Notes

Unexpected Formation of an *ortho*-Palladated Diphenylthioether

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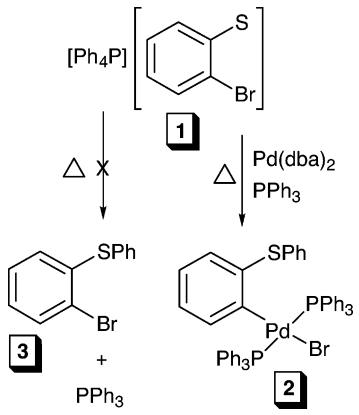
Summary: The reaction of [Ph$_4$P][BrC$_6$H$_4$S-2] with [Pd$_2$(dba)$_3$]·dba (dba = dibenzylideneacetone) in the presence of PPh$_3$ gives trans-[Pd(C$_6$H$_4$SPh-2)Br(PPh$_3$)$_2$]. A sequence of reactions consisting of oxidative addition of the tetraphenylphosphonium cation to palladium(0), reductive C−S coupling to give BrC$_6$H$_4$SPh-2, and, again, an oxidative addition of the latter to palladium(0) seems to constitute the pathway for the formation of the final palladium complex. Some experimental evidence supporting this pathway is provided. The crystal structure of trans-[Pd(C$_6$H$_4$SPh-2)Br(PPh$_3$)$_2$] has been solved by an X-ray diffraction study.

Introduction

One of our research interests involves the synthesis of *ortho*-functionalized arylpalladium complexes[1−4] and the study of their reactivity toward CO,[4−6] isonitriles,[4,5,7,8] or alkynes.[4,9,10] In this context, we prepared the tetraphenylphosphonium salt of the 2-bromobenzenethiolate anion, [PPh$_4$][BrC$_6$H$_4$S] (**1**), with the purpose of reacting it with Pd(dba)$_2$ and obtaining the first arylpalladium complexes having a negatively charged sulfur atom at the *ortho* position. We report here the unexpected results of this reaction and a proposal of the mechanism.

Scheme 1



Results and Discussion

The salt [PPh$_4$][BrC$_6$H$_4$S] (**1**) precipitated in water when 2-bromobenzenethiol was reacted with NaOH and [PPh$_4$]Cl in 1:5.5:1 molar ratios (Scheme 1). The electrospray mass spectroscopy in the negative and positive modes, the molar conductivity in acetone, and NMR spectroscopic data of **1** prove the above formulation. However, the reaction of **1** with Pd(dba)$_2$ ([Pd$_2$(dba)$_3$]·dba) and PPh$_3$ (1:2) in boiling toluene (2.5 h) did not give the expected complex *trans*-[PPh$_4$][Pd(C$_6$H$_4$S-2)Br(PPh$_3$)$_2$] but instead *trans*-[Pd(C$_6$H$_4$SPh-2)Br(PPh$_3$)$_2$] (**2**; Scheme 1). A possible explanation of this result would be that, under the reaction conditions, the salt **1** decomposes to give PPh$_3$ and BrC$_6$H$_4$SPh-2 (**3**) and the latter adds to Pd(dba)$_2$ to give **2**; in such a case only 1 equiv of PPh$_3$ would be needed. However, although the reaction goes well using 1 equiv of added PPh$_3$, when **1** was refluxed in toluene for 2.5 h, it was recovered unaltered in virtually quantitative yield.

We propose the following sequence of reactions to explain the formation of **2** (Scheme 2). First, the Ph$_4$P$^+$ cation oxidatively adds to Pd(0) to give a phenyl Pd(II)

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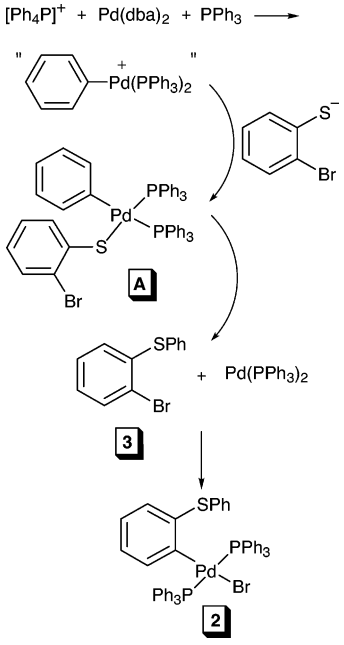
Scheme 2



derivative that reacts with the 2-bromobenzenethiolate anion to give a phenyl(2-bromophenylthiolate)Pd(II) complex, **A**. This intermediate undergoes a C−S reductive coupling to give **3** and [Pd(PPh$_3$)$_2$]. An oxidative addition process between these reagents gives **2**. This pathway also assumes the formation of **3** but through a palladium-mediated reaction.

Oxidative addition reactions of quaternary phosphonium salts to Pd(0) complexes to give organopalladium(II) complexes have been reported.[11] Such reactions are involved in aryl−aryl exchange between arylpalladium complexes and arylphosphine ligands[1,12−17] and constitute a key step in some new palladium-catalyzed syntheses of phosphines.[18−20] In fact, we have modeled this step in carrying out the reaction of [Ph$_4$P]Cl with Pd(dba)$_2$ and PPh$_3$ (molar ratio 1:0.5:1), which results in the formation of *trans*-[PdPhCl(PPh$_3$)$_2$].[13]

The proposed C−S reductive coupling process of the complex **A** to give **3** is an important step in the palladium-catalyzed synthesis of diarylthioethers from thiolates with aryl halides or triflates.[21−30]

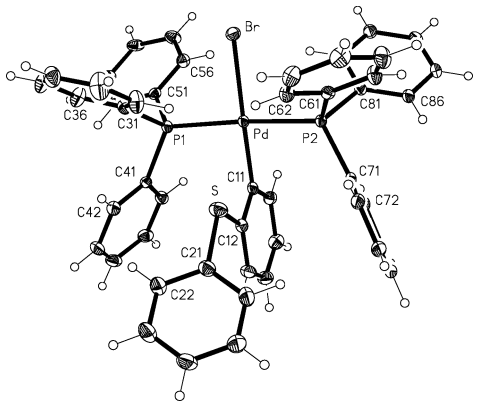


Figure 1. Molecular structure of complex **2**, with thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd−C(11) 2.016(3), Pd−P(2) 2.3337(7), Pd−P(1) 2.3366(7), Pd−Br 2.5296(3), S−C(12) 1.776(3), S−C(21) 1.780(3), C(11)−Pd−P(2) 88.21(7), C(11)−Pd−P(1) 89.47(7), P(2)−Pd−P(1) 174.75(3), C(11)−Pd−Br 177.29(8), P(2)−Pd−Br 91.633(19), P(1)−Pd−Br 90.909(19), C(12)−S−C(21) 103.87(13).

We have also reproduced the last step in the formation of **2**. Thus, we have prepared **3** by a palladium-catalyzed coupling of 2-bromobenzenethiol and iodobenzene in the presence of KO^{t}Bu (1:1.4:1), using a mixture of Pd(dba)$_2$ and 1,1′-diphenylphosphinoferrocene as the catalyst. The refluxing in toluene of a mixture of **3**, Pd(dba)$_2$, and PPh$_3$ (1.2:1:2) gave complex **2**.

The crystal and molecular structure of **2** has been determined by X-ray diffraction studies (Figure 1). The palladium atom is in a square-planar coordination with the phosphine ligands in *trans* position.

Conclusions

Although oxidative addition and reductive elimination reactions in palladium chemistry are very well-known processes, we describe here (i) one of the few examples in which a phosphonium cation is oxidatively added to Pd(0) and (ii) the first example in which two reagents are able to react through a sequence of reactions consisting of three steps: an oxidative addition giving a Pd(II) complex that suffers a reductive C−S coupling, giving a product that is able to add oxidatively to the intermediate palladium(0) complex, giving a palladated thioether. We have proposed a mechanism and modeled most of the proposed steps.

Experimental Section

Synthesis of [PPh$_4$][BrC$_6$H$_4$S] (1). A solution of NaOH (551 mg, 13.8 mmol) in water (40 mL) was slowly added to a mixture of BrC$_6$H$_4$SH-2 (470 mg, 2.49 mmol) and water (40 mL). The resulting mixture was stirred under nitrogen for 15 min, and [Ph$_4$P]Cl (933 mg, 2.49 mmol) was added. The resulting suspension was stirred for 15 min and filtered, and the solid was washed with water (3 × 5 mL) and Et$_2$O (3 × 5 mL) and dried, giving **1** as a pale yellow solid. Yield: 1.19 g,

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87%. $\Lambda_M = 126\ \Omega^{-1}\ mol^{-1}\ cm^2$. ^1H NMR (200 MHz, $CDCl_3$): δ 7.82−7.51 (several m, 20 H PPh_4 + 1 H C_6H_4), 7.14 (dd, 1 H, H2 or H5 C_6H_4, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz), 6.61 (td, 1 H, H3 or H4 C_6H_4, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz), 6.27 (td, 1 H, H3 or H4 C_6H_4, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.80 (CH, C_6H_4), 135.71 (d, CH, *para* CH's PPh_4^+, $J_{P,C} = 2.6$ Hz), 134.26 (d, CH, *meta* CH's PPh_4^+, $J_{P,C} = 10.2$ Hz), 130.75 (CH, C_6H_4), 130.71 (d, CH, *ortho* CH's PPh_4^+, $J_{P,C} = 12.8$ Hz), 125.10 (CH, C_6H_4), 118.59 (CH, C_6H_4), 117.26 (d, C, CP, $J_{P,C} = 88.7$ Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 24.3 (s, PPh_4). ESMS (MeCN) + (*m*/*z*): 339.1 (PPh_4^+). ESMS (MeCN) − (*m*/*z*): 188.6 (100), 187.3 (69) ($BrC_6H_4S^-$).

Synthesis of *trans*-[Pd(C_6H_4SPh-2)Br(PPh_3)$_2$] (2). Method A. $Pd(dba)_2$ (1.09 g, 1.90 mmol) and PPh_3 (1.00 g, 3.81 mmol) were mixed in toluene (10 mL) under nitrogen and stirred for 15 min. **1** (1.00 g, 1.90 mmol) was added, and the resulting mixture was refluxed under nitrogen for 2.5 h. Some palladium formed. The solvent was evaporated, the residue was extracted in the air with CH_2Cl_2 (4 × 5 mL), and the extracts were filtered over Celite. The red filtrate was concentrated to dryness and the residue triturated with Et_2O (20 mL), giving a solid that was separated by filtration, washed with Et_2O (3 × 5 mL), and air-dried, giving pale yellow **2**. Yield: 1.13 g, 67%.

Method B. $Pd(dba)_2$ (217 mg, 0.38 mmol) and PPh_3 (200 mg, 0.76 mmol) were dissolved in toluene (15 mL) under nitrogen and stirred for 5 min. Compound **3** (120 mg, 0.46 mmol) was added and the resulting mixture refluxed under nitrogen for 2 h. Working up as described for **1** renders **2**. Yield: 260 mg, 76%. Dec pt: 178 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.6−7.5 (m, 12 H), 7.35−7.18 (several m, 21 H), 6.96 (m, 1 H), 6.70 (dd, 2 H, C_6H_5 $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 1.7$ Hz), 6.31 (m, 2 H), 5.58 (m, 1 H, C_6H_4). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 152.40 (t, CS, C_6H_4, $J_{P,C} = 3.62$ Hz), 144.99 (t, CPd, $J_{P,C} = 3.77$ Hz), 135.00 (t, CH, *ortho* CH's PPh_3 $|^2J_{P,C} + {}^4J_{P,C}| = 12.6$ Hz), 134.86 (CH, C_6H_5), 133.17 (t, C, CS C_6H_5, $^5J_{P,C} = 1.1$ Hz), 131.45 (t, CH, *ipso* CH's PPh_3 $|^1J_{P,C} + {}^3J_{P,C}| = 45.7$ Hz), 129.75 (CH, *para* CH's PPh_3), 128.86 (CH), 128.06 (CH), 127.72 (t, CH, *meta* CH's PPh_3 $|^3J_{P,C} + {}^5J_{P,C}| = 10.2$ Hz), 124.77 (CH, C_6H_4), 123.48 (CH), 123.19 (CH). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 24.58 (s, 2 PPh_3). Anal. Calcd for $C_{48}H_{39}BrP_2PdS$: C, 64.33; H, 4.39; S, 3.58. Found: C, 63.98; H, 4.53; S, 3.41.

Synthesis of BrC_6H_4SPh-2 (3). 2-Bromobenzenethiol (0.31 mL, 488 mg, 2.57 mmol) and KO^{t}Bu (306 mg, 2.57 mmol) were mixed in toluene under nitrogen and stirred for 15 min. Then, iodobenzene (0.40 mL, 3.54 mmol), 1,1′-diphenylphosphinoferrocene (15 mg, 0.026 mmol), and $Pd(dba)_2$ (16 mg, 0.026 mmol) were added, and the resulting mixture was stirred at 50 °C for 3 days. After this time it was not necessary to work under nitrogen. The solvent was removed in vacuo, the residue was extracted with Et_2O (3 × 5 mL), and the extracts were filtered over Celite. The red filtrate was concentrated (ca. 3 mL) and purified by TLC chromatography (dichloromethane/*n*-hexane, 1:4). The band containing the product ($R_f = 0.52$) was collected and extracted with acetone. This solution was concentrated to dryness, and the residue was redissolved in Et_2O and dried with anhydrous magnesium sulfate. The suspension was filtered and the filtrate concentrated to dryness, giving **3** as a colorless oil. Yield: 660 mg, 97%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (dd, 1 H, H3 or H6 C_6H_4 $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz), 7.48−7.43 (several m, 5 H, C_6H_5), 7.14 (td, 1 H, H4 or H5 C_6H_4 $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz), 7.02 (td, 1 H, H4 or H5 C_6H_4 $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz), 6.90 (dd, 1 H, H3 or H6 C_6H_4 $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 138.8 (C), 133.5 (CH), 133.0 (CH), 132.8 (C), 129.7 (CH), 129.6 (CH), 128.5 (CH), 127.8 (CH), 127.2 (CH), 123.00 (C). FAB-MS: *m*/*z* 266 (M^+, 100%).

X-ray Crystal Structure of 2·Et_2O. A single crystal, obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **2**, was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Crystal data for **2·Et_2O**: $C_{52}H_{49}BrOP_2PdS$, $M = 970.22$, monoclinic, $a = 17.8954(12)$ Å, $b = 12.4133(8)$ Å, $c = 20.4354(14)$ Å, $\beta = 101.376(3)°$, $U = 4450.4(5)$ Å^3, $T = 143$ K, space group $P2_1/c$, $Z = 4$, μ(Mo Kα) = 1.472 mm^{-1}, 84 493 reflections measured, 11 047 unique ($R_{int} = 0.083$), which were used in all calculations. Refinement using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen) proceeded to a final $wR(F^2)$ of 0.091 (all data), $R(F)$ 0.035 for 523 parameters; max. $\Delta\rho$ 0.53 e Å^{-3}. CCDC number 228878.

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Supporting Information Available: CIF file for complex **2·Et_2O**. This material is available free of charge via the Internet at http://pubs.acs.org.

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