogeno complex with the *trans* structure in the presence of base tends to produce the diarylpalladium complex with *cis* structure via the transmetalation accompanied by *trans*-*cis* isomerization or via the isomerization of the once formed *trans*-diarylpalladium complex. Ensuing coupling of the two aryl ligands at the *cis* positions occurs easily and form biaryl as the product both in the stoichiometric and catalytic reactions.



Scheme 1. Plausible ligand exchange reactions of arylboronic acid $Ar^2B(OH)_2$ with aryl(halogeno)palladium complex, $PdAr^1X(L_2)$.

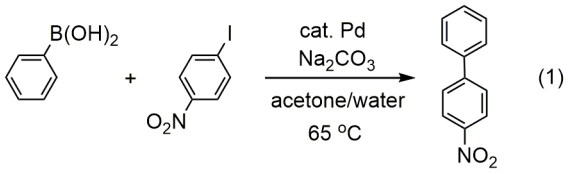
Use of arylpalladium halide complex with a *trans*-chelating binidentate ligand would fix the *trans* geometry of the square-planar complex during the transmetalation and prevent or retard coupling of the two aryl ligands attached to the Pd center. Considerable number of *trans*-chelating diphosphines ligands were reported to exhibit unique properties in the stoichiometric and catalytic reactions [12].

In this study, we studied the reaction of arylboronic acid with arylpalladium(II) halogeno complexes having a *trans*-chelating dinitrogen ligand. 1,2-Bis(2'-pyridylethylnyl)benzene) (bpeb) was used as the *trans*-bidentate dipyridyl

ligand. Its Pd complexes, react with arylboronic acids to produce the biaryls via cross-coupling, accompanied by formation of symmetric biaryl as well as formal aryl ligand exchange between the complex and arylboronic acids (Scheme 1(ii)). This paper presents details of the stoichiometric reaction and its comparison with results of the catalytic reaction using the Pd complexes.

Results and Discussion

Dichrolopalladium complex bearing 1,2-bis(2'-pyridylethylnyl)benzene (bpeb), $PdCl_2$(bpeb), catalyzes Suzuki-Miyaura coupling reaction of phenylboronic acid and 4-iodo(nitorobenzene) to yield the corresponding biaryl in 94% yield at 65 ^oC (eq 1).[13] The reaction using $Pd(OAc)_2$(bpeb) catalyst gives the product in lower yield (55%). $Pd(OCOCF_3)_2$(bpep) catalyzes the equimolar reaction of 4-iodoanisole with phenylboronic acid similarly, and the yield after 5 h varies depending on the conditions. These catalytic reactions are considered to involve formation of arylpalladium complex having bpeb ligand and succesive reactions with phenylboronic acid to afford coupling product.



(1)

cat. Pd	Yield
$PdCl_2$(bpeb)	94% (45 min)
$Pd(OAc)_2$(bpeb)	55% (45 min)
$Pd(OCOCF_3)_2$(bpeb)	72% (2 h)

The reaction of 4-iodoanisole (2.0 mmol) with phenylboronic acid (2.0 mmol) by the Pd catalyst ($PdCl_2$(bpeb), 2 μmol) yields the product in 45%. The reaction of a large excess 4-iodoanisole (10 mmol and 20 mmol) results in decrease of the product

yield (22% and 29%, respectively), while use of an excess phenylboronic acid (10 mmol) increases the product (96%). The latter reaction at 35-65 °C produced the biaryl above 82%, and plots of the observed rate constants yielded the kinetic parameters, $\Delta G^{‡}$ = 100 kJ mol^{-1}, $\Delta H^{‡}$ = 83 kJ mol^{-1}, and $\Delta S^{‡}$ = -58 J mol^{-1}K^{-1} (Table S1-S3, Figure S1). Electron-donating group at *para* position of the arylboronic acid enhances the reaction, as revealed by Hammett plots of the reaction (Figure S2). Thus, the catalytic reaction is enhanced by increase of concentration of phenylboronic acid and by introduction of electron-donating group at the *para* position of the substrate. Increase of concentration of iodoarene, however, decreases the yield of the product probably because of occurrence of an undesirable side reaction, such as deactivation of the catalyst. Large negative activation entropy of the reaction suggests an associative intermediate at the rate-determining step, and it corresponds to the reaction step of the arylpalladium intermediate with arylboronic acid.

Arylpalladium(II) iodo and acetate complexes with bpeb ligand were prepared from the precursor with tmeda, Pd(C_6H_4X-4)(I)(tmeda) (**1a**: X = OMe; **1b**: X = Me; **1c**: X = H; **1d**: X = COMe; **1e**: X = CHO; **1f**: X = COOEt; **1g**: X = NO_2; **1h**: X = F), Pd($C_6H_4F_2$-2,4)(I)(tmeda) (**1i**) and Pd(C_6H_4X-4)($OCOCF_3$)(tmeda) (**2a**: X = OMe; **2b**: X = Me; **2c**: X = H; **2d**: X = COMe **2e**: X = CHO) and Pd(C_6F_5)($OCOCF_3$)(tmeda) (**2j**). The reaction of 1,2-bis(2'-pyridylethylnyl)benzene) (bpeb) with Pd(C_6H_4OMe-4)(I)(tmeda) (**1a**) in the presence of CF_3COOH at room temperature yields Pd(C_6H_4OMe-4)(I)(bpeb) (**3a**) (86% yield) and [tmeda-H_2]$^{2+}$($OCOCF_3$)$_2$ (eq 2) via exchange of the supporting ligand. Similar reactions of bpeb with PdArI(tmeda) and with PdAr($OCOCF_3$)(tmeda) (**1b-1i, 2a-2e**, **2j**) in THF (or in CH_2Cl_2) produce the complexes with bpeb ligand, Pd(Ar)(I)(bpeb) (**3b-3i**) and Pd(Ar)($OCOCF_3$)(bpeb)

(**4a-4e**, **4j**), in 41-86% yields. The results are summarized in Table 1. Bis(trifluoroacetoxy)palladium complex, $Pd(OCOCF_3)_2$(bpeb) (**5**), was also synthesized from the reaction of bpeb with $Pd(OCOCF_3)_2$ in 40% yield. An equimolar reaction of $AgPF_6$ with **3a** in MeCN produces cationic palladium complex, $[Pd(C_6H_4OMe\text{-}4)(MeCN)(bpeb)]PF_6$ ([**6a**(MeCN)]PF_6) in 90% yield (eq 3).

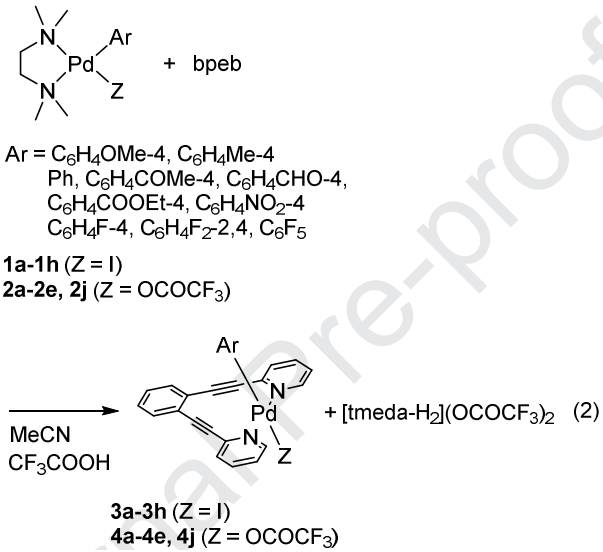
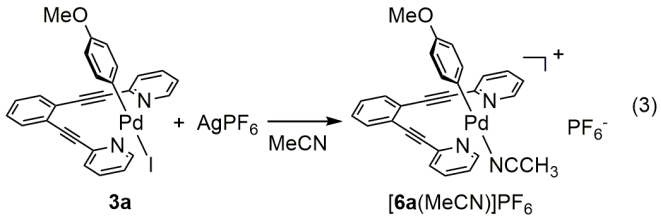


Table 1, Synthesis of **3a-3i** and **4a-4e, 4j**.

run	Complex	Z	Ar	Yield
1	**1a**	I	C_6H_4OMe-4	**3a**, 86%
2	**1b**	I	C_6H_4Me-4	**3b**, 55%
3	**1c**	I	Ph	**3c**, 86%
4	**1d**	I	C_6H_4COMe-4	**3d**, 57%
5	**1e**	I	C_6H_4CHO-4	**3e,** 55%
6	**1f**	I	C_6H_4COOEt-4	**3f**, 55%
7	**1g**	I	$C_6H_4NO_2$-4	**3g**, 84%
8	**1h**	I	C_6H_4F-4	**3h**, 60%
9	**1i**	I	$C_6H_4F_2$-2,4	**3i**, 45%
10	**2a**	$OCOCF_3$	C_6H_4OMe-4	**4a**, 59%
11	**2b**	$OCOCF_3$	C_6H_4Me-4	**4b**, 47%
12	**2c**	$OCOCF_3$	Ph	**4c**, 75%
13	**2d**	$OCOCF_3$	C_6H_4COMe-4	**4d**, 41%
14	**2e**	$OCOCF_3$	C_6H_4CHO-4	**4e**, 66%
15	**2j**	$OCOCF_3$	C_6F_5	**4j**, 41%



(3)

X-ray crystallography revealed molecular structures of $Pd(C_6H_4OMe\text{-}4)(OCOCF_3)$(bpeb) (**4a**) and $Pd(OCOCF_3)_2$(bpeb) (**5**) with a square-planar Pd center bearing *trans*-chelating bpeb ligand (Figure 1). For complex **4a**, Pd1–C1 and Pd1–O1 bonds are orthogonal (88 ^{o}) to the Pd(bpeb) plane. Pd1–C1 bond distance 1.974(3) Å is longer than that of Pd–C bond (1.92 Å) of Pd(Ph)(I)(tmeda) (**1c**) [14,15]. The O1–Pd1–O3 bond of **5** is inclined toward the Pd(bpep) plane (79 ^{o}), and the distances between O2 with H1 and H12 (O2…H1: 2.656 Å, O2…H12: 2.518 Å) of **5** are shorter than the corresponding atom distances of **4a** (O2…H8: 3.166 Å, O2…H19: 2.967 Å) and than sum of the van der Waals radii of hydrogen and oxygen atom (2.72 Å). It suggests the hydrogen bond interaction between the acetate oxygen and the pyridyl hydrogen at 2-position.

^{1}H NMR spectrum of **4a** and **5** in $CDCl_3$ contain signals of the hydrogen at the 6-position of pyridyl group at δ 9.09 and 9.15, respectively, which is at much lower magnetic field than the corresponding signal of bpeb (δ 7.64). These data suggest that complex **5**, has more significant O…H hydrogen bonding between the ligand than **4a** also in the solution. Dissolution of **4a** in CD_3CN gave rise to the ^{1}H NMR spectrum that is almost identical to the corresponding data for [**6a**(MeCN)]PF_6, indicating **4a** undergoes dissociation of the $OCOCF_3$ ligand in CD_3CN solution to form [**6a**(CD_3CN)]($OCOCF_3$). HR-ESI-MS (high resolution electrospray mass spectrum) of $Pd(OCOCF_3)(C_6H_4Me\text{-}4)$(bpeb) (**4b**) (eluent: MeCN) contains a peak of *m/z* 477.0598

which corresponds to $[Pd(C_6H_4Me\text{-}4)(bpeb)]^+$ (calcd. 477.0588), indicating facile dissociation of $OCOCF_3$ ligand from **4b**.

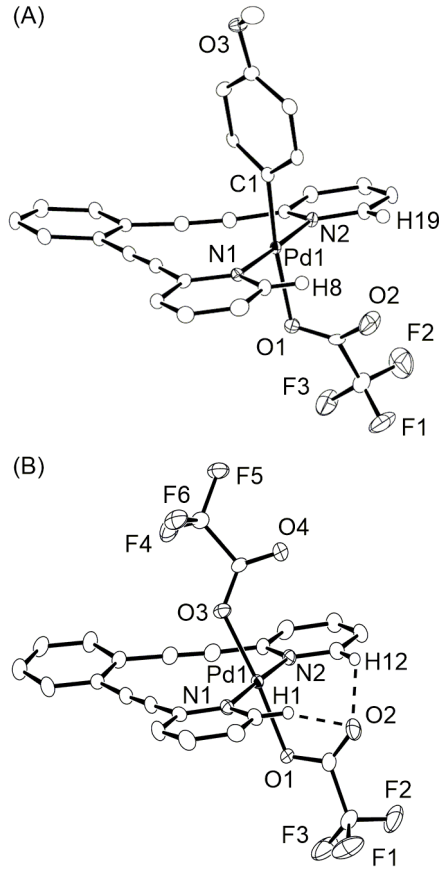
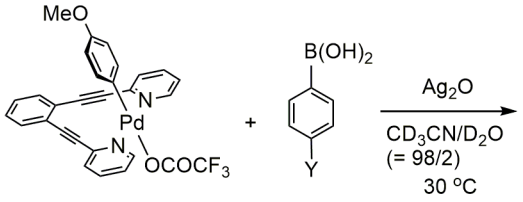


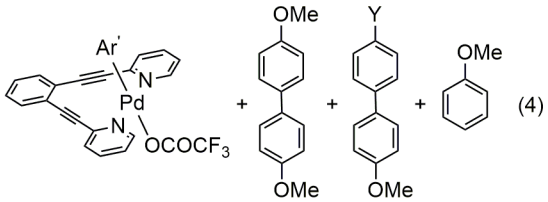
Figure 1, Molecular structure of (A) $Pd(C_6H_4OMe\text{-}4)(OCOCF_3)(bpeb)$ (**4a**) and (B) $Pd(OCOCF_3)_2(bpeb)$ (**5**) determined by X-ray crystallography (50% probability). Hydrogen atoms except H1 and H12 of **5** are omitted for clarity.

Reaction of arylboronic acids, $(4\text{-}YC_6H_4)B(OH)_2$ (**7b-7e**, Y = Me, H, COMe and CHO) with complex **4a** in the presence of Ag_2O (2 eq to **4a**) was conducted in NMR tubes. Complex **4a** reacts with **7b** to yield complex **4b** (28%) via aryl group exchange between the Pd complex and arylboronic acid (eq 4). Reaction of **7e** (50

mM) with complex **4a** in CD_3CN/D_2O (10 mM, CD_3CN/D_2O = 98/2) in the presence of Ag_2O forms a mixture of Pd(C_6H_4CHO-4)($OCOCF_3$)(bpeb) (**4e**) (90%), and coupling products, (4-$MeOC_6H_4$)$_2$ (**8a**, 17%), 4-$MeOC_6H_4$-C_6H_4CHO-4 (**8e**, 41%) and PhOMe (18%), at 30 ^oC after 52 h. The yield of the compounds were determined by comparison of the ^1H NMR peak area ratio of the compound observed at δ 3.83 (**8a**), 3.79 (**8e**), 3.76 (PhOMe), 3.52 (**4a**) and 9.67 (pyridyl proton of **4e**) with added internal standard (diphenylethane). A similar reaction of (4-$COMeC_6H_4$)$B(OH)_2$ (**7d**) with **4a** yields a mixture of Pd(C_6H_4COMe-4)($OCOCF_3$)(bpeb) (**4d**) (81%), 4-$MeOC_6H_4$-C_6H_4Y-4 (Y = OMe (**8d**, 31%), COMe (**8d**, 12%)) and PhOMe (10%) after 120 h. Reaction of (4-$CHOC_6H_4$)$B(OH)_2$ (**7e**) with **4a** in the absence of Ag_2O does not yield neither Pd complex **4e** nor the biaryl compounds.



4a Y = Me (**7b**); Y = H (**7c**); Y = COMe (**7d**); Y = CHO (**7e**)



4b **4c** **4d** **4e** — **8a** Y = Me (**8b**); Y = H (**8c**); Y = COMe (**8d**); Y = CHO (**8e**)

The Pd(II) complex obtained by the reaction is resulted from formal exchange of the aryl ligand with aryl group of the boronic acid. Figure 2 shows profile of formation of the monoarylpalladium complexes, which obeys the first-order kinetics (eq 5).

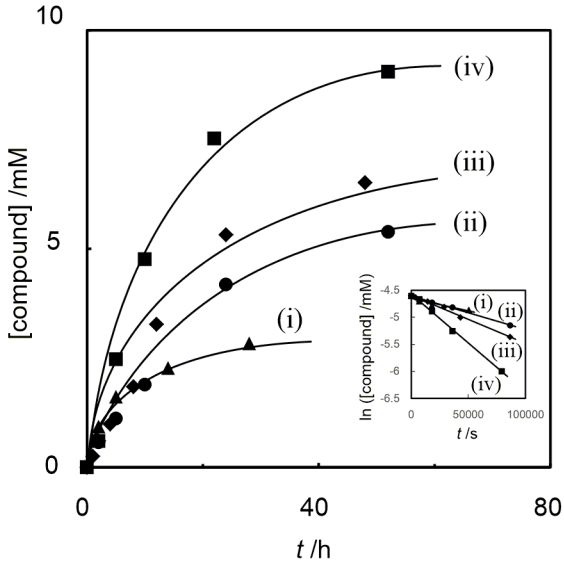


Figure 2. The profile of formation of arylpalladium complex (i) **4b**, (ii) **4c**, (iii) **4d**, and (iv) **4e**, from reaction of **4a** with **7b**, **7c**, **7d**, and **7e**, respectively.

$$Ar^1Pd(OAc)(bpeb) + Ar^2B(OH)_2 \xrightarrow{Ag_2O} Ar^1Ar^2Pd(bpeb) \quad (5)$$

$$\frac{d}{dt}[Ar^1Ar^2Pd(bpeb)] = k_{obs}[Ar^1Pd(OAc)(bpeb)]$$

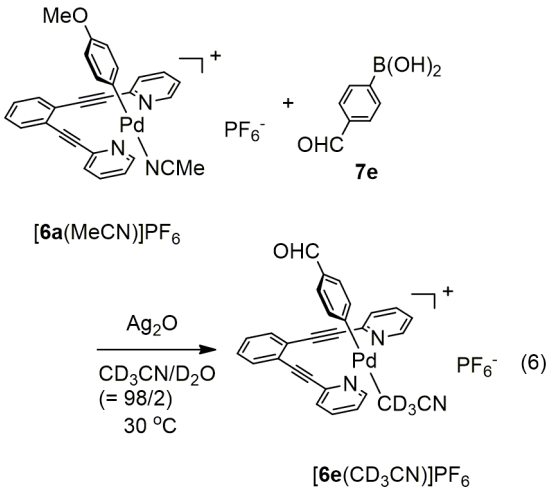
The observed rate constant for formation of **4e** was determined to be $k_{obs} = 1.8 \times 10^{-5}$ s^{-1} (30 ^oC), and the reaction of **7d** proceeds more slowly ($k_{obs} = 8.9 \times 10^{-6}$ s^{-1}). The rate-constants at 30 ^oC are included in Table 2. Electron-withdrawing substituents such as COMe and CHO groups on the arylboronic acids, increase the yield and the rate constant of the reactions with **4a** to give **4b** (28%, $k_{obs} = 1.3 \times 10^{-6}$ s^{-1}), **4c** (54%, $k_{obs} = 6.2 \times 10^{-6}$ s^{-1}), **4d** (81%, $k_{obs} = 8.9 \times 10^{-6}$ s^{-1}) and **4e** (90%, $k_{obs} = 1.3 \times 10^{-5}$ s^{-1}), respectively.

Table 2, Observed rate constants, k_{obs} (s^{-1}), for ligand exchange reaction of arylboronic acids (**7b**, **7c**, **7d**, **7e**) with **4a** (at 30 °C)

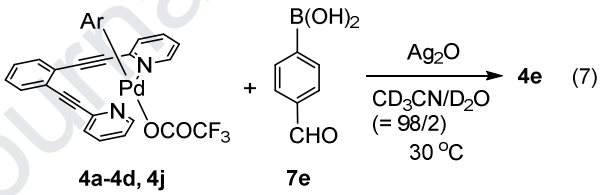
			Yield				
run	boronic acid	time	Pd complex	**8a**	biaryl	anisole	k_{obs} /s^{-1}
1	Y = Me, **7b**	28 h	28% (**4b**)	nd[a)]	nd[a)]	nd[a)]	1.3×10^{-6}
2	Y = H, **7c**	52 h	54% (**4c**)	2%	40% (**8c**)	5%	6.2×10^{-6}
3	Y = COMe, **7d**	120 h	81% (**4d**)	11%	31% (**8d**)	10%	8.9×10^{-6}
4	Y = CHO, **7e**	24 h	90% (**4e**)	17%	41% (**8e**)	18%	1.8×10^{-5}
5	Y = CHO, **7e**[b)]	52 h	71% (**4e**)	6%	9% (**8e**)	25%	1.3×10^{-5}

Addition of bpeb (1 eq to **4a**) to the reaction mixture causes no significant influence to the reaction rate, indicating that the reactions does not require partial liberation of bpeb ligand from the palladium atom.

Similar aryl ligand exchange was observed also in the reaction of **7e** with cationic palladium complex, [**6a**(MeCN)]PF_6 ([[**6a**(MeCN)]PF_6]$_0$ = 10 mM, [**7e**]$_0$ = 50 mM), in the presence of Ag_2O (2 eq amount to Pd) (eq 6). Observed rate constant, k_{obs}, and yield for formation of [Pd(4-$CHOC_6H_4$)(CD_3CN)(bpeb)]PF_6 ([**6e**(CD_3CN)]PF_6) were determined to be 1.6×10^{-4} s^{-1} and 98% (after 4 h), respectively. The reaction is retareded by addition of $NaOCOCF_3$ (k_{obs} = 7.5×10^{-5} s^{-1}, 86 % after 4 h), while the reaction in the absence of Ag_2O does not yield [**6e**(CD_3CN)]PF_6.



Dependence of the rate constants of aryl ligand exchange on the aryl ligand of the palladium complex was investigated by the reaction of $(4\text{-}CHOC_6H_4)B(OH)_2$ (**7e**) with palladium complexes having various aryl ligands, **4a**, **4b**, **4c**, **4d** and **4j**, in CD_3CN/D_2O (= 98/2) in the presence of Ag_2O at 30 ^oC (eq 7). The rate constants of the reactions, k_{obs}, estimated by ^1H NMR spectroscopy were in the range of 7.7×10^{-7} s^{-1} to 2.2×10^{-6} s^{-1}. The negative slope of the Hammett plots indicate that electron donating substituents on the aryl ligand of palladium complex enhance the aryl ligand exchange reaction (Figure 3). Results of the reactions in eqs 4 and 7 suggest that the aryl group exchange between the Pd complexes and arylboronic acids is enhanced by electron-donating substituent of the aryl ligand and electron-withdrawing substituent of the arylboronic acid.



4a-4d, 4j **7e**

Ar = C_6H_4OMe-4 (**4a**), C_6H_4Me-4 (**4b**), Ph (**4c**), C_6H_4COMe-4 (**4d**), C_6F_5 (**4j**)

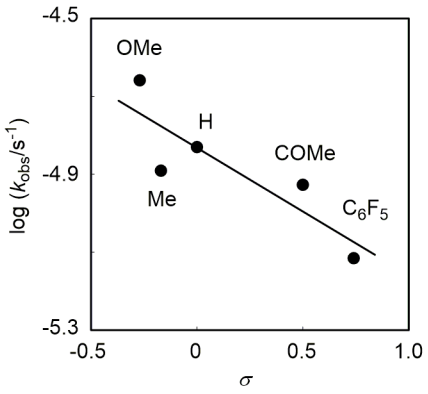
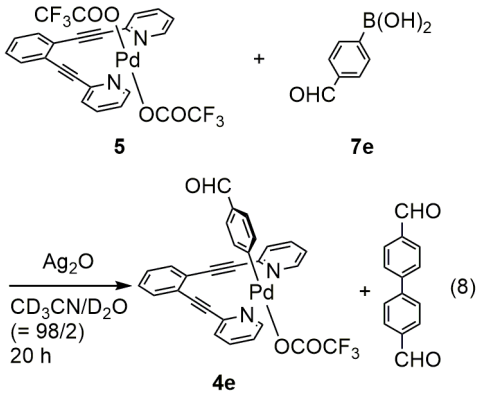


Figure 3. Hammett plots of the k_{obs} values for aryl ligand exchange reaction of **7e** with each of complex ($Pd(C_6H_4X\text{-}4)(OCOCF_3)$(bpeb) (**4a**: X = OMe; **4b**: X = Me; **4c**: X =

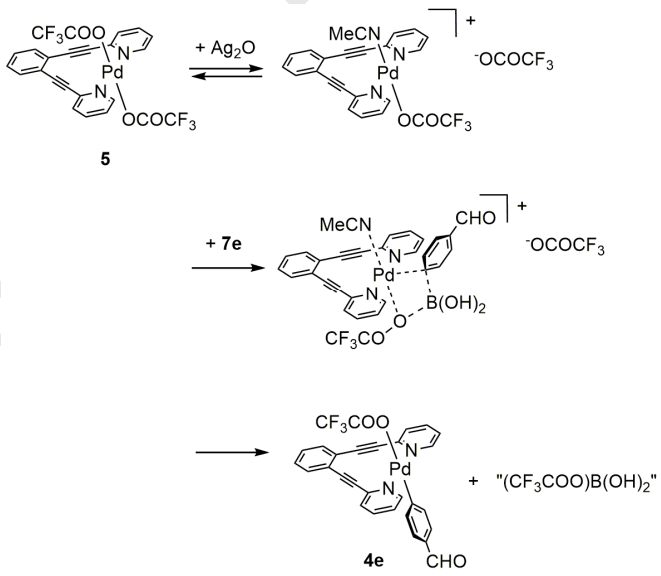
H; **4d**: X = COMe) and Pd(C_6F_5)($OCOCF_3$)(bpeb) (**4j**)).

Pd complex, Pd($OCOCF_3$)$_2$(bpeb) (**5**), reacts with **7e** in the presence of Ag_2O in CD_3CN to afford **4e** (34%, 20 h) and 4-CHOC_6H_4-C_6H_4CHO-4 (23%, 20 h) via transmetalation of aryl group from boron to palladium, as shown in eq 8. The yield of 4-CHOC_6H_4-C_6H_4CHO-4 increase to 33% after 44 h, which is ascribed to formation of Pd(C_6H_4CHO-4)$_2$(bpeb) from **4e** and **7e**. The addition of Ag_2O is indispensable to induce the reaction and the mixture of **5** and **7e** does not undergo similar reaction without Ag_2O.

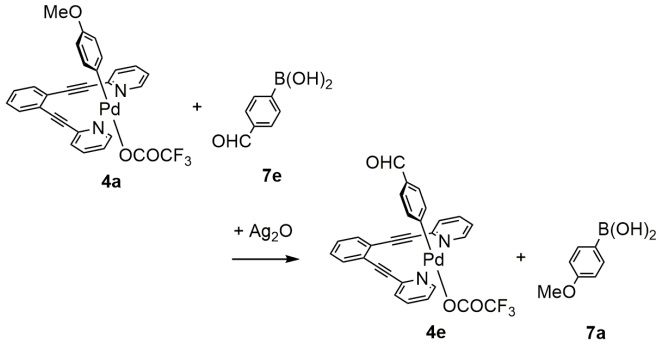


Scheme 2 depicts a possible mechanism of formation of arylpalladium complex from bis(trifluoroacetate)palladium(II) complex **5** and arylboronic acid **7e** (reaction (8)). The complex undergoes partial dissociation of a trifluoroacetate ligand with aid of Ag_2O to form the cationic palladium complex. Addition of 4-formylphenylboronic acid **7e** to the complex causes concerted activation of the Pd–O and C–B bonds of the complex and substrate and formation of new Pd–C and B–O bonds. Elimination of trifluoroacetate boronic acid results in formation of the arylpalladium complex **4e**. High oxophilic nature of the boron atom of boronic acid renders the coordination of the aryl group smoothly, similar to the proposed mechanism of activation of the arylboronic acid in the transition-metal catalyzed reactions [6].

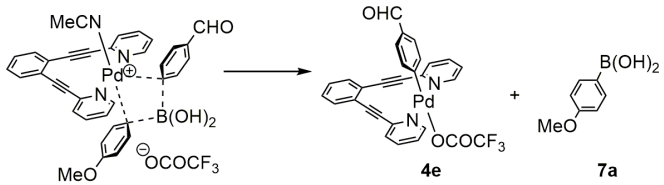
Reactions of arylboronic acid with the cationic and neutral arylpalladium(II) complexes (reactions (6) and (7)) also involve the activation of arylboronic acid and formation of a new Pd-aryl bond. Two reaction pathways can be considered. Scheme 3 shows the reaction via exchange of the aryl group between the Pd complex and boronic acid derivative. This type of simple exchange of the aryl group is not plausible because NMR spectra of the reaction mixture do not contain signals of 4-methoxyphenylboronic acid and because the formation of a new C–B bond is less favored than the formation of O–B bond. Scheme 4 shows a possible intermediate for such a reaction, but the process is less plausible than the other reaction involving activation of B–C bond that is aided by formation of B–O bond.



Scheme 2. A proposed mechanism for reaction of **5**, Ag_2O and **7e** to form **4e**.

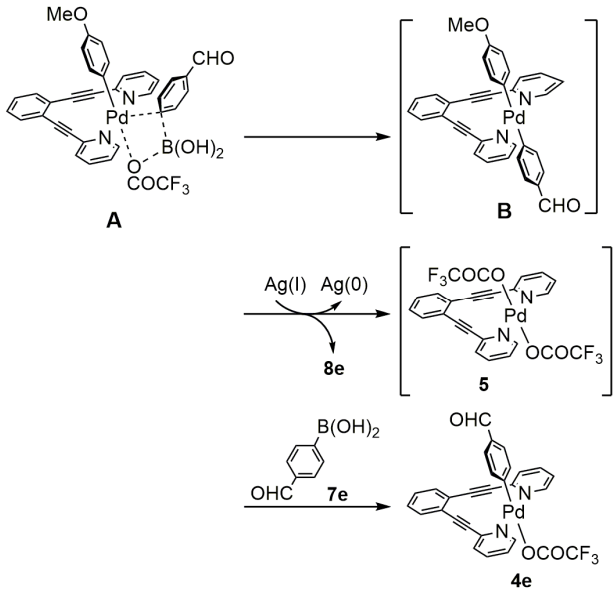


Scheme 3. A proposed mechanism for reaction of **4a**, Ag_2O and **7e** to form **4e**.



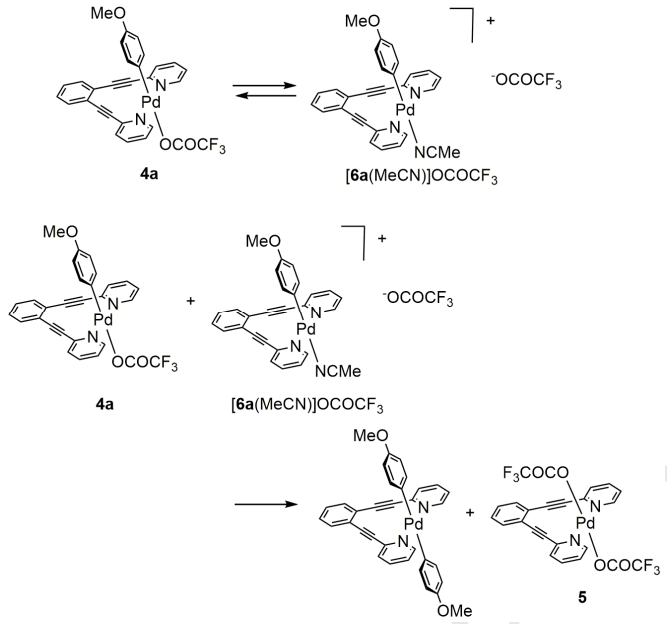
Scheme 4. The possible intermediate giving **4e** and **7a** via aryl group exchange.

The other possible mechanism for the aryl group exchange involves formation of bis(trifluoroacetate)palladium(II) complexes and its conversion into the arylpalladium(II) complex according to reaction (8) (Scheme 5). Reaction of **7e** with **4a** forms an intermediate, **A** and elimination of $(CF_3COO)B(OH)_2$ yield diarylcomplex, $Pd(C_6H_4OMe\text{-}4)(C_6H_4CHO\text{-}4)(bpeb)$ (**B**). Reductive elimination reaction of biaryl from **B** forms Pd(0) species which is oxidized by Ag(I) to form **5** and silver metal. The mechanism via intermediate **A** and **B** (Scheme 5) accounts for the formation of **8e**, and silver after completion of the reaction. The rate determining step of the reaction probably resides in intermolecular reaction of **7e** with **4a** form **B** whose stability is affected by substituents or the aryl groups on Pd and B atoms.



Scheme 5. A proposed mechanism for reaction of intermediate **A**, **7e** and Ag_2O to form **4e**.

Details of formation of dimethoxybiphenyl (**8a**) from reaction of **4a** and **7e** can be attributed to another reaction pathway. The cationic Pd(II) complexes, [PdAr(acetone)(2,2'-bpy)]BF_4, generated in situ by reaction of PdArI(2,2'-bpy) and $AgBF_4$ were reported to yield cooresponding biaryl, Ar-Ar via conproportionation of the monoarylpalladium complex [15]. The reaction shown in Scheme 6 also seems to occur in the reactions shown in eq 4, giving diarylpalladium complex and di(trifluoroacetato)palladium complex **5**, and the latter complex undergoes further reaction with arylboronic acid, as shown in reaction 8 (Scheme 2). Analogous reaction should occur between the original arylpalladium trifluoroacetate complex and the complex formed via the reaction 8 to form unsymmetrial biaryl that is formed in a higher yield than the symmetrical biaryl.



Scheme 6. A possible reactions of **4a** to give diarylpalladium complex and **5**.

In summary, we succeeded in syntheses of the arylpalladium(II) complex with bpeb ligand and X-ray crystallography of the molecule with *trans* structure. The reaction of arylboronic acid with the arylpalladium complex yields not only the cross-coupling product but also the aryl palladium complex via aryl ligand exchange reaction between the Pd and B compounds. The reaction is regarded to involve elimination of the cross-coupling product and transmetalation of the arylboronic with bis(acetaet)palladium(II) complex. Direct exchange of phenyl ligand between transition metal and main group metal were reported for the reaction of $PdPh(Me)(PEt_2Ph)_2$ and MeMgBr (or PhMgBr) affording $PdMe_2(PEt_2Ph)$ and PhMgBr (or $PdPh_2(PEt_2Ph)_2$ and MeMgBr) [16]. These Ph/Me exchange reactions were regarded to be the origin of the biphenyl as side product from the Pd-catalyzed cross-coupling reaction of PhI and MeMgBr. Intramolecular aryl ligand exchange between Pd and P was also reported in the reaction of arylpalladium(II) complex

bearing triarylphosphine ligands [17] and in the deactivation step of phosphinesulfonato Pd(II) catalyst for ethylene polymerization [18]. Also in the Suzuki-Miyaura reaction catalyzed by the *trans*-chelating ligand, undesirbal product is formed by the side reaction in the catalytic system. Studies of the stoichiometric reaction in this study clarified such side reactions, although catalytic reactions involve such process as minor paths.

Experimental Section

General. 1,2-bis(2'-pyridylethylnyl)benzene) (bpeb) [19,20], $PdCl_2$(bpeb) and PdAr(I)(tmeda) (Ar = **1a-1h**) [14,15a,21] were prepared according to the literature method. PdAr($OCOCF_3$)(tmeda) (Ar = **2a-2e, 2j**) were prepared by similar procedure reported for Pd($C_6H_4CF_3$-4)($OCOCF_3$)(tmeda) [22]. Pd(C_6H_4Me-4)($OCOCF_3$)(tmeda) (**2b**) and PdPh($OCOCF_3$)(tmeda) (**2c**) are known compound [23].

The other chemicals were commercially available and used without further purification. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian MERCURY300, JEOL EX-400 and Bruker biospinAvance III spectrometers. IR absorption spectra were recorded on Shimadzu FT/IR-8100 spectrometers. Electrospray ionization mass spectrometry (ESIMS) was recorded on a Bruker micrOTOF II. Elemental analysis was carried out with a LECO CHNS-932 CHNS or Yanaco MT-5 CHN autorecorder at Suzukakedai Materials Analysis Division, Technical Department, Tokyo Institute of Technology. X-ray crystal structure analyses of the obtained orange crystal were performed at a Rigaku AFC-10R Saturn CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations and analysis were carried out using program package Crystal Structure^{TM} for Windows [24]. Substituent constants (σ) for Hammett plots was obtained from literacture [25].

Pd(C_6H_4OMe-4)(I)(bpeb) (3a). To a THF solution (4.0 mL) of Pd(C_6H_4OMe-4)(I)(tmeda) (**1a**) (91 mg, 0.20 mmol) and bpeb (84 mg, 0.30 mmol) was added an THF (1.0 mL) solution of CF_3COOH (20 μL, 0.27 mmol) at room temperature to induce separation of Pd complex. The mixture was stirred for 30 min at room temperature. The solid was collected by filtration then washed with acetone (10 mL, 2

times) and Et_2O (10 mL) and dried in vacuo to form **3a** as yellow solid (102 mg, 0.17 mmol, 86%). Anal. Calcd for $C_{27}H_{19}N_2IPdO(H_2O)_{0.5}$: C, 51.49; H, 3.20; N, 4.45; I, 20.15%. Found: C, 51.55; H, 3.43; N, 4.40; I, 20.46%. IR (KBr disk, r.t.): δ = 2220 (C≡C) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, r.t.): δ = 3.56 (s, 3H, Me), 6.45 (d, 2H, C_6H_4OMe, *J* = 9 Hz), 7.28 (m, 2H, C_6H_4OMe, *J* = 9 Hz), 7.30 (ddd, 2H, py-5, *J* = 8, 6, 2 Hz), 7.57 (m, 2H, C_6H_4-bpeb), 7.64 (d, 2H, py-3, *J* = 8 Hz), 7.72 (ddd, py-4, 2H, *J* = 8, 8, 2 Hz), 7.83 (m, 2H, C_6H_4-bpeb), 9.84 (d, 2H, py-6, *J* = 5 Hz)) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, r.t.): δ = 31.0 (Me), 92.1(C≡C), 94.9 (C≡C), 113.0, 124.5, 125.2, 129.2, 130.1, 133.1, 133.4, 137.3, 144.8, 153.2 ppm. Low solubility of the complex prevents precise $^{13}C\{^1H\}$ NMR analysis. Due to low signal-to-noise ratio of the spectra, two ^{13}C NMR signals were not assigned.

Pd(C_6H_4Me-4)(I)(bpeb) (3b). Complex **3b** (67 mg, 0.11 mmol, 55%) was obtained from the reaction of Pd(C_6H_4Me-4)(I)(tmeda) (**1b**) (88 mg, 0.20 mmol), bpeb (84 mg, 0.30 mmol) and CF_3COOH (20 μL, 0.27 mmol) by the similar procedure of **3a**. Anal. Calcd for $C_{27}H_{19}N_2IPd(H_2O)_{0.5}$: C, 52.83; H, 3.28; N, 4.56%. Found: C, 52.76; H, 3.68; N, 4.47%. IR (KBr disk, r.t.): ν = 2224 (C≡C) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, r.t.): δ = 2.12 (s, 3H, Me), 6.45 (d, 2H, C_6H_4-4-Me, *J* = 9 Hz), 7.29 (ddd, 2H, py-5, *J* = 8, 6, 2 Hz), 7.30 (d, 2H, C_6H_4-4-Me, *J* = 9 Hz), 7.57 (m, 2H, C_6H_4-bpeb), 7.64 (d, 2H, 3-py, *J* = 8 Hz), 7.72 (ddd, 2H, 4-py, *J* = 8, 8, 2 Hz), 7.83 (m, 2H, C_6H_4), 8.99 (dd, 2H, py-6, *J* = 5 Hz) ppm. Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement.

PdPh(I)(bpeb) (3c). Complex **3c** (102 mg, 0.17 mmol, 86%) was obtained from the

reaction of PdPh(I)(tmeda) (**1c**) (85.0 mg, 0.20 mmol), bpeb (84 mg, 0.30 mmol) and CF_3COOH (20 μL, 0.27 mmol) by the similar procedure of **3c**. To a CH_2Cl_2 solution (4.0 mL) of PdPh(I)(tmeda) (**1c**) (85.0 mg, 0.20 mmol) and bpeb (84 mg, 0.30 mmol) was added an CH_2Cl_2 (1.0 mL) solution of CF_3COOH (20 μL, 0.27 mmol) at room temperature to induce separation of Pd complex. The mixture was stirred for 3 h at room temperature. The solid was collected by filtration then washed with acetone (10 mL, 2 times) and Et_2O (10 mL) and dried in vacuo to form **3c** as yellow solid (102 mg, 0.17 mmol, 86%). Anal. Calcd for $C_{26}H_{17}N_2IPd$: C, 52.86; H, 2.90; N, 4.74%. Found: C, 52.95; H, 3.19; N, 4.68%. IR (KBr disk, r.t.): ν = 2224 (C≡C) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, r.t.): δ = 6.73 (m, 1H, *para*-Ph), 6.79 (m, 2H, *meta*-Ph), 7.31 (ddd, 2H, py-5, *J* = 7, 5, 1 Hz), 7.44 (dd, 2H, *ortho*-Ph, *J* = 8, 1 Hz), 7.58 (m, 2H, C_6H_4), 7.65 (ddd, 2H, 3-py, *J* = 8, 2, 1 Hz), 7.73 (ddd, 2H, 4-py, *J* = 8, 8, 2 Hz), 7.84 (m, 2H, C_6H_4), 8.99 (dd, 2H, py-6, *J* = 5, 1 Hz) ppm. Low solubility of the complex prevented $^{13}C\{^1H\}$ NMR measurement.

Pd(C_6H_4COMe-4)(I)(bpeb) (3d). Complex **3d** (72 mg, 0.11 mmol, 57%) was obtained from the reaction of Pd(C_6H_4COMe-4)(I)(tmeda) (**1d**) (93 mg, 0.20 mmol), bpeb (84 mg, 0.30 mmol) and CF_3COOH (20 μL, 0.27 mmol) in THF (4.0 mL) for 1 h by the similar procedure of **3a**. Anal. Calcd for $C_{28}H_{19}N_2IPdO(H_2O)_{0.5}$: C, 52.40; H, 3.14; N, 4.36%. Found: C, 52.74; H, 3.21; N, 4.37%. IR (KBr disk, r.t.): ν = 1674 (C=O), 2222 (C≡C) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, r. t.): δ = 2.35 (s, 3H, Me), 7.32 (ddd, 2H, py-5, *J* = 8, 6, 2 Hz), 7.36 (d, 2H, C_6H_4COMe, *J* = 8 Hz), 7.59 (m, 2H, C_6H_4-bpeb), 7.63 (d, 2H, C_6H_4COMe, *J* = 8 Hz), 7.66 (ddd, 2H, py-3, *J* = 8, 2, 1 Hz), 7.73 (ddd, 2H, py-4, *J* = 8, 8, 2 Hz), 7.85 (m, 2H, C_6H_4-bpeb), 8.99 (ddd, 2H, py-6, *J* =

6, 1, 1 Hz) ppm. Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement.

Pd(C_6H_4CHO-4)(I)(bpeb) (3e). Complex **3e** (135 mg, 0.22 mmol, 55%) was obtained from the reaction of Pd(C_6H_4CHO-4)(I)(tmeda) (**1e**) (187 mg, 0.40 mmol), bpeb (0.44 mg, 123 mmol) and CF_3COOH (50 μL, 0.68 mmol) in THF (10 mL) for 2 h by the similar procedure of **3a**. Anal. Calcd for ^1H NMR (300 MHz, $CDCl_3$, r.t.): δ 7.27 (d, 2H, *ortho*-C_6H_4-4-CO, *J* = 8.2 Hz), 7.32 (ddd, 2H, py-5, *J* = 7.4, 5.8, 1.6 Hz), 7.60 (dd, 2H, C_6H_4, *J* = 3.3, 5.8 Hz), 7.66 (d, 2H, py-3, *J* = 7.1 Hz), 7.71-7.77 (m, 4H, *meta*-C_6H_4-4-CO, py-4), 7.85 (dd, 2H, C_6H_4, *J* = 3.3, 5.8 Hz), 7.98 (d, 2H, py-6, *J* = 5.8 Hz), 9.69 (s, 2H, CHO).

Pd(C_6H_4COOEt-4)(I)(bpeb) (3f). Complex **3f** (75 mg, 0.11 mmol, 55%) was obtained from the reaction of Pd(C_6H_4COOEt-4)(I)(tmeda) (**1f**) (100 mg, 0.20 mmol), bpeb (84 mg, 0.30 mmol) and CF_3COOH (20 μL, 0.27 mmol) in THF (4.0 mL) for 10 min by the similar procedure of **3a**. Anal. Calcd for $C_{29}H_{21}N_2IO_2Pd$: C, 52.55; H, 3.19; N, 4.23%. Found: C, 52.49; H, 3.80; N, 4.30%. IR (KBr disk, r.t.): ν = 2217 (C≡C) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, r.t.): δ = 1.23 (t, 3H, Me, *J* = 7 Hz), 4.17 (q, 2H, CH_2, *J* = 7 Hz), 7.31 (ddd, 2H, py-5, *J* = 7, 6, 2 Hz), 7.42 (d, 2H, C_6H_4COOEt, *J* = 8 Hz), 7.59 (m, 2H, C_6H_4-bpeb), 7.60 (d, 2H, C_6H_4COOEt, *J* = 8 Hz), 7.65 (ddd, 2H, py-3, *J* = 8, 2, 1 Hz), 7.73 (ddd, 2H, py-4, *J* = 7, 7, 2 Hz), 7.84 (m, 2H, C_6H_4-bpeb), 8.98 (ddd, 2H, py-6, *J* = 6, 1, 1 Hz) ppm.

Pd($C_6H_4NO_2$-4)(I)(bpeb) (3g). Complex **3g** (532 mg, 0.84 mmol, 84%) was obtained from the reaction of Pd($C_6H_4NO_2$-4)(I)(tmeda) (**1g**) (471 mg, 1.0 mmol), bpeb (280 mg, 1.0 mmol) and CF_3COOH (100 μL, 1.4 mmol) in THF (55 mL) for 4 h by the similar

procedure of **3a**. Anal. Calcd for $C_{26}H_{16}N_3IPdO_2$: C, 49.12; H, 2.54; N, 6.61%. Found: C, 49.48; H, 2.80; N, 6.31%. ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ = 7.29 (ddd, 2H, py-5, *J* = 7, 6, 2 Hz), 7.56 (m, 2H, C_6H_4-bpeb), 7.62-7.72 (8H, $C_6H_4NO_2$, 3-py, 4-py), 7.79 (m, 2H, C_6H_4-bpeb), 8.98 (d, 2H, py-6, *J* = 5 Hz) ppm. Low solubility of the complex prevents ^{13}C{^{1}H} NMR measurement.

Pd(C_6H_4F-4)(I)(bpeb) (3h). Complex **3h** (73 mg, 0.12 mmol, 60%) was obtained from the reaction of Pd(C_6H_4F-4)(I)(tmeda) (**1h**) (89 mg, 0.20 mmol), bpeb (84 mg, 0.30 mmol) and CF_3COOH (20 μL, 0.27 mmol) in THF (4.0 mL) for 10 min by the similar procedure of **3a**. Anal. Calcd for $C_{26}H_{16}N_2FIPd(H_2O)_{0.25}$: C, 50.92; H, 2.71; N, 4.57; F, 20.69%. Found: C, 51.16; H, 3.10; N, 4.62; F, 20.67%. IR (KBr disk, r.t.): ν = 2220 (C≡C) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, r.t.): δ = 6.60 (d, 2H, C_6H_4F, *J*(HH) = 9 Hz, *J*(FH) = 10 Hz), 7.33 (ddd, 2H, py-5, *J*(HH) = 7, 6, 2 Hz), 7.40 (d, 2H, C_6H_4F, *J*(HH) = 9 Hz, *J*(FH) = 6 Hz), 7.59 (m, 2H, C_6H_4-bpeb), 7.67 (ddd, 2H, py-3, *J*(HH) = 8, 2, 1 Hz), 7.75 (ddd, 2H, py-4, *J*(HH) = 8, 8, 2 Hz), 7.85 (m, 2H, C_6H_4-bpeb), 8.99 (ddd, 2H, py-6, *J*(HH) = 6, 2, 1 Hz) ppm. Low solubility of the complex prevents ^{13}C{^{1}H} NMR measurement.

Pd(C_6H_3F-2,4)(I)(bpeb) (3i). Complex **3i** (56 mg, 0.089 mmol, 45%) was obtained from the reaction of Pd(C_6H_3F-2,4)(I)(tmeda) (**1i**) (92 mg, 0.20 mmol), bpeb (84 mg, 0.30 mmol) and CF_3COOH (20 μL, 0.27 mmol) in THF (4.0 mL) for 2 h by the similar procedure of **3a**. Anal. Calcd for $C_{26}H_{15}N_2F_2IPd$: C, 49.83; H, 2.41; N, 4.47%. Found: C, 50.07; H, 2.74; N, 4.38%. IR (KBr disk, r.t.): ν = 2226 (C≡C) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, r. t.): δ = 6.38 (m, 1H, $C_6H_3F_2$), 6.44 (m, 1H, $C_6H_3F_2$), 7.30

(ddd, 2H, py-5, *J*(HH) = 9, 6, 2 Hz), 7.47 (m, 1H, $C_6H_3F_2$), 7.59 (m, 2H, C_6H_4-bpeb), 7.64 (ddd, 2H, py-3, *J*(HH) = 8, 2, 1 Hz), 7.72 (ddd, 2H, py-4, *J*(HH) = 7, 7, 2 Hz), 7.84 (m, 2H, C_6H_4-bpeb), 9.05 (d, 2H, py-6, *J*(HH) = 6 Hz) ppm. Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement.

Pd(OCOCF$_3$)(Ph)(bpeb) (4c). To a THF solution (20 mL) of PdPh(I)(tmeda) (**1c**) (426 mg, 1.0 mmol) was added $AgOCOCF_3$ (221 mg, 1.0 mmol) at room temperature to induce separation of AgI. The mixture was stirred for 2 h at room temperature and the insoluble solid was removed by filtration. The reaction mixture was concentrated to ca. 5 mL under reduced pressure to yield Pd(OCOCF$_3$)(Ph)(tmeda) (**2c**) in situ which is used without further purification. The complex Pd(OCOCF$_3$)(Ph)(tmeda) (**2c**) were not isolated because of the gradual degradation. Data of **2c:** Anal. Calcd for $C_{15}H_{23}F_3N_2O_3Pd$: C, 40.69; H, 5.24; N, 6.33%. Found: C, 40.96; H, 5.07; N, 6.05%. ^1H NMR (300 MHz, $CDCl_3$, r.t.): δ = 2.51 (s, 6H, NMe), 2.57-2.62 (m, 8H, CH_2, NMe), 2.72-2.76 (m, 2H, CH_2), 3.72 (s, 3H, OMe), 6.62 (d, 2H, *ortho*-C_6H_4, *J* = 9 Hz), 7.25 (d, 2H, *meta*-C_6H_4, *J* = 9 Hz). IR (KBr disk, r.t.): ν 1680 (C=O) cm^{-1}). To the reaction mixture containing **2c** was added bpeb (308 mg, 1.1 mmol) and CF_3COOH (100 μL, 1.35 mmol) in THF (5.0 mL) at room temperature for 1 h. The solid formed was collected by filtration and washed with THF and dried in vacuo to form **4c** as white powder (427 mg, 0.75 mmol, 75%). Anal. Calcd for $C_{28}H_{17}F_3N_2O_2Pd(H_2O)_{0.5}$: C, 57.40; H, 3.10; N, 4.78%. Found: C, 57.32; H, 3.05; N, 4.78%. HR-ESI-MS (eluent; MeCN): *m*/*z* calcd for $C_{26}H_{17}N_2Pd$: 463.0431 ($[M - OCOCF_3]^+$); found 463.0439. IR (KBr disk, r.t.): ν = 2220 (C≡C), 1680 (C=O) cm^{-1}. ^1H NMR (300 MHz, CD_3CN, r.t.): δ = 6.72-6.81 (m, 3H, *para*-Ph, *meta*-Ph), 7.42 (d, 2H, *ortho*-Ph, *J* = 7 Hz), 7.48 (dd, 2H,

py-5, J = 6, 6 Hz), 7.67 (m, 2H, C_6H_4), 7.81 (d, 2H, 3-py, J = 7 Hz), 7.79-7.84 (2H, py-4, C_6H_4), 8.96 (d, 2H, py-6, J = 5 Hz) ppm. Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement.

Pd(OCOCF$_3$)(C$_6$H$_4$OMe-4)(bpeb) (4a). Complex **4a** (720 mg, 0.12 mmol, 59%) was obtained as gray powder from the reaction of Pd(OCOCF$_3$)(C$_6$H$_4$OMe-4)(tmeda) (**2a**) generated in situ from Pd(C$_6$H$_4$OMe-4)(I)(tmeda) (**1a**) (933 mg, 2.1 mmol) and AgOCOCF$_3$ by the similar procedure of **4a**. Anal. Calcd for $C_{29}H_{19}F_3N_2O_3Pd(H_2O)_{0.25}$: C, 56.97; H, 3.21; F, 9.32; N, 4.58%. Found: C, 57.02; H, 3.31; F, 9.52; N, 4.60%. HR-ESI-MS (eluent; MeCN): m/z calcd for $C_{27}H_{19}N_2OPd$: 493.0537 ($[M - OCOCF_3]^+$); found 493.0544. IR (KBr disk, r.t.): ν = 2224 (C≡C), 1678 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, r.t.): δ = 3.59 (s, 3H, OMe), 6.47 (d, 2H, *ortho*-C$_6H_4$-4-OMe, J = 9 Hz), 7.21-7.34 (4H, *meta*-C$_6H_4$-4-OMe, py-5), 7.54 (m, 2H, C_6H_4), 7.61 (d, 2H, py-3, J = 7.1 Hz) 7.70 (m, 2H, py-4), 7.79 (m, 2H, C_6H_4), 9.09 (d, 2H, py-6, J = 5 Hz) ppm. Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement.

Pd(OCOCF$_3$)(C$_6$H$_4$Me-4)(bpeb) (4b). Complex **4b** (247 mg, 0.42 mmol, 47%) was obtained as gray powder from the reaction of Pd(OCOCF$_3$)(C$_6$H$_4$Me-4)(tmeda) (**2b**) generated in situ from Pd(C$_6$H$_4$Me-4)(I)(tmeda) (**1b**) (441 mg, 1.0 mmol) and AgOCOCF$_3$ by the similar procedure of **4a**. Anal. Calcd for $C_{29}H_{19}F_3N_2O_2Pd(H_2O)$: C, 57.20; H, 3.48; N, 4.60%. Found: C, 57.31; H, 3.28; N, 4.63%. HR-ESI-MS (eluent; MeCN): m/z calcd for $C_{27}H_{19}N_2Pd$: 477.0588 ($[M - OCOCF_3]^+$); found 477.0598. IR (KBr disk, r.t.): ν = 2226 (C≡C), 1681 (C=O) cm^{-1}. ^1H NMR (300 MHz, CD_3CN, r.t.):

δ = 2.04 (s, 3H, Me), 6.63 (d, 2H, *meta*-C_6H_4-Me, J = 8 Hz), 7.26 (d, 2H, *ortho*-C_6H_4-Me, J = 8 Hz), 7.47 (dd, 2H, py-5, J = 6, 6 Hz), 7.69 (m, 2H, C_6H_4-bpeb, J = 6, 3 Hz), 7.81 (d, 2H, py-3, J = 8 Hz), 7.94 (m, 6H, C_6H_4, py-4), 8.94 (d, 2H, py-6, J = 5 Hz). Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement.

Pd(OCOCF$_3$)(C$_6$H$_4$COMe-4)(bpeb) (4d). Complex **4d** (100 mg, 0.16 mmol, 41%) was obtained as gray powder from the reaction of Pd(OCOCF$_3$)(C$_6$H$_4$COMe-4)(tmeda) (**2d**) generated in situ from Pd(C$_6$H$_4$COMe-4)(I)(tmeda) (**1d**) (182 mg, 0.40 mmol) and AgOCOCF$_3$ by the similar procedure of **4a**. Data of **4d**. Anal. Calcd for $C_{30}H_{19}F_3N_2O_3Pd(H_2O)_2$: C, 55.02; H, 3.54; N, 4.28%. Found: C, 54.49; H, 3.14; N, 4.17%. HR-ESI-MS (eluent; MeCN): *m*/*z* calcd for $C_{28}H_{19}N_2OPd$: 505.0537 ([M – $OCOCF_3]^+$); found 505.0541. IR (KBr disk, r.t.): ν = 2224 (C≡C), 1678 cm^{-1}. ^1H NMR (300 MHz, CD_3CN, r.t.): δ = 2.36 (s, 3H, Me), 7.36 (d, 2H, *ortho*-C_6H_4-4-COMe, J = 9 Hz), 7.49 (dd, 2H, py-5, J = 7 Hz), 7.64 (d, 2H, *meta*-C_6H_4-4-COMe, J = 8 Hz), 7.70 (m, 2H, C_6H_4-bpeb, J = 3, 6 Hz), 7.82 (d, 2H, py-3, J = 7 Hz), 7.92-7.95 (4H, C_6H_4, py-4), 8.98 (d, 2H, py-6, J = 5 Hz) ppm. Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement.

Pd(OCOCF$_3$)(C$_6$H$_4$CHO-4)(bpeb) (4e). Complex **4e** (185 mg, 0.31 mmol, 66%) was obtained as gray powder from the reaction of Pd(OCOCF$_3$)(C$_6$H$_4$CHO-4)(tmeda) (**2e**) generated in situ from Pd(C$_6$H$_4$CHO-4)(I)(tmeda) (**1e**) (277 mg, 0.50 mmol) and AgOCOCF$_3$ by the similar procedure of **4a**. Data of **4e**. Anal. Calcd for $C_{29}H_{17}F_3N_2O_3Pd(H_2O)$: C, 55.92; H, 2.83; N, 4.63%. Found: C, 55.67; H, 2.92; N, 4.49%. HR-ESI-MS (eluent; MeCN): *m*/*z* calcd for $C_{27}H_{17}N_2OPd$: 491.0381 ([M –

$OCOCF_3]^+$); found 491.0384. IR (KBr disk, r.t.): ν = 2837 (C-H), 2745 (C-H), 2223 (C≡C), 1682 (C=O) cm^{-1}. ^1H NMR (300 MHz, CD_3CN, r.t.): δ = 7.28 (d, 2H, *ortho*-C_6H_4-4-CO, J = 8 Hz), 7.49 (dd, 2H, py-5, J = 7 Hz), 7.70 (m, 2H, C_6H_4), 7.75 (d, 2H, *meta*-C_6H_4-4-CO, J = 8 Hz), 7.82 (d, 2H, py-3, J = 8 Hz), 7.91-7.95 (m, 4H, C_6H_4, py-4), 8.99 (d, 2H, py-6, J = 5 Hz), 9.68 (s, 1H, COH) ppm. Low solubility of the complex prevents $^{13}C\{^1H\}$ NMR measurement. HRESIMS (eluent: acetone): *m/z* Calcd for $C_{27}H_{17}N_2OPd$ $[M\text{-}OCOCF_3]^+$: 491.0381. Found: 491.0366.

Pd(OCOCF$_3$)(C$_6$F$_5$)(bpeb) (4j). Complex **4j** (138 mg, 0.21 mmol, 41%) was obtained as gray powder from the reaction of $Pd(OCOCF_3)(C_6F_5)$(tmeda) (**2j**) generated in situ from $Pd(C_6F_5)(I)$(tmeda) (258 mg, 0.50 mmol) and $AgOCOCF_3$ by the similar procedure of **4a**. data of **2i**, ^1H NMR data (300 MHz, $CDCl_3$, r.t.): δ = 2.65 (s, 6H, Me), 2.69 (s, 6H, Me), 2.73-2.75 (m, 2H, CH_2), 2.78 (s, 2H, CH_2). data of **4i**, Anal. Calcd for $C_{28}H_{12}F_8N_2O_2Pd$: C, 50.43; H, 1.81; N, 4.20%. Found: C, 50.59; H, 2.30; N: 3.98%. HR-ESI-MS (eluent; MeCN): *m/z* calcd for $C_{26}H_{12}N_2F_5Pd$: 552.9960 ($[M - OCOCF_3]^+$); found 552.9961. IR (KBr disk, r.t.): ν = 2224 (C≡C), 1681 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, r.t.): δ = 7.30 (ddd, 2H, py-5, J = 7, 6, 2 Hz), 7.54 (m, 2H, C_6H_4), 7.64 (d, 2H, py-3, J = 7 Hz), 7.74–7.80 (4H, C_6H_4, py-4), 9.01 (d, 2H, py-6, J = 5 Hz) ppm.

Pd(OCOCF$_3$)$_2$(bpeb) (5). To a THF solution (12.0 mL) of $Pd(OCOCF_3)_2$ (332 mg, 1.00 mmol) and bpeb (336 mg, 1.20 mmol) was stirred for 1 h at room temperature. The evaporation of the solvent yield crude product which was washed with toluene, Et_2O and CH_2Cl_2 to yield **5** as yellow solid (246 mg, 0.40 mmol, 40%). Anal. Calcd

for $C_{24}H_{12}N_2F_6O_4Pd$: C, 47.04; H, 1.97; N, 4.57; F, 18.60%. Found: C, 47.69; H, 2.08; N, 4.79; F, 18.26% ^{1}H NMR (300 MHz, $CDCl_3$, r.t.): δ = 7.38 (ddd, 2H, C_5H_4N, J = 7, 6, 1 Hz), 7.56 (dd, 2H, C_6H_4, J = 6, 3 Hz), 7.67 (d, 2H, C_5H_4N, J = 8 Hz), 7.81-7.86 (m, 4H, C_6H_4, C_5H_4N), 9.15 (d, 2H, C_5H_4N, J = 4 Hz) ppm.

Typical procedure of reaction of arylboronic acids, (4-YC_6H_4)$B(OH)_2$ (7b-7e, Y = Me, H, COMe and CHO) with complex 4a. Complex **4a** (6.1 mg, 10 μmol), Ag_2O (4.6 mg, 20 μmol), arylboronic acids, (4-YC_6H_4)$B(OH)_2$ (**7b-7e**, Y = Me, H, COMe and CHO, 50 μmol) and 1,2-diphenylethane (0.7 mg, 4 μmol (internal standard)) were charged to a NMR tube. After addition of CD_3CN/D_2O (0.98 mL/0.02 mL) to the mixture, the ^{1}H NMR spectrum was recorded. The reaction temperature is maintained at 50 °C by a thermostatic oil bath. Concentration of the compounds was calculated from ^{1}H NMR peak area ratio among OMe of **4a** (δ 3.52), C_5H_4N of resulting complex (δ 8.91-8.96) and CH_2 of internal standard (1,2-diphenylethane).

Typical procedure of reaction of (4-$CHOC_6H_4$)$B(OH)_2$ (7e) with complex 4a-4d, 4j. Complexes, **4a-4d** and **4j** (10 μmol), Ag_2O (4.6 mg, 20 μmol), arylboronic acids, (4-$CHOC_6H_4$)$B(OH)_2$ (**7e**, 7.5 mg, 50 μmol) and 1,2-diphenylethane (0.7 mg, 4 μmol (internal standard)) were charged to a NMR tube. After addition of CD_3CN/D_2O (0.98 mL/0.02 mL) to the mixture, the ^{1}H NMR spectrum was recorded. The reaction temperature is maintained at 50 °C by a thermostatic oil bath. Concentration of the compounds was calculated from ^{1}H NMR peak area ratio between CHO of **4e** and CH_2 of the internal standard (1,2-diphenylethane).

Crystal structure determination.

Yellow crystals of **4a** and **5** suitable for X-ray diffraction study were obtained by recrystallization from CH_2Cl_2/Et_2O at room temperature. CCDC nos. 1555703 and 1555704 contain the supplementary crystallographic data for **4a** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi.

References

[1] (a) D. V. Partyka, Chem. Rev. 111 (2011) 1529-1595; (b) K. Osakada, Transmetalation. in Current Methods in Inorganic Chemistry, 3. Fundamentals of Molecular Catalysis; H. Kurosawa, A. Yamamoto, Eds.; Elsevier Science: Amsterdam, Chapter 5 (2003) pp 233-291.

[2] (a) A. Suzuki, J. Organomet. Chem. 576 (1999) 147-168; (b) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457-2483.

[3] (a) Y. Nishihara, H. Onodera, K. Osakada, J. Chem. Soc., Chem. Commun. (2004) 192-193; (b) K. Osakada, H. Onodera, Y. Nishihara, Organometallics 24 (2005) 190-192; (c) Y. Suzaki, K. Osakada, Organometallics 23 (2004) 5081-5084; (d) I. Pantcheva, Y. Nishihara, K. Osakada, Organometallics 24 (2005) 3815-3817.

[4] (a) A. A. C. Braga, N. H. Morgon, G. Ujaque, F. Maseras, J. Am. Chem. Soc. 127 (2005) 9298-9307; (b) A. A. C. Braga, N. H. Morgon, G. Ujaque, A. Lledós, F. Maseras, J. Organomet. Chem. 691 (2006) 4459-4466; (c) A. A. C. Braga, G. Ujaque, F. Maseras, Organometallics 25 (2006) 3647-3658.

[5] (a) P. Zhao, C. D. Incarvito, J. F. Hartwig, J. Am. Chem. Soc. 129 (2007) 1876-1877; (b) B. P. Carrow, J. F. Hartwig, J. Am. Chem. Soc. 133 (2011) 2116-2119.

[6] (a) C. Amatore, A. Jutand, G. Le Duc, Chem.-Eur. J. 17 (2011) 2492-2503; (b) C. Amatore, A. Jutand, G. Le Duc, Chem.-Eur. J. 18 (2012) 6616-6625; (c) C. Amatore, G. Le Duc, A. Jutand, Chem.-Eur. J. 19 (2013) 10082-10093; (d) G. Laurence, A. Jutand, Synthesis 49 (2017) 1182-1189.

[7] M. A. Ortuño, A. Lledós, F. Maseras, G. Ujaque, ChemCatChem 6 (2014) 3132-3138.

[8] (a) M. Hofer, E. Gomez-Bengoa, C. Nevado, Organometallics 33 (2014) 1328-1332; (b) R. Kumar, A. Linden, C. Nevado, J. Am. Chem. Soc. 148 (2016) 13790-13793.

[9] A. A. Thomas, S. E. Denmark, Science 352 (2016) 329-332.

[10] (a) F. Fu. J. Xiang, H. Cheng, L. Cheng, H. Chong, S. Wang, P. Li, S. Wei, M. Zhu, Y. Li, ACS Catal. 7 (2017) 1860-1867; (b) J. M. Neely, M. J. Bezdek, P. J. Chirik, ACS Cent. Sci. 2 (2016) 935-942; (c) A. K. L. Yuen, C. A. Hutton, Tetrahedron Lett. 46 (2005) 7899-7903; (d) J. del Pozo, G. Salas, R. Álvarez, J. A. Casares, P. Espinet, Organometallics 35 (2016) 3604-3611; (e) J. Li, L. Jin, C. Liu, A. Lei, Org. Chem. Front. 1 (2014) 50-53.

[11] T. Nishikata, Y. Yamamoto, N. Miyaura, Organometallics 23 (2004) 4317-4324.

[12] Z. Freixa, P. W. N. M. van Leeuwen, Coord. Chem. Rev. 252 (2008) 1755-1786.

[13] A similar reaction using Ag_2O instead of Na_2CO_3 proceed slowly and yield the biaryl in 19% after 1 h.

[14] B. A. Markies, A. J. Canty, W. de Graaf, J. Boersma, M. D. Janssen, M. P. Hogerheide, W. J. J. Smeets, A. L. Spek, G. van Koten, J. Organomet. Chem. 482 (1994) 191-199.

[15] (a) T. Yagyu, M. Hamada, K. Osakada, T. Yamamoto, Organometallics 20 (2001) 1087-1101; (b) Y. Suzaki, K. Osakada, Organometallics 22 (2003) 2193-2195; (c) Y. Suzaki, M. Shirokawa, T. Yagyu, K. Osakada, Eur. J. Inorg. Chem. 31 (2015) 421-429.

[16] (a) F. Ozawa, K. Kurihara, M. Fujimori, T. Hidaka, T. Toyoshima, A. Yamamoto, Organometallics 8 (1989) 180-188; (b) F. Ozawa, T. Ito, Y. Nakamura, A. Yamamoto, Bull. Chem. Soc. Jpn. 54 (1981) 1868-1880.

[17] (a) K.-C. Kong, C.-H. Cheng, J. Am. Chem. Soc. 113 (1991) 6313-6315; (b) F. E. Goodson, T. I. Wallow, B. M. Novak, J. Am. Chem. Soc. 119 (1997) 12441-12453.

[18] T. Rünzi, U. Tritschler, P. Roesle, I. Göttker-Schnetmann, H. M. Möller, L. Caporaso, A. Poater, L. Cavallo, S. Mecking, Organometallics 31 (2012) 8388-8406.

[19] (a) E. Bosch, C. L. Barnes, Inorg. Chem. 40 (2001) 3097-3100; (b) N. L. Brennan, C. L. Barnes, E. Bosch, Inorg. Chim. Acta 363 (2010) 3987-3992.

[20] M. Jung, Y. Suzaki, T. Saito, K. Shimada, K. Osakada, Polyhedron 40 (2012) 168-174.

[21] (a) N. Mintcheva, M. Tanabe, K. Osakada, Organometallics 26 (2007) 1402; (b) D. Kruis, B. A. Markies, A. J. Canty, J. Boersma, G. van Koten, J. Organomet. Chem. 532 (1997) 235-242; (c) K. Osakada, R. Sakata, T. Yamamoto, Organometallics 16 (1997) 5354-5364.

[22] N. D. Ball, J. B. Gary, Y. Ye, M. S. Sanford, J. Am. Chem. Soc. 133 (2011) 7577-7584.

[23] Y.-J. Kim, D.-H. Kim, S.-W. Song, T. Son, Bull. Korean Chem. Soc. 19 (1998) 125-128.

[24] Crystal Structure: Crystal analysis package, Rigaku and Rigaku/MSC (2000–).

[25] C. Hansch, A. Leo, R. W. Taft, Chem. Rev. 91 (1991) 165.

Highlights for

Catalytic and Stoichiometric Reactions of Arylpalladium(II) Complexes Bearing a *trans*-Chelating Dinitrogen Ligand with Arylboronic Acids

Yuji Suzaki, Takashi Saito, Kohtaro Osakada*

i) Palladium complexes bearing a *trans*-chelating dinitrogen ligand have been synthesized.

ii) The new complexes show function as homogeneous catalysts for Suzaki-Miyaura coupling reaction.

iii) The stoichiometric reaction of the new complexes with arylboronic acids result in exchange of the aryl lignads.