Cross-coupling of polychloroarenes with phenylboronic acid and organozinc compounds catalyzed by palladium complexes*

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Hexachlorobenzene and 1,2,4,5-tetrachlorobenzene react with phenylboronic acid by a C–C cross-coupling mechanism with a $Pd(dba)_2/P(Bu^t)_3$ system (dba is dibenzylideneacetone) or palladium-azole complexes as catalysts, or with organozine compounds in the presence of $Pd(PPh_3)_4$ to afford substitution products of one or two chlorine atoms in moderate yields.

Key words: polychloroarenes, hexachlorobenzene, biaryls, tolans, cross-coupling, phenylboronic acid, organozine compounds, palladium catalysts, imidazolium salts, 1,3-bis(1-tetrazolyl)benzene.

Great attention is given to the development of methods for the catalytic activation of C-Cl bonds in C-C cross-coupling reactions due to a large pool of industrially accessible chloroaromatic compounds. It has recently been shown that transition metal complexes with bulky phosphine ligands¹ and heterocyclic carbene ligands of the imidazole type² can serve as efficient catalysts of chloroarene reactions. Using these complexes, monochloroarenes of different structures, including sterically hindered, were involved in C-C cross-coupling. At the same time, information on the reactions of polychloroarenes catalyzed by transition metal complexes is scarce. The cross-coupling products of o-dichlorobenzene with phenylboronic acid³ and Grignard reagents⁴ were synthesized in the presence of nickel or palladium complexes. The reaction of 2,4,6-trichloro-1,3,5-triiodobenzene with phenylacetylene in the presence of Pd(PPh₃)₄ and CuI afforded the substitution product of three iodine atoms and one chlorine atom, whereas the organozinc alkyne derivatives were used for the exhaustive substitution of all halogens.⁵

The C–C cross-coupling of polychloroarenes containing more than three chlorine atoms, to the best of our knowledge, has not been studied. Meanwhile, these reactions can be of significance as alternative methods for the transformation of toxic chlorine-containing compounds (insecticides, polychlorobiphenyls, polychlorodioxins, *etc.*) into useful products.

To understand whether highly chlorinated polychloroarenes can be involved in C–C cross-coupling in the present work, we studied for the first time the reactions of 1,2,4,5-tetrachloro- (1) and hexachlorobenzenes (2) with phenylboronic acid and organozinc benzene and phenylacetylene derivatives in catalytic systems including Pd complexes with different phosphine and azole ligands. We expected that the mutual activating effect of the chlorine atoms in compounds 1 and 2 would facilitate crosscoupling in comparison with monochloroarenes, which require special catalytic systems.

However, it turned out that polychloroarenes 1 and 2 do not react with arylboronic acids and terminal acetylenes under the conditions typical of aryl bromides and iodides. For instance, an attempt to perform the Suzuki reaction in the $Pd(PPh_3)_4$ -dimethoxyethane-Na₂CO₃ (aq) system⁶ resulted only in homocoupling of arylboronic acids to form symmetrical biphenyls. Similar homocoupling of phenylacetylene to 1,4-diphenylbuta-1,3diyne was also observed when the Sonogashira reaction was carried out in the Pd(PPh₃)₄-CuI-Prⁱ₂NH system,⁵ while the starting compounds returned unchanged from the Pd(PPh₂)₄—pyrrolidine system.⁷ Cross-coupling products are formed only in trace amounts in the reaction of tetrachlorobenzene 1 with phenylboronic acid in the presence of NiCl₂(dppf) (dppf is 1,1'-diphenylphosphinoferrocene) or NiCl₂(PPh₃)₂ and K_3PO_4 in dioxane.^{3a} Negative results were obtained when pentachloroacetophenone containing an electron-withdrawing substituent was involved in the Suzuki reaction [PhB(OH)₂, $Pd(PPh_3)_4$, Na_2CO_3 (aq)]. Probably, the low reactivity of polychloroarenes is caused by both the C-Cl bond stability and steric hindrance from other chlorine atoms. The role of steric factors is confirmed by the reluctance (under the above-indicated conditions) of pentachloroiodobenzene containing the reactive C-I bond.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 4, pp. 947-951, April, 2005.

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^{*} Dedicated to Corresponding Member of the Russian Academy of Sciences E. P. Serebryakov on the occasion of his 70th birthday.

Thus, we had to search for a solution of the problem in two directions including the use of more active catalytic systems and a more reactive nucleophilic counter-component, for example, organozinc compounds.⁸ Indeed, we found that polychloroarenes 1 and 2 react with phenylboronic acid in the $Pd(dba)_2-But_3P-K_3PO_4$ system^{1c} (dba is dibenzylideneacetone) to form a mixture of substitution products of one (3, 4) and two chlorine atoms in moderate yields (Scheme 1, Table 1). Similar results were obtained when the catalytic system containing easily oxidizable But_3P was replaced by new, simple, and convenient systems based on $Pd(OAc)_2$ in combination with 1,3-bis(1-tetrazolyl)benzene (1,3-TetC₆H₄)⁹ or 1,3-diarylimidazolium chlorides (IMes • HCl or IPr • HCl) with bulky aryl substituents.^{2f-h}

It is of interest that the conversion of tetrachlorobenzene **1** with the $Pd(dba)_2$ — Bu^t_3P system (entry *1*) is much higher than that of hexachlorobenzene **2** (entry *8*), which can be related to lower spatial accessibility of the chlorine atoms in the latter. A similar tendency is seen for the $Pd(OAc)_2$ —IMes · HCl and $Pd(OAc)_2$ —IPr · HCl systems (entries 3—5): unlike almost inert (under these con-



IPr · HCl



Reagents and conditions: *a*. PhB(OH)₂, Pd(dba)₂, Bu^t₃P, K₃PO₄, toluene, Δ , 24 h; *b*. PhB(OH)₂, Pd(OAc)₂, 1,3-Tet₂C₆H₄, K₃PO₄, 18-crown-6, DMF, Δ , 8 h; *c*. PhB(OH)₂, Pd(OAc)₂, 1,3-IMes · HCl or IPr · HCl, Cs₂CO₃, dioxane, Δ , 8 h; *d*. PhZnCl, Pd(PPh₃)₄, THF, Δ , 24 h; *e*. PhC=CZnCl, Pd(PPh₃)₄, THF, Δ , 24 h.

Entry	Starting polychloroarene	Nucleophilic component	Catalytic system	Composition of mixture according to GC-MS data, mol.%			
				Monosub- stituted product	Disub- stituted products	Unconsumed starting compound	Other components
1	$C_6H_2Cl_4$	PhB(OH) ₂	$Pd(dba)_2 - Bu^t_3P - K_3PO_4$	66 (3)	$5 + 11^{a}$	18	_
2	$C_6H_2Cl_4$	PhB(OH) ₂	$Pd(OAc)_{2}$ - 1,3-Tet ₂ C ₆ H ₄ - K ₃ PO ₄ - 18-crown-6	11 (3)	2 ^{<i>a</i>}	87	_
3	$C_6H_2Cl_4$	PhB(OH) ₂	Pd(OAc) ₂ – IMes•HCl– K_2CO_3 –	7 (3)	4 ^{<i>a</i>}	82	1 (Ph ₃ C ₆ H ₂ Cl) ^{<i>b</i>} , 6 (Ph—Ph) ^{<i>c</i>}
4	$C_6H_2Cl_4$	PhB(OH) ₂	$Pd(OAc)_2 - IMes \cdot HCl - Cs_2 CO_2$	6 (3)	$13 + 3^{a}$	69	9 ($Ph_3C_6H_2Cl$) ^d
5	$C_6H_2Cl_4$	PhB(OH) ₂	$Pd(OAc)_2 - $ IPr·HCl-	22 (3)	$5 + 3^{a}$	70	_
6	$C_6H_2Cl_4$	PhZnCl	$Pd(PPh_3)_4$	52 (3)	$2 + 3^{a}$	23	16 (Ph-Ph) ^c , 4 (Cl ₂ H ₂ C $_{\epsilon}$ -C $_{\epsilon}$ H ₂ Cl ₂) ^d
7	CcH2CL	PhC≡CZnCl	Pd(PPh ₂) ₄	21 (5)		30	49 (PhC=C $-$ C=CPh) ^e
8	C_6Cl_6	PhB(OH) ₂	$Pd(dba)_2$ - Bu ^t ₃ P-K ₃ PO ₄	19 (4)	$10 + 8^{f}$	63	_
9	C ₆ Cl ₆	PhB(OH) ₂	$Pd(OAc)_2-$ 1,3-Tet ₂ C ₆ H ₄ - K ₃ PO ₄ - 18-crown-6	27 (4)	$10 + 6^{f}$	44	13 (Ph—Ph) ^c
10	C ₆ Cl ₆	PhZnCl	$Pd(PPh_3)_4$	67 (4)	4 ^f	11	9 (C ₆ HCl ₅) ^g , 6 (Ph—Ph) ^c , 3 (PhC ₆ HCl ₄) ^h
11	C_6Cl_6	PhC≡CZnCl	Pd(PPh ₃) ₄	45 (6)	_	42	13 $(PhC \equiv C - C \equiv CPh)^e$

Table 1. Results of cross-coupling of polychloroarenes 1 and 2 in the Suzuki and Negishi reactions

Note. Mass numbers of some components for ${}^{35}Cl([M^+])$, m/z: a 298, b 340, c 154, d 358, e 202, f 366, g 248, h 290. The isotope clusters of peaks of the molecular ions corresponded to the number of chlorine atoms in a molecule.

ditions) compound 2, tetrachlorobenzene 1 forms small amounts of cross-coupling products. To the contrary, in the $Pd(OAc)_2$ —1,3-TetC₆H₄ catalytic system, hexachlorobenzene 2 (entry 9) affords cross-coupling products in somewhat higher yields than chloroarene 1 (entry 2). It is most likely that the decisive role belongs here to electronic factors. We have shown that in the case of the bis-tetrazolic ligand 1,3-TetC₆H₄, K₃PO₄ in combination with a crown ether can successfully be used as a base instead of the earlier proposed⁹ hygroscopic potassium *tert*-butoxide. In the absence of a crown ether and when K₃PO₄ is replaced by K₂CO₃ or Cs₂CO₃, virtually no reaction occurs.

Higher yields of products **3** and **4** were achieved in the $Pd(PPh_3)_4$ -catalyzed reactions of polychloroarenes **1** and **2** with phenylzinc chloride (the Negishi reaction), which is a considerably stronger nucleophile than phenylboronic acid. The use of the organozinc reagent made it

possible to substitute the phenylacetylene fragment for the chlorine atoms in polychloroarenes 1 and 2 (see Scheme 1). Unlike the reaction with phenylboronic acid, side processes such as homocoupling of the nucleophilic and electrophilic components and reductive dechlorination are more pronounced in the reactions of polychloroarenes 1 and 2 with organozinc compounds (see Table 1, entries 6, 7, 10, and 11).

Thus, we have shown for the first time that highly chlorinated polychloroarenes can be involved in the C–C cross-coupling reactions catalyzed by Pd complexes. Higher yields are obtained with highly active catalytic systems with bulky phosphine and azole ligands or with organoelement compounds with pronounced nucleophilic properties as cross-coupling components. The results obtained can be used to develop methods for processing ecologically hazardous polychloroarenes to non-toxic and little toxic compounds. At the same time, problems of regiochemistry of chlorine atom substitution in non-symmetrical polychloroarenes or enhancement of chemoselectivity of the reactions remain unsolved and require further investigation.

Experimental

Melting points were uncorrected. NMR spectra were recorded on a Bruker AM-300 spectrometer in CDCl₃ at 300.13 MHz (¹H) and 75.47 MHz (¹³C). GC-MS spectra were obtained on an MS Finnigan MAT ITD-700 instrument (EI, 70 eV) using a Pye Unicam 104 chromatograph (Ultra-1 column (Hewlett-Packard) 25000×0.2 mm, injector temperature 280 °C, temperature programming: 80 °C (1 min) \rightarrow 280 °C, heating rate 10 deg min⁻¹, carrier gas helium, 1 mL min⁻¹). Mass numbers are presented for the ³⁵Cl isotopes. GLC analysis was carried out on an Agilent Technologies 6890 chromatograph (HP-5MS capillary column 30000×0.25 mm, injector and flame-ionization detector temperature 280 °C, temperature programming $60 \rightarrow 300$ °C (5 min), 10 deg min⁻¹, carrier gas helium, 2 mL min⁻¹). Surface areas of chromatographic peaks were corrected taking into account the number of carbon atoms in a molecule, and then molar fractions of components were calculated. Elemental analysis was carried out at the Analytical Laboratory of the N. D. Zelinsky Institute of Organic Chemistry (Russian Academy of Sciences). Hexane and CH₂Cl₂ were freshly distilled, and THF was dehydrated by refluxing over sodium in the presence of benzophenone followed by distillation under argon. 1,2,4,5-Tetrachlorobenzene 1 (Acros), hexachlorobenzene 2 (Aldrich), and 1,3-dimesitylimidazolium chloride (Acros) were used as purchased. Bromobenzene and phenylacetylene were used freshly distilled. 1,3-Bis(1-tetrazolyl)benzene⁹ and 1,3-di(2,6-diisopropylphenyl)imidazolium chloride¹⁰ were prepared by known procedures. Pentachloroacetophenone and pentachloroiodobenzene have been synthesized previously.¹¹ TLC analysis was carried out on aluminum plates with Kieselgel 60 F₂₅₄ (Merck, 1.05554) using a hexane-CH₂Cl₂ (1:1) mixture as eluent. Column chromatography was carried out on silica gel L (100/160).

Polychlorobiphenyls 3 and 4. *A*. A mixture of polychloroarene (1 mmol), phenylboronic acid (1 mmol), $Pd(dba)_2$ (0.05 mmol), tri-*tert*-butylphosphine (0.1 mmol), K_3PO_4 (2.5 mmol), and toluene (5 mL) was stirred for 24 h under nitrogen at 80 °C. An aliquot of the reaction mixture was filtered through a silica gel layer and analyzed by TLC and GC-MS.

B. A Schlenk flask was loaded with $Pd(OAc)_2$ (8 mg, 0.036 mmol), 1,3-bis(1-tetrazolyl)benzene (8 mg, 0.037 mmol), K_3PO_4 (233 mg, 1.1 mmol), and 18-crown-6 (16 mg, 0.061 mmol). DMF (2 mL) was added under argon, and oxygen was removed from the mixture by evacuation and filling with argon. The mixture was heated for 1 h at 90 °C and then cooled to ~20 °C, polychloroarene **1** or **2** (0.5 mmol) was added, and the mixture was stirred for 10 min. Phenylboronic acid (66 mg, 0.546 mmol) and DMF (3 mL) were added. The mixture was stirred for 7 h at 90 °C. An aliquot of the reaction mixture was withdrawn from which DMF was removed *in vacuo*, and the residue was dissolved in benzene. The resulting slurry was filtered through a silica gel layer, and the filtrate was analyzed by GC-MS.

C. A Schlenk flask was loaded with $Pd(OAc)_2$ (13 mg, 0.058 mmol), 1,3-dimesitylimidazolium or 1,3-di(2,6-diisopropylphenyl)imidazolium chloride (0.135 mmol), and Cs_2CO_3 (659 mg, 2.03 mmol). Dioxane (2 mL) was added under argon, and oxygen was removed from the mixture by evacuation and filling with argon. The mixture was heated for 1 h at 80 °C and then cooled to ~20 °C. Polychloroarene 1 or 2 (1 mmol) and a solution of phenylboronic acid (185 mg, 1.53 mmol) in dioxane (2 mL) were added, and the mixture was stirred for 7 h at 95 °C. An aliquot of the reaction mixture was worked up and analyzed by GC-MS as before. In some experiments, other bases were used instead of Cs_2CO_3 (see Table 1).

D. The Negishi cross-coupling was carried out according to a published procedure.¹² n-Butyllithium (2.0 mL, 3.2 mmol) as a 1.6 M solution in hexane (Merck) was added at -78 °C under nitrogen to a solution of bromobenzene (504 mg, 3.2 mmol) in anhydrous THF (8 mL). The mixture was stirred for 20 min. To phenyllithium thus obtained a solution of anhydrous zinc chloride (436 mg, 3.2 mmol, Aldrich) in THF (4 mL) was added, cooling was removed, and the mixture was warmed to ~20 °C and stirred at this temperature for 20 min. Then polychloroarene (2 mmol) was rapidly added to the mixture under nitrogen, and after 10 min a solution of Pd(PPh₃)₄ (116 mg, 0.1 mmol) in THF (1 mL) was added. The mixture was refluxed for 24 h, cooled, diluted with toluene, and washed with 5% HCl and then a solution of NaHCO₃ until the washings became clear. The organic layer was dried with CaCl₂. An aliquot of the reaction mixture was concentrated, suspended in benzene, passed through a silica gel layer, and analyzed by GLC and GC-MS. The main portion was concentrated and subjected to column chromatography using CH_2Cl_2 (10%) in hexane as eluent.

2,4,5-Trichlorobiphenyl (3). M.p. 73–74 °C (*cf.* Ref. 13: m.p. 74–76 °C). ¹H NMR, δ : 7.32–7.50 (m, 6 H); 7.60 (s, 1 H). ¹³C NMR, δ : 128.28 (C(2')H μ C(4')H); 129.16 (C(3')H); 131.05 (C(5)Cl); 131.16 (C(6)H); 131.33 and 131.95 (C(2)Cl and C(4)Cl); 132.32 (C(3)H); 137.24 (C(1')); 140.38 (C(1)). Mass spectrum, *m*/*z*: 256 [M]⁺. The spectral characteristics are similar to those published earlier.¹⁴

2,3,4,5,6-Pentachlorobiphenyl (4). M.p. 122–124 °C (*cf.* Ref. 15: m.p. 122–124 °C). ¹H NMR, δ : 7.18 (m, 2 H); 7.49 (m, 3 H). ¹³C NMR, δ : 128.65, 128.71, 128.83 (all CH); 131.93 (C(3)Cl); 132.86 (C(2)Cl); 133.11 (C(4)Cl); 137.18 (C(1')), 140.47 (C(1)). Mass spectrum, *m/z*: 324 [M]⁺. The spectral characteristics are similar to those published earlier.¹⁴

Piolychlorotolans 5 and **6** were synthesized by the reaction of polychloroarenes **1** and **2**, respectively, with ethynylphenylzinc chloride in the presence of $Pd(PPh_3)$ according to method **D** using phenylacetylene instead of bromobenzene.

2,4,5-Trichlorotolan (5). M.p. 118–120 °C. Found (%): C, 59.83; H, 2.59. $C_{14}H_7Cl_3$. Calculated (%): C, 59.72; H, 2.51. ¹H NMR, δ : 7.38, 7.51 (both m, 3 H each); 7.62 (s, 1 H). ¹³C NMR, δ : 84.21 (=<u>C</u>Ph); 96.38 (=<u>C</u>₆H₂Cl₃); 122.15 (C(1')); 123.13 (C(1)); 128.43 (C(3')H); 129.12 (C(4')H); 130.60 (C(3)H); 130.88 (C(5)Cl); 131.77 (C(2')H); 132.83 (C(4)Cl); 133.73 (C(6)H); 134.59 (C(2)Cl). Mass spectrum, *m/z*: 280 [M]⁺.

2,3,4,5,6-Pentachlorotolan (6). M.p. 189–190 °C. ¹H NMR, δ: 7.40 (m, 3 H); 7.62 (m, 2 H). ¹³C NMR, δ: 83.26 (=<u>C</u>Ph); 101.93 (=<u>C</u>C₆Cl₅); 121.82 (C(1')); 124.13 (C(1)); 128.53 (C(3')H); 129.66 (C(4')H); 131.78 (C(3)Cl); 131.99 (C(2')H); 133.19 (C(4)Cl); 134.43 (C(2)Cl). Mass spectrum, m/z: 348 [M]⁺.

The authors thank A. Z. Voskoboinikov, A. Yu. Lebedev, A. N. Kasatkin, and D. S. Chekmarev for help in the work.

This work was financially supported by the Russian Academy of Sciences (Fundamental Research Program No. 1, Division of Chemistry and Materials Sciences, Russian Academy of Sciences) and the Russian Science Support Foundation.

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Received April 1, 2005