Pd(II) Trifluoroacetate Complexes Containing Chelating Phosphine Ligands: Synthesis, Structures, and Catalysis

Kun-Woo Kim,[†] Yong-Joo Kim,[†,*] Hye Jin Lim,[‡] and Soon W. Lee[‡]

[†]*Department of Chemistry, Kangnung-Wonju National University, Gangneung 210-702, Korea.*
**E-mail: yjkim@kangnung.ac.kr*
[‡]*Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*

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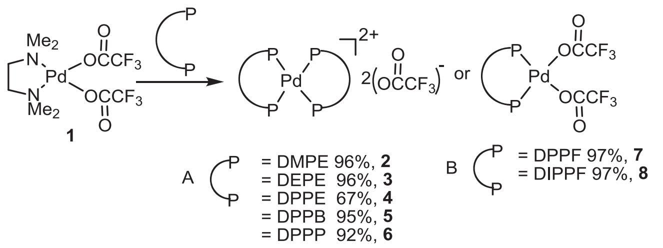
Carboxylates coordinate to transition metals in a terminal, chelating, or bridging mode through their oxygen atoms, and serve as active ligands in various catalytic reactions.[1–3] Transition-metal complexes having a trifluoroacetate (TFA) ligand are well known to have higher solubility and crystallinity than the corresponding acetate counterparts depending on the metal identity. In particular, TFA complexes of late transition metals are efficient catalysts in several organic reactions, including polymerization of isocyanide or butadiene and copolymerization of CO and olefin.[4–7] Moreover, such complexes exhibit higher efficiency than the corresponding acetate complexes in the aerobic oxidation of organic substrates, enamide formation by vinyl transfer, or oxidative cyclization of organic substrates in the presence of Pd catalysts.[8–11] Although many catalytic Suzuki–Miyaura C—C coupling reactions have been reported, those involving late-transition-metal–TFA complexes are still rare.[12–15] For this reason, we attempted to develop a new synthetic route to Pd–TFA complexes possessing chelating phosphine ligands for use in such coupling reactions. In this work, we prepared a series of Pd(II)–TFA–(chelating diphosphine) complexes and examined their catalytic C—C coupling reactions of aryl halides and arylboronic acids.

We first prepared a Pd(II)–TFA–TMEDA complex (TMEDA = *N*,*N*,*N*′,*N*′-dimethyl ethylene diamine), [Pd(TMEDA)(TFA)$_2$] (**1**), by the metathesis of [PdCl$_2$(TMEDA)] and 2 equiv of [Ag(TFA)]. Subsequently, the ligand replacement of complex **1** was investigated with one or two equivalents of chelating phosphine, including DMPE, DEPE, 1,2-Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2, DPPE; n = 3, DPPP; n = 4, DPPB), and the ferrocene-bridged phosphines DPPF and DIPPF (1,1′-bis(diphenyl or diisoporpyl)phosphine ferrocene). These reactions afforded ionic bis(diphosphine) Pd(II) complexes [Pd(P~P)$_2$](TFA)$_2$ (type A, **2–6**) or neutral mono(diphosphine) Pd(II)–TFA complexes [Pd(P~P)(TFA)$_2$] (type B, **7** and **8**) in high yields (Scheme 1).

Chemical compositions of complexes **2–8** strongly indicate that sterically hindered and less basic chelating phosphines such as DPPF or DIPPF prefer to form mono(diphosphine) compounds. Isolated bis(chelating phosphine)–Pd(II)–TFA complexes are poorly soluble in organic solvents.



Scheme 1. Syntheses of Pd(II) trifluoroacetates.

All products were characterized by spectroscopy (IR and NMR) and elemental analysis, together with X-ray crystallography for complexes **2** and **7**. The IR spectra display characteristic stretching C—O and C—F bands at 1671–1711 and at 1105–1190 cm^{-1}, respectively. Details on crystal data of complexes are summarized in Supporting Information (see Table S1). Figure 1 shows the cationic part of complex **2**·H$_2$O, in which two CF$_3$COO$^-$ counterions and one lattice water are omitted for clarity.

The molecular structure of **7** is given in Figure 2, which shows a Pd(II) metal, a DPPF ligand, and two CF$_3$COO$^-$ ligands. Two Cp rings in the DPPF ligand are not perfectly parallel, with a dihedral angle of 4.4(4)°. The Pd···Fe separation of 4.1932(8) Å indicates no direct interactions between these two metals.

We examined the ligand exchange reaction of complex **8** with 2 equiv of NaN$_3$ in CH$_2$Cl$_2$ (Scheme 2). The reaction readily proceeded to give a Pd(II) azide complex, [(DIPPF)Pd(N$_3$)$_2$] (**9**), as an orange crystal in quantitative yield, which was characterized by spectroscopic data and elemental analysis. The IR spectrum of **9** shows a strong absorption band at 2045 cm^{-1}, a characteristic peak of the N$_3$ group.

Recently, several Suzuki–Miyaura C—C coupling reactions employing Pd(II)–TFA complexes containing C–N donor or pincer-type (PCP) ligands were reported.[14,15] However, the corresponding reactions with bis(chelating phosphine) analogs are relatively rare. In this context, we evaluated the catalytic activity of several complexes (**1**, **2**, **6–8**, and **9**) for the coupling reactions (catalysts in Chart 1 and Scheme 3). In order to find the optimum conditions for

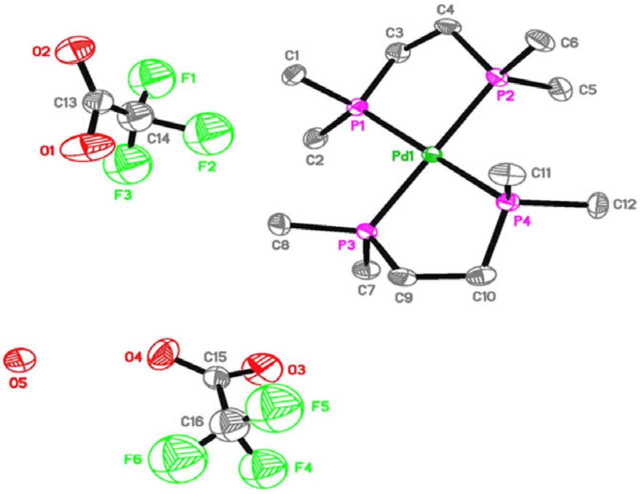


Figure 1. ORTEP drawing of the cationic part of complex $2 \cdot H_2O$. Selected bond lengths (Å) and bond angles (°) in complex $2 \cdot H_2O$: Pd1—P4 2.312(2), Pd1—P1 2.315(2), Pd1—P3 2.315(2), Pd1—P2 2.316(2); P4—Pd1—P1175.87(5), P4—Pd1—P3 83.97(8), P1—Pd1—P3 95.80(4), P1—Pd1—P2 84.50(8).

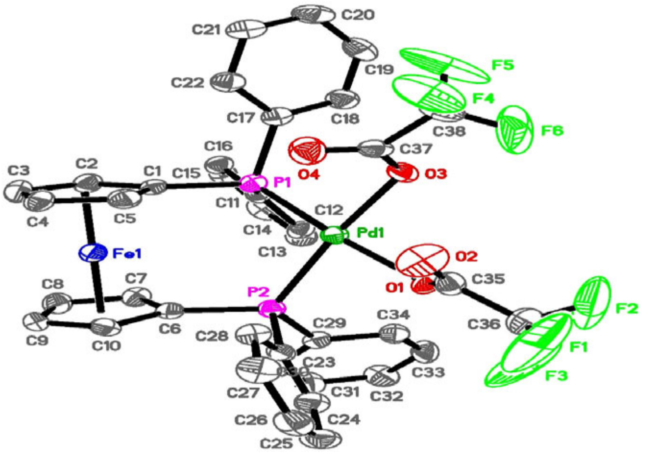
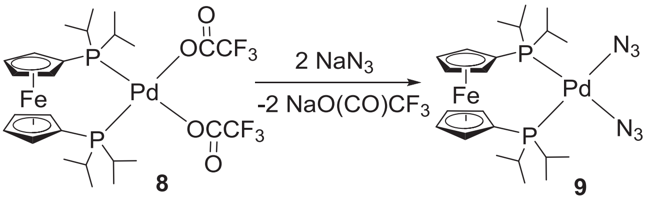


Figure 2. ORTEP drawing of complex **7**. Selected bond lengths (Å) and bond angles (°): Pd1—O3 2.071(3), Pd1—O1 2.088(3), Pd1—P1 2.244(1), Pd1—P2 2.261(1); O3—Pd1—O1 86.9(1), O3—Pd1—P1 91.30(9), O3—Pd1—P2 170.80(9), P1—Pd1—P2 97.38(5).



Scheme 2. Reaction of **8** with NaN_3.

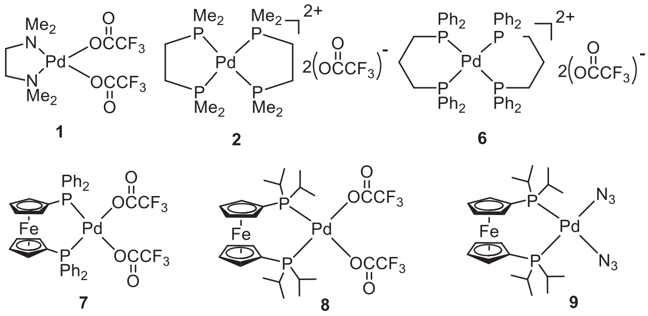
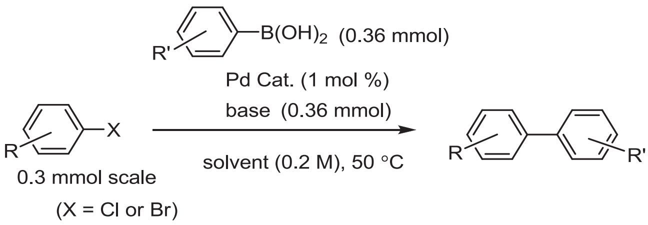


Chart 1. Catalysts for Suzuki–Miyaura C—C coupling



Scheme 3. Suzuki–Miyaura C—C couplings.

the reactions, we first examined the reaction of *p*-chloro (or bromo) acetophenone, phenylboronic acid, and various bases in the mole ratio of 1:1.2:1.2 in several solvents in air. The reaction conditions and product yields are listed in Table 1, in which entry 5 (complex **8**) exhibits relatively high activity when *p*-chloro acetophenone (entries 1–15) is the substrate. Furthermore, even in the case of *p*-bromo acetophenone (entries 16–21), the activity (entry 20) of complex **8** is higher than that of the other complexes. Slightly higher activity of **8** compared to **7** may be due to the fact that complex **8** having the more basic DIPPF ligand than the DPPF possesses a more electron-rich metal center to stabilize an M–C(sp^2) bond in the oxidative addition product of aryl halides. According to entries 1–21 in Table 1, *p*-bromo acetophenone is more reactive than *p*-chloro acetophenone, and mono(diphosphine) Pd–TFA complexes are more efficient catalysts than bis(diphosphine) analogs. On the basis of the above catalytic activities, we utilized complex **8** for further catalytic C—C coupling reactions.

Entries 1–13 in Table 2 show the results of the C—C coupling reactions of various aryl bromides and phenylboronic acid in ethanol/H_2O at 50 °C in air. As expected, the coupling products were obtained in moderate to good yields, which are comparable to those for other known Pd-catalyzed reactions. In addition, the same coupling reactions using varied aryl boronic acids exhibited good activities. However, entries 12 and 13 gave poor yields, probably due to the deactivation of the phenyl ring by the organic substituents or aryl moieties. Entry 17 also gave very low yield, but we cannot give a clear explanation at this moment. Therefore, our results suggest that Pd(II)–TFA complexes having a single chelating phosphine ligand can serve as efficient catalysts for the C—C coupling reactions involving aryl bromide with organoboronic acid.

In summary, we prepared several Pd(II)–TFA complexes having one or two chelating phosphines, and one of them showed a high catalytic activity in the Suzuki–Miyaura C—C coupling reactions of aryl bromide and aryl boronic acid at 50 °C in air.

Table 1. Optimization for Suzuki–Miyaura cross-coupling reactions of 4-chloro (or bromo) acetophenone with phenylboronic acid in air.

Entry	Catalyst	Solvent	Base	T (°C)	t (h)	Isolated yield (%)
1	**1**	EtOH/H_2O	Cs_2CO_3	50	1	36
2	**2**	EtOH/H_2O	Cs_2CO_3	50	1	35
3	**6**	EtOH/H_2O	Cs_2CO_3	50	1	41
4	**7**	EtOH/H_2O	Cs_2CO_3	50	1	46
5	**8**	EtOH/H_2O	Cs_2CO_3	50	1	61
6	**9**	EtOH/H_2O	Cs_2CO_3	50	1	34
7	**8**	EtOH/H_2O	K_2CO_3	50	1	47
8	**8**	EtOH/H_2O	Na_2CO_3	50	1	39
9	**8**	EtOH/H_2O	KO^tBu	50	1	38
10	**8**	THF	Cs_2CO_3	50	1	42
11	**8**	MeOH	Cs_2CO_3	50	1	42
12	**8**	MeOH/H_2O	Cs_2CO_3	50	1	36
13	**8**	EtOH	Cs_2CO_3	50	1	32
14	**8**	DMF	Cs_2CO_3	50	1	18
15	**8**	EtOH/H_2O	Cs_2CO_3	r-t	6	14
16[a]	**1**	EtOH/H_2O	Cs_2CO_3	50	1	87
17[a]	**2**	EtOH/H_2O	Cs_2CO_3	50	1	83
18[a]	**6**	EtOH/H_2O	Cs_2CO_3	50	1	89
19[a]	**7**	EtOH/H_2O	Cs_2CO_3	50	1	99(88)[b]
20[a]	**8**	EtOH/H_2O	Cs_2CO_3	50	1	99(97) [b]
21[a]	**9**	EtOH/H_2O	Cs_2CO_3	50	1	95

[a] 4-Bromoacetophenone was used.
[b] 0.5 h stirring.

Experimental

All manipulations of air-sensitive compounds were performed under N_2 or Ar using Schlenk-line techniques. THF and diethyl ether were distilled from sodium benzophenone. Elemental analyses were performed at the analytical laboratories at Kangnung-Wonju National University. IR spectra were recorded using a Perkin-Elmer BX spectrophotometer (Waltham, MA, USA). NMR (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectra were obtained in $CDCl_3$ using a JEOL Lamda 300 MHz spectrometer (Tokyo, Japan). Chemical shifts were referenced to internal Me_4Si and to external 85% H_3PO_4. X-ray reflection data were obtained at either the Korea Basic Science Institute (Seoul Center) and the Cooperative Center for Research Facilities at Sungkyunkwan University. $[PdCl_2(TMEDA)]$ was prepared by the literature method.[16]

Preparation of $[Pd(TFA)_2(TMEDA)]$ (1). A solution of $AgOCOCF_3$ (0.331 g, 1.51 mmol) dissolved in H_2O (2 mL) was added to a Schlenk flask containing $[PdCl_2(TMEDA)]$ (0.200 g, 0.69 mmol) in CH_2Cl_2 (30 mL). After stirring the reaction mixture for 2 h at room temperature, white solids precipitated. The mixture was filtered to remove the salts and dried over $CaCl_2$. The solvent was completely removed under vacuum. The resulting residue was solidified with hexane. The solids were washed with *n*-hexane (2 mL × 2) to give crude solids, which were recrystallized from CH_2Cl_2/hexane to give compound **1**. The complex **1** was also prepared from $[Pd(TFA)_2]$ and TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) under reflux.[9]

Preparation of $[Pd(P\sim P)_2](TFA)_2$ (P~P = DMPE, DEPE, DPPE, DPPB, 2–6) and $[(P\sim P)Pd(TFA)_2]$ (P~P = DPPF, 7; DIPPF, 8). DMPE (102 µL, 0.616 mmol) was slowly added to a yellow suspension of $[Pd(TFA)_2(TMEDA)]$ (0.138 g, 0.31 mmol) in CH_2Cl_2 (3 mL). An initial suspension turned gray. After stirring the reaction mixture for 2 h at room temperature, the solvent was removed under vacuum, and washed with *n*-hexane. The crude solid was recrystallized from CH_2Cl_2/hexane to give $[Pd(P\sim P)_2](TFA)_2$ (P~P = DMPE), **2** (0.192 g, 99%). Complexes **3–8** were analogously prepared. Analytical and spectroscopic data are available as Supporting Information.

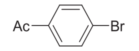
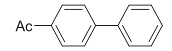
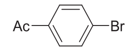
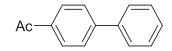
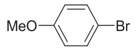
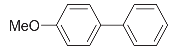
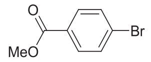
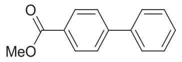
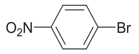
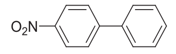
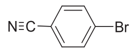
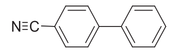
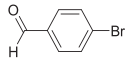
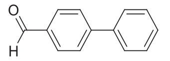
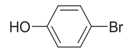
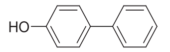
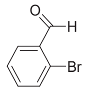
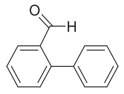
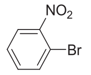
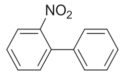
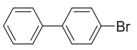
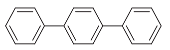
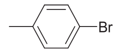
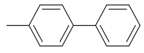
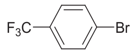
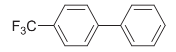
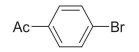
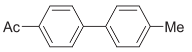
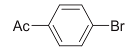
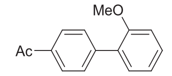
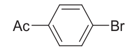
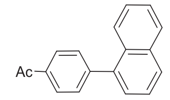
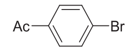
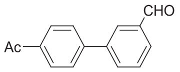
Preparation of $[(DIPPF)Pd(N_3)_2]$ (9). NaN_3 (0.011g, 0. 16 mmol) dissolved in H_2O (1 mL) was slowly added to a red solution of **8** (0.059 g, 0.08 mmol) in CH_2Cl_2 (3 mL). After stirring the reaction mixture for 1 h at room temperature, the solvent was removed under vacuum and extracted with CH_2Cl_2. The collected solution was evaporated to give a crude product, which was recrystallized from CH_2Cl_2/hexane to give orange crystals of compound **9** (0.046 g, 96%).

General Procedure for Suzuki–Miyaura Cross-Coupling Reactions. Experimental details and spectral data for the organic compounds are described in Supporting information.

X-ray Structure Determination. Details on X-ray structure determination are described in Supporting information.

Acknowledgments. This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the

Table 2. Cross-coupling reactions of arylbromide and arylboronic acid catalyzed by complex **8**.

Entry	Aryl bromide	Product	Isolated yield
1			99
2			93
3			98
4			98
5			97
6			96
7			94
8			89
9			80
10			79
11			75
12			54
13			47
14			99
15			89
16			83
17			36

[a] Catalyst 0.5 mol %.

[b] 4-Methylboronic acid was used.

[c] 2-Methoxyphenyl boronic acid was used.

[d] Naphtalene-1-boronic acid was used.

[e] 3-Formylphenyl boronic acid was used.

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Supporting Information. Analytical, spectroscopic, and crystallographic data are available from the supporting information.

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