Bis(tetrazolyl)benzenes as ligands in the Suzuki reaction: promoters or inhibitors?

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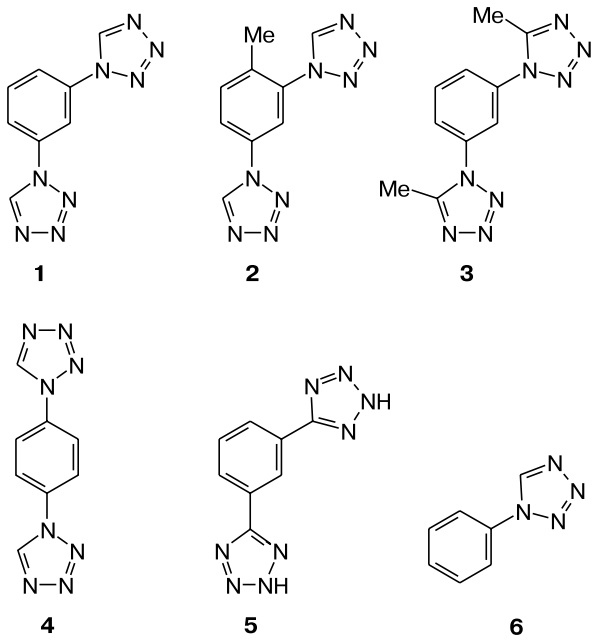
The Suzuki cross-coupling with phenylboronic acid in the presence of the $Pd(OAc)_2/K_3PO_4$/DMF catalytic system was successful for aryl bromides and somewhat poorer for aryl chlorides. Addition of 1,3-bis(tetrazol-1-yl)benzene or its analogs lowered the yields of biaryls.

Key words: cross-coupling, the Suzuki reaction, polychloroarenes, biaryls, 1,3-bis(tetrazol-1-yl)benzene, tetrazoles, phenylboronic acid.

During the past two decades, the Suzuki reaction has been widely recognized as a convenient method for bond formation between sp^2-hybridized C atoms. The Suzuki reaction easily occurs with aryl bromides and aryl iodides (see surveys[1]). However, much more accessible aryl chlorides, especially non-activated ones, are less reactive and their cross-coupling requires special (often expensive) catalysts containing sterically hindered phosphine[2] or *N*-heterocyclic carbene[3] ligands. Examples of ligands of other types employed in this reaction are few.[4] That is why a search for more accessible and less expensive catalytic systems for cross-coupling reactions, especially with non-activated chloroarenes, remains of topical interest. Recently,[5] 1,3-bis(tetrazol-1-yl)benzene (**1**) has been proposed as a promising pincer ligand for the Suzuki cross-coupling, ensuring satisfactory yields of the target products even from non-activated aryl chlorides. This ligand is easy to prepare, is stable in air, and can *in situ* form catalytically active metal complexes with palladium acetate.[5]

In the present work, we compared compound **1** with its five structural analogs **2**—**6** as ligands for Pd-catalyzed Suzuki reactions of aryl halides **7a**—**j** and, in particular, polychloroarenes **7c**—**f,i,j** with phenylboronic acid (Scheme 1). Earlier, compounds **2**—**6** have not been used as ligands in palladium-catalyzed cross-coupling reactions. The reaction conditions were the same as specified in Ref. 5 (DMF, 100 °C, K_3PO_4, 18-crown-6, preliminary activation of $Pd(OAc)_2$ in the presence of the ligand; see Table 1). In some cases, Bu_4NBr was used instead of 18-crown-6 or the process was carried out without a phase-transfer catalyst (PTC).



It turned out that with ligands **2**, **3**, and **6** in the reaction of 4-bromoanisole (**7a**) with $PhB(OH)_2$, the yield of 4-methoxybiphenyl (**8a**) is higher (entries *2*—*5*, *8*) than that in the presence of ligand **1** (entry *1*). However, with bis(tetrazolyl)benzenes **4** and **5**, which are isomeric with compound **1**, the yield of product **8a** was appreciably lower (entries *6*, *7*). The quantitative yields of cross-coupling product **8a** were unexpectedly attained in blank experiments without ligands or a phase-transfer catalyst (entries *9*, *10*). Similar tendencies were observed in the reactions of 4-bromotoluene (**7b**) (entries *11*—*14*), although

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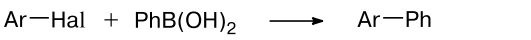
Scheme 1



7a—j **8a—j**

7,8	Ar	Hal in 7	7,8	Ar	Hal in 7
a	4-$MeOC_6H_4$	Br	**f**	C_6Cl_5	Cl
b	4-MeC_6H_4	Br (**7b**), Cl (**7´b**)	**g**	4-AcC_6H_4	Cl
c	2-ClC_6H_4	Cl	**h**	2-AcC_6H_4	Cl
d	4-ClC_6H_4	Cl	**i**	2-Ac-5-ClC_6H_3	Cl
e	2,4,5-$Cl_3C_6H_2$	Cl	**j**	AcC_6Cl_4	Cl

Reagents and conditions: $Pd(OAc)_2$, K_3PO_4, DMF, Δ, additives (see Table 1).

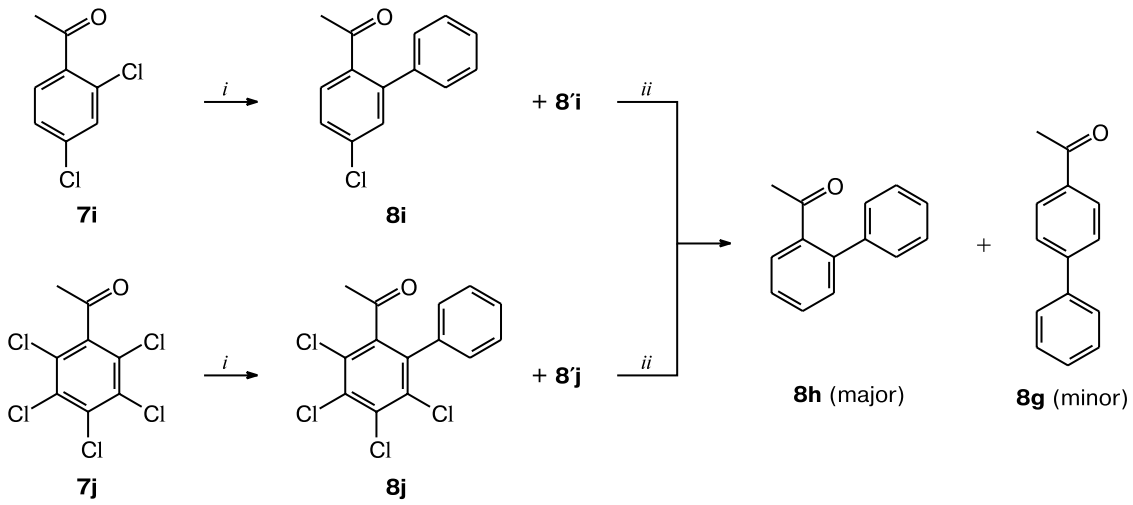
without such a large difference between the yields of 4-methylbiphenyl (**8b**) under different conditions.

The study of the Suzuki reaction with other substrates confirmed that tetrazole ligands **1—5** inhibit rather than promote cross-coupling of aryl halides under the conditions used. The inhibitive effects of compounds **1—5** were especially pronounced in reactions with less reactive chloroarenes (entries *15—32*). The reaction is doubly affected by PTC: they can both increase (*e.g.*, **8e**) and decrease the yields of cross-coupling products (**8f**). Apparently, transfer of inorganic ions at elevated temperatures in a polar solvent (DMF) can occur without intermediacy of 18-crown-6 or Bu_4NBr; in addition, probable coordination of crown ether by palladium makes the catalyst less active, which is especially pronounced for poorly reactive polychlorobenzenes (entries *19*, *20*, *22*, *23*).

One can assume that when heated in DMF, $Pd(OAc)_2$ liberates finely dispersed (possibly nanosized) palladium capable of catalyzing cross-coupling (*cf.* Refs 6, 7). Apparently, coordination of pincer *meta*-disubstituted ligands **1—3** by palladium lowers its activity. The stronger inhibitive effect of compound **1** compared to that of analog **3** can be tentatively associated with possible C-deprotonation of the tetrazole ring followed by coordination of the carbanion by palladium (similar to the formation of heterocyclic carbene complexes of palladium; *cf.* Refs 3). The methyl group in the phenyl ring of ligand **2** probably presents steric hindrances to the conformation required for coordination by palladium. Although *para*-disubstituted derivative **4** cannot act as a pincer ligand, it also inhibits the reaction (this phenomenon calls for further investigation). Ligand **5**, which is an N—H acid, is deprotonated under the reaction conditions and the resulting anion probably interacts with palladium to give a catalytically inert complex. Monodentate 1-phenyltetrazole (**6**) is a weak complexone and hence does not inhibit the reaction.

In contrast to nonactivated chloroarenes, mono- and dichloroacetophenones **7g—i** gave the corresponding cross-coupling products **8g—i** in high yields (entries *33—40*). Pentachloroacetophenone **7j** proved to be less reactive (entries *41*, *42*) because of the steric hindrances created by the Cl atoms in the *ortho*-position relative to the reactive site. According to the GC-MS data, the reactions with polychloroacetophenones **7i,j** gave mixtures of isomeric monosubstitution products. The structures of major products **8i,j** were determined in additional chemical experiments. For this purpose, mixtures of products of the cross-coupling of 2,4-dichloroacetophenone (**7i**) and pentachloroacetophenone (**7j**) with phenylboronic acid were subjected to reductive dechlorination[8] into known phenylacetophenones (Scheme 2). The major isomer in the reduction products was identified as 2-phenylacetophenone (**8h**) by capillary GLC

Scheme 2



Reagents and conditions: *i.* $PhB(OH)_2$, K_3PO_4, DMF, [Pd]. *ii.* H_2, Pd/C, MeOH, Et_3N; **8´i** and **8´j** are the corresponding isomers.

Table 1. Influence of the additives on the yields of the cross-coupling products from ArHal in the $Pd(OAc)_2/K_3PO_4$/DMF system[a]

Entry	ArHal	Additives	Yields of the cross-coupling products[b] (%)	Composition of the mixture (GC-MS data) (mol.%)		
				Products of the cross-coupling	Unreacted compound **7**	Ph_2[c]
1	**7a**	**1** + 18-crown-6	49	47 (**8a**)	48	5
2		**2** + 18-crown-6	75	74 (**8a**)	23	3
3		**3** + 18-crown-6	82	82 (**8a**)	17	1
4		**3** + Bu_4NBr	100	100 (**8a**)	—	Traces
5		**3**	100	100 (**8a**)	Traces	—
6		**4** + 18-crown-6	37	36 (**8a**)	61	3
7		**5** + 18-crown-6	6	5 (**8a**)	94	2
8		**6** + 18-crown-6	100	100 (**8a**)	—	—
9		18-Crown-6	100	100 (**8a**)	—	—
10		—	100	100 (**8a**)	—	—
11	**7b**	**1** + 18-crown-6	95	93 (**8b**)	5	2
12		**2** + 18-crown-6	92	92 (**8b**)	8	Traces
13		**3** + 18-crown-6	92	92 (**8b**)	8	Traces
14		—	100	100 (**8b**)	—	Traces
15	**7´b**	**1** + Bu_4NBr	—	—	95	5
16		**3** + 18-crown-6	9	9 (**8b**)	90	1
17		18-Crown-6	16	16 (**8b**)	83	1
18	**7c**	**3** + 18-crown-6	1	1 (**8c**)	98	1
19		18-Crown-6	2	2 (**8c**)	98	Traces
20		—	21	21 (**8c**)	79	—
21	**7d**	**3** + 18-crown-6	7	7 (**8d**)	92	1
22		18-Crown-6	8	8 (**8d**)	92	—
23		—	76	76 (**8d**)	24	—
24	**7e**	**1** + 18-crown-6	Σ 13	11 (**8e**), 2 ($Ph_2C_6H_2Cl_2$)	87	—
25		**3** + 18-crown-6	Σ 30	27 (**8e**), 3 ($Ph_2C_6H_2Cl_2$)	70	—
26		**6** + 18-crown-6	21	20 (**8e**)	76	4
27		18-Crown-6	Σ 69	57 (**8e**), 3+2+7 ($Ph_2C_6H_2Cl_2$)	31	—
28		—	Σ 58	42 (**8e**), 5+6 ($Ph_2C_6H_2Cl_2$)	39	8
29	**7f**	**1** + 18-crown-6	Σ 21	11 (**8f**), 5 (PhC_6HCl_4)	51 (C_6Cl_6) + 10 (C_6HCl_5)	23
30		**4** + 18-crown-6	—	—	90	10
31		18-Crown-6	Σ 32	16 (**8f**), 3 ($Ph_2C_6HCl_3$), 4 ($Ph_2C_6Cl_4$)	50	27
32		—	Σ 78	17 (**8f**), 7 ($Ph_2C_6HCl_3$), 13+4+4 ($Ph_2C_6Cl_4$), 5+4 ($Ph_3C_6Cl_3$), 6 ($Ph_3C_6HCl_2$)	17	21
33	**7g**	**3** + 18-crown-6	97	92 (**8g**)	3	5
34		**4** + 18-crown-6	—	—	100	
35		18-Crown-6	100	100 (**8g**)		
36	**7h**	**3** + 18-crown-6	95	91 (**8h**)	5	4
37		18-Crown-6	95	95 (**8h**)	5	—
38	**7i**	**1** + 18-crown-6	Σ 100	75 (**8i**) + 10 (**8´i**)[d], 15 ($AcC_6H_3Ph_2$)	—	—
39		**3** + 18-crown-6	Σ 100	14 (**8i**), 62 ($AcC_6H_3Ph_2$)	—	24
40		18-Crown-6	Σ 100	51 (**8i**) + 7 (**8´i**)[d], 17 ($AcC_6H_3Ph_2$)		25
41	**7j**	**3** + 18-crown-6	17	11 (**8j**)	53	36
42		18-Crown-6	37	20 (**8j**) + 4 (**8´j**)[d]	42	34

[a] Reaction conditions: 8 mol.% $Pd(OAc)_2$, 8 mol.% ligands **1**—**6**, 12 mol.% phase-transfer catalysts, $PhB(OH)_2$ (1.1 equiv.), K_3PO_4 (4 equiv.), DMF, 95 °C, 7—8 h.

[b] With respect to the starting ArHal without considering the content of biphenyl (product of the homocoupling of phenylboronic acid).

[c] The product of the homocoupling of phenylboronic acid.

[d] The isomers of substituent positions in the phenyl ring.

(comparison with an authentic sample obtained from 2-chloroacetophenone (**7h**)). The minor reduction product was 4-phenylacetophenone (**8g**) identical with the cross-coupling product from 4-chloroacetophenone (**7g**) and phenylboronic acid.

The *ortho*-position of the acetyl group in the major cross-coupling products **8i,j** (especially **8i**) was unexpected since the Cl atom in the *para*-position of 2,4-dichloroacetophenone (**7i**) is sterically more accessible. Here, electron activation of the Cl atom *ortho* to the acetyl group may be decisive. The only close literature example is $NiCl_2(PPh_3)_2$-catalyzed cross-coupling of 2,4-dichlorobenzaldehyde with $PhB(OH)_2$, with predominant replacement of the Cl atom in the *para*-position.[9] The reactivities of the *ortho*- and *para*-positioned halogen atoms can be indirectly compared by using data[2d,3e,10,11] on cross-coupling of chloro- and bromobenzenes containing an electron-withdrawing group in the *ortho*- and *para*-positions under identical conditions. In most cases, the yields of the *para*-isomers have been reported to be higher.[2d,11]

To conclude, we disproved the data[5] by demonstrating that pincer-type bistetrazole ligands inhibit rather than promote cross-coupling reactions of aryl halides with phenylboronic acid in DMF. The results obtained can be explained in terms of ligandless palladium catalysis.[6,7]

Experimental

GC-MS spectra were recorded on a Agilent Technologies 85973 Network instrument (EI, 70 eV) connected to a Agilent Technologies 6890 chromatograph (HP-5MS capillary column 30 000×0.25 mm, injector and flame ionization detector temperature 280 °C, temperature programming: 60 °C (5 min) and then rise to 300 °C (10 deg min^{-1}), helium as a carrier gas, 2 mL min^{-1}. During the analysis, the total ionic current and the signal from the flame ionization detector were measured in parallel. The areas under chromatographic peaks were corrected for the number of the carbon atoms in the molecule and then the mole fractions of the components were calculated. Elemental analysis was carried out at the analytical laboratory of the Institute of Organic Chemistry, Russian Academy of Sciences. Dimethylformamide was successively distilled over P_2O_5 and K_2CO_3. 1,2,4,5-Tetrachlorobenzene (**7e**) (Acros) and hexachlorobenzene (**7f**) (Aldrich) were used as purchased. Pentachloroacetophenone was synthesized earlier.[12] Bis(tetrazol-1-yl)benzenes **1** and **4** and 1-phenyltetrazole (**6**) were prepared according to a known procedure.[13]

4-Methyl-1,3-bis(tetrazol-1-yl)benzene (2). A round-bottom flask fitted with a reflux condenser was charged with sodium azide (2.27 g, 35 mmol), a solution of triethyl orthoformate (4.87 g, 33 mmol) in glacial acetic acid (20 mL), and 2,4-diaminotoluene (1.3 g, 11 mmol) and the mixture was refluxed with stirring for 6 h. The mixture was then cooled and diluted with water (50 mL). The precipitate that formed was filtered off, washed with water, and dried in air to give compound **2** (0.71 g, 28%) as a light gray powder, m.p. 183—184 °C. Found (%): C, 47.23; H, 3.74; N, 48.95. $C_9H_8N_8$. Calculated (%): C, 47.37; H, 3.53; N, 49.10. ^{1}H NMR (DMSO-d_6), δ: 2.26 (s, 3 H); 7.83, 8.14 (both d, 1 H each, J = 8.1 Hz); 8.25, 9.95, 10.15 (all s, 1 H each). ^{13}C NMR (DMSO-d_6), δ: 17.1 (CH_3); 119.0 (=CH); 122.8 (=CH); 132.3 (=C); 133.1 (=CH); 133.6 (=C); 134.9 (=C); 142.3 (=CH); 144.6 (=CH).

1,3-Bis(5-methyltetrazol-1-yl)benzene (3) was obtained analogously from sodium azide (1.46 g, 22.5 mmol), 1,3-phenylenediamine (0.756 g, 7 mmol), AcOH (13 mL), and trimethyl orthoacetate (2.52 g, 21 mmol). The yield was 0.59 g (35%), a light gray powder, m.p. 226—227 °C. Found (%): C, 49.65; H, 4.39; N, 46.26. $C_{10}H_{10}N_8$. Calculated (%): C, 49.58; H, 4.16; N, 46.26. ^{1}H NMR (DMSO-d_6), δ: 2.64 (s, 6 H); 7.90—8.40 (m, 3 H); 8.12 (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 9.3 (CH_3); 121.2 (=CH); 126.5 (=CH); 131.4 (=CH); 134.4 (=C); 152.4 (=C).

1,3-Bis(tetrazol-5-yl)benzene (5). A round-bottom flask fitted with a reflux condenser was charged with isophthalonitrile (0.71 g, 5.5 mmol), sodium azide (0.75 g, 13 mmol), NH_4Cl (0.68 g, 13 mmol), and DMF (5 mL). The mixture was refluxed with stirring for 20 h. Then the solvent was removed *in vacuo*, water was added, and the resulting precipitate was filtered off and purified by column chromatography on silica gel with 3% MeOH in CH_2Cl_2 as the eluent. The yield of compound **5** was 0.838 g (74%), m.p. 278—280 °C (*cf.* Ref. 14: m.p. 290 °C). ^{1}H NMR (DMSO-d_6), δ: 7.49 (t, 1 H, J = 8.1 Hz); 7.98 (d, 2 H, J = 8.1 Hz); 8.67 (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 124.2, 126.2, 129.4, 131.0, 160.2.

Cross-coupling reactions. ***A.*** A Schlenk tube was charged with $Pd(OAc)_2$ (9 mg, 0.040 mmol), a ligand **1**—**6** (0.041 mmol), K_3PO_4 (339 mg, 1.6 mmol), and 18-crown-6 (16 mg, 0.06 mmol). Dimethylformamide (1 mL) was added under argon and the tube was deaerated by pumping and filling with argon. The mixture was heated at 95 °C for 1 h and cooled to ~20 °C. An appropriate haloarene **7** (0.5 mmol) (see Table 1) was added and the mixture was stirred for 10 min. Then phenylboronic acid (66 mg, 0.55 mmol) and DMF (1 mL) were added and stirring was continued at 95 °C for 7 h. A probe was withdrawn from the reaction mixture and concentrated *in vacuo* and the residue was dissolved in benzene, filtered through a layer of silica gel, and analyzed by GC-MS. In some cases, an equivalent amount of Bu_4NBr was used instead of 18-crown-6 or the reaction was carried out without a phase-transfer catalyst.

B. In the ligandless method, the other components specified in method ***A*** were mixed simultaneously, the tube was deaerated by pumping—argon filling, and the mixture was stirred at 95 °C for 7—8 h.

Reaction products were identified from mass spectra, as well as by comparing their retention times with those of authentic samples (compounds **8e** and **8f** have been earlier[15] isolated in the individual state). The mass numbers of the molecular ion peaks (given for the ^{35}Cl nuclei; the isotope clusters correlated with the number of Cl atoms in the molecule) for cross-coupling products are: **7e**, $PhC_6H_2Cl_3$ (256), $Ph_2C_6H_2Cl_2$ (298); **7f**, PhC_6Cl_5 (324), $Ph_2C_6Cl_4$ (366), $Ph_3C_6Cl_3$ (408), PhC_6HCl_4 (290), $Ph_2C_6HCl_3$ (332), $Ph_3C_6HCl_2$ (374); **7g**, 4-PhC_6H_4Ac (196); **7h**, 2-PhC_6H_4Ac (196); **7i**, 2-Ph-4-ClC_6H_3Ac (230), 4-Ph-2-ClC_6H_3Ac (230), 2,4-$Ph_2C_6H_3Ac$ (272); **7j**, PhC_6Cl_4Ac (332).

Reductive hydrodechlorination of polychlorobiaryls 8. A crude cross-coupling product (*ca.* 50 mg) was dissolved in MeOH (3 mL) and placed in a round-bottom flask. The flask was charged with 10% Pd/C (50 mg) (Alfa) and triethylamine (0.2 mL) and

deaerated by flushing hydrogen from a balloon. Hydrogenation was carried out at ~20 °C. Usually, the reaction was completed in 1—2 h (monitoring by GLC). On longer hydrogenation, the oxo groups in acetyl-containing biaryls **8i,j** were reduced to the corresponding sec-OH groups (Table 1, entries *40*, *42*).

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