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Synthesis and structural characterization of the first unsymmetrical diarylpalladium complex *trans*-Pd(C_6F_5)(2,4,6-$C_6F_3H_2$)(PEt_3)$_2$, derived from transmetallation between 2,4,6-trifluorophenylboronic acid and *trans*-Pd(C_6F_5)I(PEt_3)$_2$

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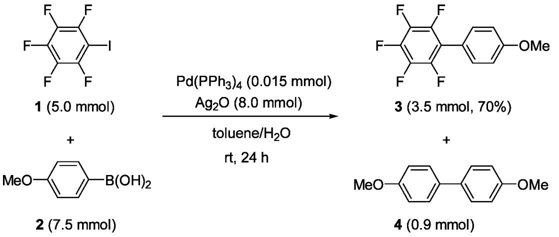
The reactions of 2,4,6-trifluorophenylboronic acid with aryl(iodo)palladium(II) complexes, *trans*-Pd(C_6F_5)I(PR_3)$_2$ (PR_3 = PEt_3, PMe_2Ph, $PMePh_2$) in the presence of Ag_2O afforded *trans*-Pd(C_6F_5)(2,4,6-$C_6F_3H_2$)(PR_3)$_2$ which are stabilized by fluorine atoms in the *ortho* positions.

Palladium catalyzed cross-coupling reactions of aryl halides and arylboronic acids (Suzuki–Miyaura reaction)[1,2] constitute an exciting development in synthetic organic chemistry. Still the mechanistic features of this reaction are not as clear as those of cross-coupling reactions employing organomagnesium[3] and organotin compounds.[4] The proposed catalytic cycle[5] involves: (a) oxidative addition of aryl halides to the Pd(0) catalyst; (b) transmetallation of an aryl group form boron to palladium forming intermediate *trans*-diarylpalladium(II) complexes; (c) isomerization of the *trans* to the *cis*; and (d) reductive elimination of unsymmetrical biaryl products thereby regenerating the catalyst. Among these individual reactions, transmetallation is of a special interest. This process likely plays a key role in a large number of important cross-coupling reactions including cleavage of carbon–metal bonds and formation of new C–C bonds. Due to facile reductive elimination, no reports describing the isolation and full characterization of intermediate diarylpalladium complexes via the transmetallation of arylboronic acids with arylpalladium halides have appeared.[6] On the other hand, Canary et al. have reported the observation by electrospray ionization mass spectroscopy (ESI-MS) of diarylpalladium complexes derived from a mixture of arylboronic acids and aryl(halogeno)palladium(II) complexes. However, the observed spectra are contaminated with the starting Pd complex.[7] Independently, we isolated diarylplatinum complexes in the transmetallation of organosilicon compounds thereby realizing that Ag_2O can accelerate the transmetallation.[8] In this paper we report preliminary results on the reactions of various arylboronic acids with aryl(iodo)palladium(II) complexes in the presence of Ag_2O[9] including the first characterization of an umsymmetrical diarylpalladium(II) complex by X-ray diffraction.

We first examined the catalytic reaction of pentafluoroiodobenzene (**1**) with 4-methoxyphenylboronic acid (**2**) in the presence of 3 mol% of Pd(PPh_3)$_4$ in toluene–H_2O and found the corresponding cross-coupled product **3** in 70% NMR yield, along with some homo-coupled product **4** derived from the added arylboronic acids (Scheme 1). We hypothesized that the generation of cross-coupled products occurred *via* smooth reductive elimination similar to the catalytic reaction. Reaction in THF–H_2O co-solvent system gave the almost same result.



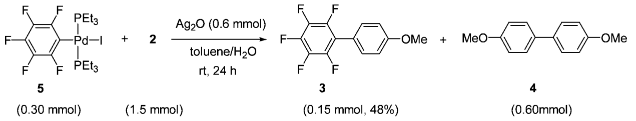
Scheme 1

To isolate the intermediate the rate of reductive elimination was decreased by employing a more basic PEt_3-ligated palladium complex. Thus, when a mixture of *trans*-Pd(C_6F_5)I(PEt_3)$_2$ (**5**) and arylboronic acid **2** in the presence of Ag_2O was stirred in toluene–H_2O for 24 h at room temperature, the identical products shown in Scheme 1 were formed, albeit with a lower yield of the cross-coupled product **3** and a higher yield of the homo-coupled product **4** (Scheme 2). We observed the formation of an unidentified palladium complex, indicating that reductive elimination of the cross-coupling product **3** was certainly suppressed, probably due to a strong basicity of PEt_3 ligands. However, our attempt to isolate and characterize the unsymmetrical diarylpalladium complex was unsuccessful as long as we used 4-methoxyphenylboronic acid as the substrate.

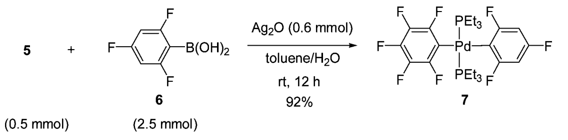
On the other hand, this observation led us to investigate the reaction of 2,4,6-trifluorophenylboronic acid (**6**) with **5**. The florine atoms in the ortho positions are expected to retard reductive elimination of the initially formed diarylpalladium complex. With this strategy a new unsymmetrical diarylpalladium complex, *trans*-Pd(C_6F_5)(2,4,6-$C_6F_3H_2$)(PEt_3)$_2$ (**7**), was isolated in 92% yield (Scheme 3).†

The structure of **7** was determined by X-ray analysis of a single crystal grown from slow evaporation of hexane solution.‡ As seen in Fig. 1, the molecular structure of **7** shows a palladium atom in an approximately square-planar environment. The aryl planes lie perpendicular to the coordination plane, similar to the square-planar *trans*-diarylpalladium(II) complex.[10]

To the best of our knowledge, no report of the synthesis of a stable unsymmetrical diarylpalladium(II) complex by transmetallation in the reactions of arylboronic acids and transition metal complexes has appeared.[11] In the solid state, **7** can be stored in air for months, without any sign of decomposition. Even upon heating at 100 °C for 24 h in toluene-d_6, complex **7** does not produce a cross-coupled product. Since no signal assigned to a cis isomer was observed during heating, the fluorine substituents in the ortho position retard trans-cis isomerization leading towards reductive elimination. The ^1H, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **7** in rigorously dry solvents, *e.g.*, C_6D_6, $CDCl_3$, and CD_2Cl_2, indicate that all ligands on the Pd atom are inert and that reductive elimination of biaryl does not occur. The $^{31}P\{^1H\}$ NMR spectrum of **7** in C_6D_6 consists of a singlet at δ 15.88, which is typical of Pd(II) complexes possessing two *trans* phosphine ligands. The *ipso*



Scheme 2



Scheme 3

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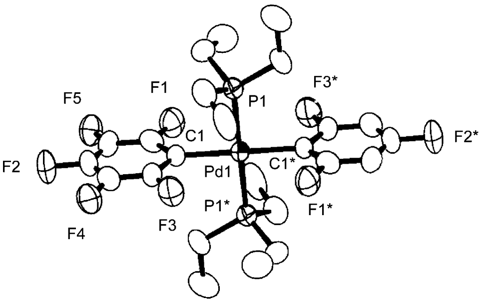

Fig. 1 An ORTEP drawing of **7** with 50% thermal ellipsoidal plotting. The molecule has crystallographic C_2 symmetry within the molecule. Atoms with asterisks are crystallographically equivalent to those having the same numbers without asterisks. Fluorine (F4* and F5*) with occupancies of 0.5 and hydrogen atoms were omitted for clarity. Selected interatomic distances (Å) and angles (°): Pd1–C1 2.066(6), Pd1–P1 2.310(2), P1–Pd1–C1 88.5(2), P1–Pd1–C1* = 91.5(2).

carbon signals of the aryl ligands are observed as triplets at δ 121.30 and 126.67. These NMR data are similar to those of the previously reported *trans*-$PdAr_2(PEt_3)_2$[12] and are consistent with the trans structure in solution.

We evaluated the transmetallation rate by the reactions of 2,4,6-trifluorophenylboronic acid with *trans*-$Pd(C_6F_5)I(PR_3)_2$ (PR_3 = PEt_3, PMe_2Ph, $PMePh_2$) forming *trans*-$Pd(C_6F_5)$(2,4,6-$C_6F_3H_2$)$(PR_3)_2$ (**7**: PR_3 = PEt_3; **8**: PR_3 = PMe_2Ph; **9**: PR_3 = $PMePh_2$). The observed rates of formation of diarylpalldium(II) complexes increase in the following order, **7** (12 h) < **8** (3 h) < **9** (40 min) at room temperature. This result correlates with the order of pK_a of the phosphine ligand, *e.g.* PEt_3 (8.65) < PMe_2Ph (6.50) < $PMePh_2$ (4.65).[13]

The reaction of Ag_2O with **5** (1.2 : 1.0 molar ratio) in toluene–H_2O generated *trans*-$Pd(C_6F_5)(OH)(PEt_3)_2$ (**10**) with concomitant generation of AgI. The $^{31}P\{^1H\}$ NMR measurement of the above reaction mixture in C_6D_6 showed that a signal of the starting material **5** at δ 16.41 decreased with apparance of a new signal at δ 18.50, which is identical with that of **10**, synthesized independently.[14] The ^1H NMR spectrum of **10** exhibits a resonance at δ −2.40, diagnostic of the Pd–OH, while the $^{13}C\{^1H\}$ NMR signal of the PCH_2 carbon appears at δ 14.19 as an apparent triplet due to virtual coupling, indicating *trans* positions of two phosphorus atoms. These results suggest an explanation for the role of Ag_2O, which promotes to replace the iodo ligand of **5** with a OH group of H_2O to afford **10**, the intermediate of transmetallation. Further details of the mechanism of transmetallation are still unclear.

In summary, we have successfully isolated diarylpalladium complexes **7–9** from the reactions of arylboronic acids with aryl(iodo)palladium(II) complexes. This methodology provides a novel and potentially practical synthetic method for unsymmetrical diaryl complexes of Pd, which are normally synthesized using organolithium and organomagnesium compounds.[15] Extensive exploration of this approach using the analogous arylboronates to illuminate more mechanistic details of the Suzuki–Miyaura cross-coupling reaction will be reported in due course.

Notes and references

† *Selected data.* For **7**: colorless crystals, yield 92%. δ_H (300 MHz, C_6D_6): 0.80 (dt, J = 16 Hz, 8 Hz, 18H, CH_3), 1.02 (m, 12H, PCH_2), 6.51 (dd, J = 9 Hz, 5 Hz, 2H, C_6H_2). δ_P (121.5 MHz, C_6D_6, 85% H_3PO_4): 15.88 (s). δ_F (282.3 MHz, C_6D_6): −82.45 (s, 2F), −112.14 (d, J = 24 Hz, 2F), −115.92 (m, 1F), −158.60 (t, J = 20 Hz, 1F), −160.51 (m, 2F). Anal. Calc. for $C_{24}H_{32}F_8P_2Pd$: C, 44.98; H, 5.03; F, 23.72. Found: C, 44.90; H, 4.94; F, 24.06%. For **8**: colorless crystals, yield 77%. δ_H (300 MHz, C_6D_6): 0.98 (apparent triplet by virtual coupling, 12H, PCH_3), 6.39 (dd, J = 9 Hz, J = 5 Hz, 2H, $C_6H_2F_3$), 6.87–6.95 (m, 6H, Ph), 7.00–7.07 (m, 4H, Ph). δ_P (121.5 MHz, C_6D_6, 85% H_3PO_4): −4.54 (s). δ_F (282.3 MHz, C_6D_6): −84.91 (t, J = 5 Hz, 2F), −114.41(d, J = 24 Hz, 2F), −115.99 (t, J = 7 Hz, 1F), −159.51 (t, J = 21 Hz, 1F), −161.00 (m, 2F). Anal. Calc. for $C_{28}H_{24}F_8P_2Pd$: C, 49.40; H, 3.55; F, 22.32. Found: C, 49.14; H, 3.75; F, 22.33%. For **9**: colorless crystals, yield 47%. δ_H (300 MHz, C_6D_6): 1.46 (apparent triplet by virtual coupling, 6H, CH_3), 6.15 (dd, J = 9 Hz, J = 5 Hz, 2H, $C_6H_2F_3$), 6.88–6.93 (m, 12H, Ph), 7.30–7.37 (m, 8H, Ph). δ_P (121.5 MHz, C_6D_6, 85% H_3PO_4): 9.77 (s). δ_F (282.3 MHz, C_6D_6): −83.29 (t, J = 5 Hz, 2F), −113.23 (d, J = 23 Hz, 2F), −116.50 (t, J = 9 Hz, 1F), −160.28 (t, J = 20 Hz, 1F), −160.95 (m, 2F). Anal. Calc. for $C_{38}H_{28}F_8P_2Pd$: C, 56.70; H, 3.51; F, 18.88. Found: C, 56.50; H, 3.71; F, 19.24%.

‡ *Crystal data.* For **7**: $C_{24}H_{32}F_8P_2Pd$, M = 640.85, monoclinic, space group $P2_1/n$, a = 12.309(4), b = 12.207(5), c = 9.460(3) Å, β = 104.81(3)°, V = 1374.2(8) Å^3, Z = 2, T = 298 K, μ(Mo–Kα) = 8.57 cm^{-1}, Rigaku AFC7R diffractometer, 1739 measured reflections (2θmax = 55.0°). At convergence, $R1$ = 0.032, $wR2$ = 0.037, and GOF = 2.02 for 169 variables refined against all 1077 unique reflections. A space group $C2/m$ is excluded by the presence of reflections ($I > 10\sigma(I)$) that do not obey the reflection conditions of C (or I) lattice. CCDC 216136. See http://www.rsc.org/suppdata/cc/b3/b308741g/ for crystallographic data in .cif or other electronic format.

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