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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

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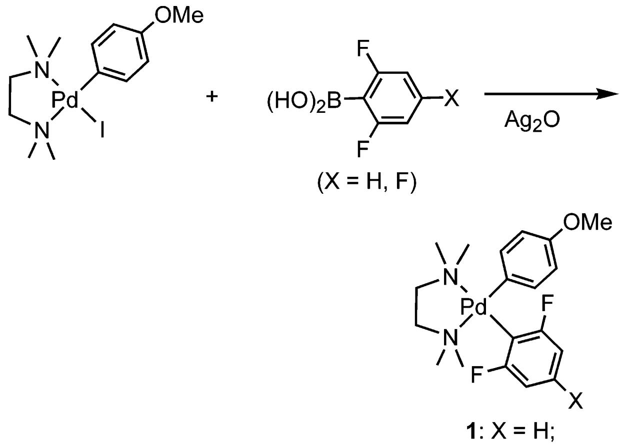
Summary: (2,4,6-Trifluorophenyl)- and (2,6-difluorophenyl)boronic acids react with $PdI(C_6H_4O\text{-}4\text{-}Me)(tmen)$ *(tmen = N,N,N′,N′-tetramethylethylenediamine) in the presence of* Ag_2O *to produce cis-diarylpalladium complexes with a tmen ligand via intermolecular transfer of the fluorophenyl 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 $[Pd(dppe)(MeCN)_2]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane) in the presence of PPh_3 to form $[PdPh(dppe)(PPh_3)]^+$ via transfer of the phenyl group from B to Pd.[2] A monophenylpalladium complex with a similar structure, $[PdPh(dppe)(L)]^+$ (L = solvent, etc.), is a plausible intermediate in 1,4-addition reactions of arylboronic acids with α,β-unsaturated ketones catalyzed by $[Pd(dppe)(MeCN)_2]^{2+}$. 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*-$Pd(C_6F_5)I(PEt_3)_2$ afforded the transmetalation product *trans*-$Pd(C_6H_2\text{-}2,4,6\text{-}F_3)(C_6F_5)(PEt_3)_2$.[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 (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 $PdI(C_6H_4\text{-}4\text{-}OMe)(tmen)$ 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, $Pd(C_6H_3\text{-}2,6\text{-}F_2)(C_6H_4\text{-}4\text{-}OMe)(tmen)$ (**1**) and $Pd(C_6H_2\text{-}2,4,6\text{-}F_3)(C_6H_4O\text{-}4\text{-}Me)(tmen)$ (**2**), respectively. Complexes **1** and **2** give satisfactory 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



(1)

1: X = H;
2: X= F

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[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.

10.1021/om049217i CCC: $30.25

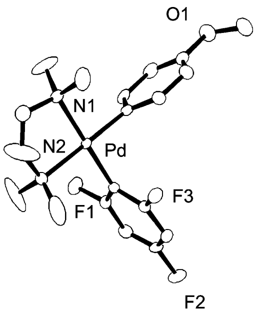
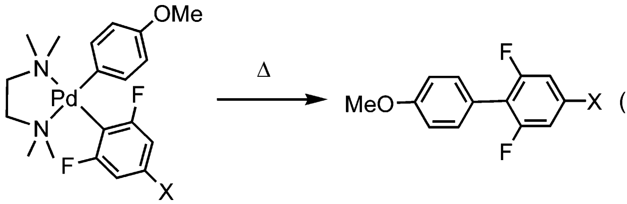


Figure 1. ORTEP drawing of **2** with 30% ellipsoidal plots. Selected bond distances (Å) and angles (deg): Pd1−N1 = 2.168(3), Pd1−N2 = 2.177(3), Pd1−C1 = 2.000(3), Pd1−C8 = 2.000(3); N1−Pd1−N2 = 83.9(1), N1−Pd1−C1 = 94.6(1), N1−Pd1−C8 = 178.1(1), N2−Pd1−C1 = 178.5(1), N2−Pd1−C8 = 96.0(1), C1−Pd1−C8 = 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(C_6H_4-4-OMe)(tmen) does not lead to isolation of the diarylpalladium complex but forms the coupling product, $MeOC_6H_4-C_6H_3F_2$, directly. Smooth transmetalation does not occur in the reaction of (2,4,6-trifluorophenyl)boronic acid using $AgBF_4$ instead of Ag_2O, suggesting that Ag_2O activates not only the Pd−I bond but also the C−B bond.

Heating a C_6D_6 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 $\Delta H^{\ddagger} = 101$ kJ mol^{-1}, $\Delta S^{\ddagger} = -10$ J mol^{-1} K^{-1}, and $\Delta G^{\ddagger} = 103$ 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 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 (1.12×10^{-4} s^{-1}) and without the additive (1.24×10^{-4} s^{-1}) do not differ significantly from each other. Thus, the Pd metal formed during the reaction does not affect the reaction rate.[6]



(2)

1: X = H;
2: X= F

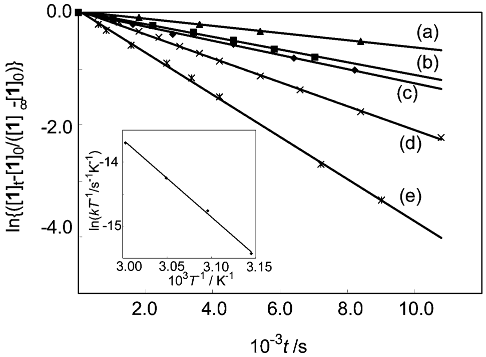


Figure 2. First-order plots of the thermally induced reductive elimination of 2,6-difluoro-4′-methoxybiphenyl from complex **1**: (a) at 45 °C; (b) with added diethyl fumarate at 50 °C; (c) at 50 °C; (d) at 55 °C; (e) at 60 °C. An Eyring plot is shown in the inset.

The diarylpalladium complexes *trans*-PdAr$_2$(PEt$_2$Ph)$_2$ (Ar = Ph, *m*-C_6H_4Me) 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 nitro[12] substituents at the ligand or are stabilized by a chelating anchor group[13] of the aryl ligands. In this study, the combination of the fluorinated and nonfluorinated aryl ligands and the tmen ligand enabled both isolation of the *cis*-diarylpalladium complexes and thermally induced reductive elimination of biaryl under mild conditions.

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(5) Crystal data and details of the structure refinement of **2**: $C_{19}H_{25}F_3N_2OPd$, $M_r = 460.81$, $1.2 \times 1.1 \times 0.7$ mm, monoclinic, $a = 8.730(4)$ Å, $b = 14.057(7)$ Å, $c = 16.033(8)$ Å, $\beta = 100.229(6)°$, $V = 1936.2(16)$ Å^3, $P2_1/c$ (No. 14), $Z = 4$, $D_{calcd} = 1.581$ g cm^{-3}, $F(000) = 936.00$, μ(Mo Kα) = 9.96 cm^{-1}, Mo Kα ($\lambda = 0.710\ 70$ Å), 12 292 total reflections measured, 4193 unique reflections ($R_{int} = 0.026$), 3555 observations ($I > 3.00\sigma(I)$), 260 variables, $R(I > 3.00\sigma(I)) = 0.040$, $R_w(I > 3.00\sigma(I)) = 0.056$, GOF = 1.114.

(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, 0.92×10^{-4} 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.; Forniés, 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.; Miravitlles, 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) Forniés, J.; Navarro, R.; Sicilia, V.; Tomas, M. *Inorg. Chem.* **1993**, *32*, 3675. (c) Edelbach, B. L.; Vicic, D. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4784.

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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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