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New class of pincer ligands: phosphite esters of 1,3-di(hydroxy)arenes in cyclopalladation reaction

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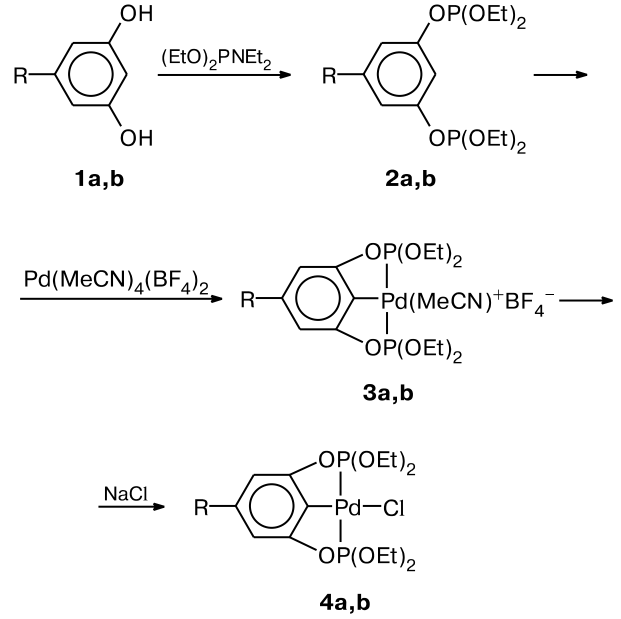
The cyclometallation reaction consists in the replacement of the hydrogen atom with a metal atom proceeding with retention of coordination of the metal atom by an electron-donating atom in the same molecule. Ligands containing two electron-donating atoms in positions suitable for the simultaneous closure of two five- or six-membered rings are referred to as *pincer* ligands. Cyclometallation of pincer ligands is well studied for arenes containing benzyl-type *meta*-substituents with the sulfide sulfur atom, the R_2P or R_2N groups as ligating centers. Palladium, platinum, and rhodium are most often used of all metals (see the review[1]).

Recently, Pd complexes with 2,5-di(dialkylphosphinomethyl)ferrocenes as pincer ligands have been described.[2] In the present study, we report the synthesis of a new class of pincer ligands for cyclometallation, *viz.*, bis(phosphite) esters of 1,3-dihydroxyarenes. Earlier,[3,4] we have developed a new synthetic method, *viz.*, cyclopalladation of alkyl aryl phosphites, which makes it possible to perform this reaction with phenols belonging to an important and abundant class of compounds and provides a way of modifying natural phenols. We studied cyclopalladation of resorcinol bis(alkoxyphosphite) **2a** under various conditions and found that the reaction with the cationic reagent, *viz.*, bis(acetonitrile)palladium fluoroborate, involves selective palladation at position 2 to form pincer cyclopalladated fluoroborate **3a**. We failed to isolate the analytically pure product even after its transformation into more stable chloride **4a**, because the process was complicated by competitive hydrolysis and oxidation of the phosphorus atom. The ^{31}P and ^{1}H NMR spectra of compound **4a** confirm the pincer structure of the product. Both phosphorus atoms are equivalent, the signal for the P atom (δ(P) 142) being typical of cyclopalladated phenol phosphites.[4] The signals for the aryl protons appear as one doublet and one triplet with an intensity ratio of 2 : 1. In the ^{1}H NMR spectrum of compound **4a**, splitting of the signal on the phosphorus atom is observed only for the H(5) proton, but not for H(4) and H(6) due to collinearity of the C—H(5) and O—P bonds ($^{3}J_{H,H}$ = 8.28 Hz, $^{5}J_{H,P}$ = 1.92 Hz). The maximum purity of the "pincer" product isolated after repeated reprecipitations was no higher than 90%, whereas chromatography afforded phosphate and metallic Pd. Under conventional conditions, cyclopalladation with palladium chloride or acetate gave rise to a mixture, with products of $P^{III} \rightarrow P^{V}$ oxidation predominating.

Alkyl phosphite ester of 5-R-substituted resorcinol **2b** (phloroglucinol, R = OH) behaves analogously.



R = H (**1a—4a**), OH (**1b**, **3b**), OP(OEt)$_2$ (**2b**, **4b**)

To summarize, we constructed a new class of ligands for pincer metallation, in which phosphite P^{III} atoms are involved in coordination bonds. Cyclopalladated phosphites have attracted recent attention as active catalysts for the Heck reaction.[5] However, a few pincer ligands described earlier contain a phosphinite fragment rather than a phosphite group (*i.e.*, they contain one P—O bond and two P—C bonds).

The ^{1}H and ^{31}P NMR spectra were recorded on Bruker WP-200 SY and Bruker 400 HX instruments in $CDCl_3$ and

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CD_3CN. The solvents were purified according to standard procedures.

3-[(Diethoxyphosphino)oxy]phenyl diethyl phosphite (2a). A mixture of resorcinol (0.51 g, 4.88 mmol) and $(EtO)_2PNEt_2$ (1.88 g, 9.76 mmol) in anhydrous acetonitrile (2 mL) was heated on an oil bath in an argon stream at 100 °C for 5 h and then at the same temperature *in vacuo* for 5 h. Compound **2a** was obtained in a yield of 1.58 g (98%). Found (%): C, 48.17; H, 6.70; P, 17.45. $C_{14}H_{24}P_2O_6$. Calculated (%): C, 48.00; H, 6.91; P, 17.69. ^1H NMR (CD_3CN), δ: 1.33 (t, 12 H, $(C\underline{H}_3CH_2O)_2P$, J = 7.2 Hz); 4.02—4.11 (m, 8 H, $(CH_3C\underline{H}_2O)_2P$); 6.83 (d, 3 H, C_6H_3, J = 8.1 Hz); 7.27 (t, 1 H, C_6H_3, J = 8.1 Hz). ^{31}P NMR (CD_3CN), δ: 134. **3,5-Bis-[(diethoxyphosphino)oxy]phenyl diethyl phosphite (2b)** was synthesized analogously. Found (%): C, 44.35; H, 6.91; P, 19.05. $C_{18}H_{33}P_3O_9$. Calculated (%): C, 44.43; H, 6,84; P, 19.11. ^1H NMR ($CDC1_3$), δ: 1.27 (t, 18 H, $(C\underline{H}_3CH_2O)_2P$, J = 7.2 Hz); 3.98 (m, 12 H, $(CH_3C\underline{H}_2O)_2P$); 6.50 (s, 3 H, C_6H_3). ^{31}P NMR ($CDC1_3$), δ: 134.

1,3-Bis[(diethoxyphosphino)oxy]phenylpalladium chloride (4a). A suspension of $PdCl_2$ (0.2268 g, 1.28 mmol) in anhydrous acetonitrile (35 mL) was refluxed in an argon stream until $PdCl_2$ was completely dissolved. Then a solution of $AgBF_4$ (0.5 g, 2.57 mmol) in anhydrous CH_3CN (12 mL) was added. The reaction solution was refluxed for 2 h and cooled to room temperature. The precipitate of AgCl that formed was filtered off. The filtrate was added to compound **2a** (0.45 g, 1.28 mmol) and the mixture was refluxed under argon for 4 h. Then the precipitate was filtered off, the solvent was removed, and solid white product **3a** was obtained in a yield of 1.0 g. Compound **3a** was dissolved in anhydrous CH_2Cl_2, a saturated aqueous NaCl solution was added, and the mixture was stirred for 24 h. The organic layer was separated, dried over K_2CO_3, and concentrated to a small volume, after which hexane was added. The solid white precipitate that immediately formed was filtered off and discarded. The filtrate was concentrated to dryness. Compound **4a** was obtained in 55% yield. ^1H NMR ($CDC1_3$), δ: 1.4 (t, 12 H, $(C\underline{H}_3CH_2O)_2P$, J = 7.0 Hz); 4.32—4.41 (m, 8 H, $(CH_3C\underline{H}_2O)_2P$); 6.67 (d, 2 H, C_6H_3, J = 8.0 Hz); 7.12 (t, 1 H, C_6H_3, J = 8.0 Hz). **1,3,5-Tris[(diethoxyphosphino)oxy]phenylpalladium chloride (4b):** was prepared analogously. ^1H NMR ($CDC1_3$), δ: (t, 18 H, $(C\underline{H}_3CH_2O)_2P$, J = 7.1 Hz); 4.35 (m, 12 H, $(CH_3C\underline{H}_2O)_2P$); 6.25 (s, 2 H, C_6H_3).

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