

Diarylpalladium Complexes with a Cis Structure. Formation via Transmetalation of Arylboronic Acids with an Aryliodopalladium Complex and Intramolecular Coupling of the Aryl Ligands, Affording Unsymmetrical Biaryls

Kohtaro Osakada,* Hiroyuki Onodera, and Yasushi Nishihara†

Chemical Resources Laboratory, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

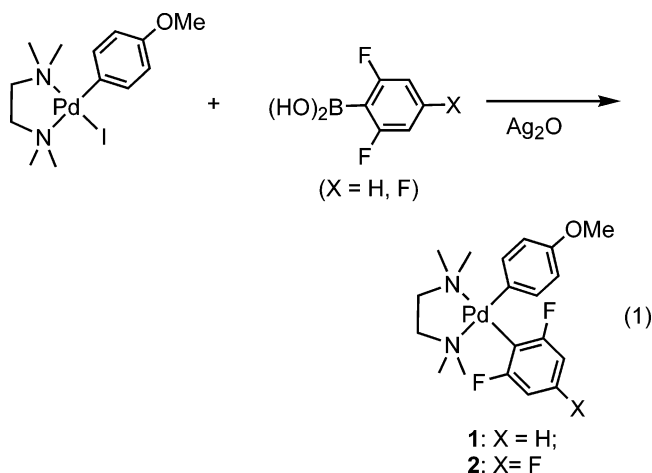
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Summary: (2,4,6-Trifluorophenyl)- and (2,6-difluorophenyl)boronic acids react with $\text{PdI}(\text{C}_6\text{H}_4\text{O}-4\text{-Me})(\text{tmen})$ ($\text{tmen} = N,N,N',N'$ -tetramethylethylenediamine) in the presence of Ag_2O to produce *cis*-diarylpalladium complexes with a *tmen* ligand via intermolecular transfer of the fluorophenyl group from B to Pd. The isolated complexes undergo coupling of the two aryl ligands upon heating the solution to 45–60 °C to afford unsymmetrical biaryls.

The reactions of organolithium, -magnesium, and -aluminum compounds with halogeno transition-metal complexes provide a useful method for the preparation of alkyl and aryl complexes of late transition metals. Reports of the preparation of organotransition-metal complexes via the reactions of organoboronic acids with halogeno transition-metal complexes are much less common, although organoboronic acids are employed as the convenient source of an aryl or alkenyl group in the C–C bond-forming reactions catalyzed by Pd and Rh complexes.¹ Since organoboronic acids contain nonpolar and stable C–B bonds, the above catalytic reactions often require addition of a base such as OH^- , which activates the C–B bond and/or the transition-metal–halogen bond. Very recently, Miyaura reported the reaction of phenylboronic acid with $[\text{Pd}(\text{dppe})(\text{MeCN})_2]^{2+}$ ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) in the presence of PPh_3 to form $[\text{PdPh}(\text{dppe})(\text{PPh}_3)]^+$ via transfer of the phenyl group from B to Pd.² A monophenylpalladium complex with a similar structure, $[\text{PdPh}(\text{dppe})(\text{L})]^+$ ($\text{L} = \text{solvent, etc.}$), is a plausible intermediate in 1,4-addition reactions of arylboronic acids with α,β -unsaturated ketones catalyzed by $[\text{Pd}(\text{dppe})(\text{MeCN})_2]^{2+}$. Transmetalation of an arylboronic acid with a monoarylpalladium complex, giving diarylpalladium species, and the subsequent coupling of the two aryl ligands are believed to be involved in the Pd-catalyzed cross-coupling reaction of aryl halides with organoboronic acids (Suzuki–Miyaura reaction). The existence of a diarylpalladium complex in the reaction mixture of arylboronic acid with an arylhalogenopalladium complex

was demonstrated by ESI/MS characterization.³ We recently found that the reaction of (2,4,6-trifluorophenyl)boronic acid with *trans*- $\text{Pd}(\text{C}_6\text{F}_5)\text{I}(\text{PEt}_3)_2$ afforded the transmetalation product *trans*- $\text{Pd}(\text{C}_6\text{H}_2\text{-2,4,6-F}_3)(\text{C}_6\text{F}_5)(\text{PEt}_3)_2$.⁴ The isolated diarylpalladium complex, however, did not undergo smooth coupling of the two aryl ligands, due to the stable Pd–C bond and *trans* geometry of the complex. In this paper, we report the reaction of a fluorine-free arylpalladium complex having *tmen* ($\text{tmen} = N,N,N',N'$ -tetramethylethylenediamine) with di- and trifluorinated phenylboronic acids to form the isolable *cis*-diarylpalladium complexes and their reductive elimination of biaryls on gentle heating.

Complex $\text{PdI}(\text{C}_6\text{H}_4\text{-4-OMe})(\text{tmen})$ reacts with (2,6-difluorophenyl)- and (2,4,6-trifluorophenyl)boronic acids in the presence of Ag_2O and H_2O to produce Pd complexes with a *cis* structure, $\text{Pd}(\text{C}_6\text{H}_3\text{-2,6-F}_2)(\text{C}_6\text{H}_4\text{-4-OMe})(\text{tmen})$ (**1**) and $\text{Pd}(\text{C}_6\text{H}_2\text{-2,4,6-F}_3)(\text{C}_6\text{H}_4\text{O}-4\text{-Me})(\text{tmen})$ (**2**), respectively. Complexes **1** and **2** give satis-



factory results of elemental analyses and NMR (^1H , ^{13}C , and ^{19}F) spectra. Figure 1 shows the molecular structure of **2** determined by X-ray crystallography.⁵ The molecule has a square-planar coordination around the Pd center. The two Pd–C bond distances are quite similar to each other. The Pd–N1 bond (2.168(3) Å) is shorter than the

† Present address: Department of Chemistry, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan.

(1) Miyaura, N. *Adv. Met.-Org. Chem.* **1998**, 6, 187.

(2) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, 23, 4317.

(3) Aliprantis, A. O.; Canary, J. W. *J. Am. Chem. Soc.* **1994**, 116, 6985.

(4) Nishihara, Y.; Onodera, H.; Osakada, K. *Chem. Commun.* **2004**, 192.

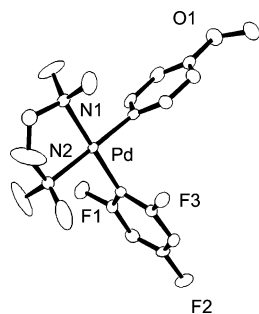
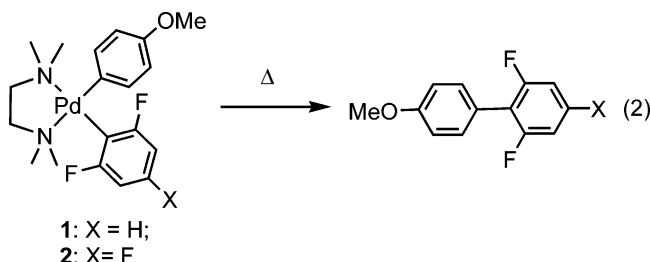


Figure 1. ORTEP drawing of **2** with 30% ellipsoidal plots. Selected bond distances (Å) and angles (deg): Pd1–N1 = 2.168(3), Pd1–N2 = 2.177(3), Pd1–C1 = 2.000(3), Pd1–C8 = 2.000(3); N1–Pd1–N2 = 83.9(1), N1–Pd1–C1 = 94.6(1), N1–Pd1–C8 = 178.1(1), N2–Pd1–C1 = 178.5(1), N2–Pd1–C8 = 96.0(1), C1–Pd1–C8 = 85.4(1).

Pd–N2 bond (2.177(3) Å), indicating that the trans influence of the 2,4,6-trifluorophenyl ligand is less than that of the 4-methoxyphenyl ligand. The reactions in eq 1 form the complexes in high yields after 3 h at room temperature, but a longer reaction causes partial formation of the biaryl caused by coupling of the two aryl groups. Analogous reaction of (2,4-difluorophenyl)-boronic acid with PdI(C₆H₄-4-OMe)(tmen) does not lead to isolation of the diarylpalladium complex but forms the coupling product, MeOC₆H₄–C₆H₃F₂, directly. Smooth transmetalation does not occur in the reaction of (2,4,6-trifluorophenyl)boronic acid using AgBF₄ instead of Ag₂O, suggesting that Ag₂O activates not only the Pd–I bond but also the C–B bond.

Heating a C₆D₆ solution of **1** at 50 °C produces 4-methoxy-2',6'-difluorobiphenyl via coupling of the two aryl ligands in 94% yield, as shown in eq 2. The ¹H NMR



spectra of the reaction mixture indicate the formation of the biaryl as the sole aromatic product. 4,4'-Dimethoxybiphenyl, which could be formed by intermolecular coupling or intermolecular scrambling of the aryl ligands, does not exist in the reaction mixture. Figure 2 depicts first-order plots of the reaction monitored by ¹H NMR spectra. The reaction of **1** obeys first-order kinetics with the kinetic parameters $\Delta H^\ddagger = 101 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -10 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta G^\ddagger = 103 \text{ kJ mol}^{-1}$ at 25 °C. Formation of the biaryl from a thermal reaction of **2** is complete after 3 days at 50 °C and is much slower than the thermal decomposition of **1**. The above reactions accompany deposition of Pd metal, which is inhibited

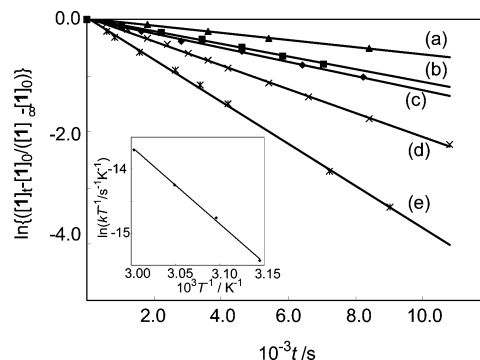


Figure 2. First-order plots of the thermally induced reductive elimination of 2,6-difluoro-4'-methoxybiphenyl from complex **1**: (a) at 45 °C; (b) with added diethyl fumarate at 50 °C; (c) at 50 °C; (d) at 55 °C; (e) at 60 °C. An Eyring plot is shown in the inset.

by addition of diethyl fumarate (8-fold molar amount of Pd, 0.15 mM). The rate constants of the reactions with addition of diethyl fumarate ($1.12 \times 10^{-4} \text{ s}^{-1}$) and without the additive ($1.24 \times 10^{-4} \text{ s}^{-1}$) do not differ significantly from each other. Thus, the Pd metal formed during the reaction does not affect the reaction rate.⁶

The diarylpalladium complexes *trans*-PdAr₂(PEt₂Ph)₂ (Ar = Ph, *m*-C₆H₄Me) have been reported in the literature.⁷ They are stable, due to the trans structure, although addition of aryl halides to their solutions results in formation of biaryls via the *cis*-diarylpalladium intermediates, which undergo reductive elimination of the products. Coupling of aryl ligands at *cis* positions of square-planar complexes of group 10 metals was reported to take place much more easily than that of *cis*-dialkyl complexes.^{8–10} The *cis*-diarylpalladium complexes reported so far contain fluoro, chloro,¹¹ and nitro¹² substituents at the ligand or are stabilized by a chelating anchor group¹³ of the aryl ligands. In this study, the combination of the fluorinated and non-fluorinated aryl ligands and the tmen ligand enabled both isolation of the *cis*-diarylpalladium complexes and thermally induced reductive elimination of biaryl under mild conditions.

(6) The reaction of **1** at 50 °C with added excess tmen (5-fold molar amount of Pd) gives rise to the observed rate constant, $0.92 \times 10^{-4} \text{ s}^{-1}$. This result suggests that tmen influences the reaction rate to a small extent.

(7) (a) Nakazawa, H.; Ozawa, F.; Yamamoto, A. *Organometallics* **1983**, 2, 241. (b) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, 5, 2144. (c) Ozawa, F.; Hidaka, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1987**, 330, 253.

(8) Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *Organometallics* **1994**, 13, 2053.

(9) (a) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1310. (b) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1977**, 1892.

(10) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, 2, 1466.

(11) (a) Uson, R.; Fornies, J.; Navarro, R. *J. Organomet. Chem.* **1975**, 96, 307. (b) Deacon, G. B.; Grayson, I. L. *Transition Met. Chem.* **1983**, 8, 131. (c) Ruiz, J.; Rodriguez, V.; López, G.; Casabó, J.; Molins, E.; Miravittles, C. *Organometallics* **1999**, 18, 1177. (d) Herberhold, M.; Schmalz, T.; Milius, W.; Wolfgang, M.; Wrackmeyer, B. *Inorg. Chim. Acta* **2003**, 352, 51.

(12) Vicente, J.; Chicote, M. T.; Martin, J.; Artigao, M.; Solans, X.; Font-Altaba, M.; Aguiló, M. *J. Chem. Soc., Dalton Trans.* **1988**, 141.

(13) (a) Cornioley-Deuschel, C.; Ward, T.; von Zelewsky, A. *Helv. Chim. Acta* **1988**, 71, 130. (b) Fornies, J.; Navarro, R.; Sicilia, V.; Tomas, M. *Inorg. Chem.* **1993**, 32, 3675. (c) Edelbach, B. L.; Vivic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, 17, 4784.

(5) Crystal data and details of the structure refinement of **2**: C₁₉H₂₅F₃N₂OPd, *M_r* = 460.81, 1.2 × 1.1 × 0.7 mm, monoclinic, *a* = 8.730(4) Å, *b* = 14.057(7) Å, *c* = 16.033(8) Å, β = 100.229(6)°, *V* = 1936.2(16) Å³, *P*2₁/c (No. 14), *Z* = 4, *D_{calc}* = 1.581 g cm⁻³, *F*(000) = 936.00, μ(Mo Kα) = 9.96 cm⁻¹, Mo Kα (λ = 0.710 70 Å), 12 292 total reflections measured, 4193 unique reflections (*R_{int}* = 0.026), 3555 observations (*I* > 3.00σ(*I*)), 260 variables, *R*(*I* > 3.00σ(*I*)) = 0.040, *R_w*(*I* > 3.00σ(*I*)) = 0.056, GOF = 1.114.

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Supporting Information Available: Text giving additional experimental details and characterization data and tables giving crystallographic data of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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