Oxidative Ligand Coupling of Tetraarylborates Promoted by Chlorosilane and Molecular Oxygen

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Oxidative ligand coupling of organoborates is promoted by chlorosilane and molecular oxygen. When tetraarylborate compounds are treated with Ph_2SiCl_2 or $PhSiCl_3$ in acetonitrile under an oxygen atmosphere, the corresponding biaryls are obtained in good yields. Use of unsymmetrical borates results in the selective formation of unsymmetrical biaryls.

Alkenyltrialkylborates undergo formal ligand coupling reactions induced by I_2 or BrCN, giving the corresponding alkylated alkenes, and the reactions have been applied to stereoselective alkene synthesis.[1] Recently, we reported that oxovanadium(V) compounds can induce the ligand coupling of alkenyltrialkylborates.[2,3] As for the oxidative transformation of tetraarylborates, biaryl formation has been reported to occur by electrochemical,[4] photochemical,[5] and chemical oxidation, for example with Ir(IV).[6] In this paper we demonstrate a novel oxidative ligand coupling of tetraarylborates promoted by chlorosilane and molecular oxygen.

When $NaBPh_4$ (**1a**) was treated with Me_3SiOTf in acetonitrile, the color of the solution changed from colorless to pale yellow immediately. Under an argon atmosphere, no further reaction was detected, but formation of biphenyl (**2a**) was observed under an oxygen atmosphere in 30% yield. In the absence of Me_3SiOTf, **2a** was produced only in 5% yield even under an oxygen atmosphere (eq 1).

$$\underset{\mathbf{1a}}{\mathrm{NaBPh_4}} \xrightarrow[\mathrm{CH_3CN,\ rt,\ 5\ h}]{} \underset{\mathbf{2a}}{\mathrm{Ph{-}Ph}} \quad (1)$$

under Ar	trace
under O_2	5%
Me_3SiOTf, under Ar	1%
Me_3SiOTf, under O_2	30%

The influence of halosilanes was monitored by employing various silicon compounds in the biphenyl formation from $NaBPh_4$. The representative results are shown in Table 1. When Me_3SiCl was used, **2a** was obtained only in 6% yield (entry 1), but the reaction with Ph_3SiCl afforded **2a** in 42% yield (entry 3). Next, the substituent effect of R_2SiX_2 was examined to reveal that the more phenyl groups introduced on silicon increase the yield of **2a** (entries 4–6). However, introduction of a diethylamino group did not promote the coupling reaction as shown in entry 7. In order to confirm whether ligand scrambling between boron and silicon occurs, the reaction with $(4\text{-}MeC_6H_4)_2SiCl_2$ was carried out. NMR analysis showed that **2a** and 4,4'-dimethylbiphenyl (**2c**) were produced in 91% and 11% yields, respectively, and no 4-methylbiphenyl (**2d**) was detected (entry 8). The result indicates that the ligand coupling reaction not only occurs in the organoborate compound but also in the organosilicon compound as a minor process.[7] On the other hand, no ligand cross-coupling between boron and silicon compounds occurred. $PhSiCl_3$ was more effective to promote the coupling reaction than $MeSiCl_3$ (entries 9 and 10).

Table 1. Effect of the silicon reagents

$$\underset{\mathbf{1a}}{\mathrm{NaBPh_4}} \xrightarrow[\mathrm{CH_3CN,\ rt,\ 5\ h}]{\substack{\text{Silicon reagent}\\ \mathrm{O_2}\text{ atmosphere}}} \underset{\mathbf{2a}}{\mathrm{Ph{-}Ph}}$$

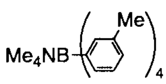
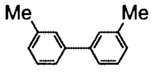
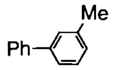
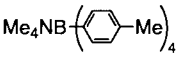
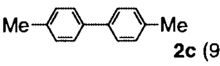
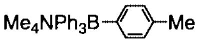
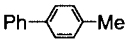
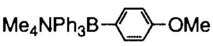
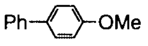
Entry	Silicon reagent	**2a** (Yield / %)
1	Me_3SiCl	6
2	Me_3SiOTf	30
3	Ph_3SiCl	42
4	Me_2SiCl_2	35
5	$PhMeSiCl_2$	48
6	Ph_2SiCl_2	76
7	$Ph_2SiCl(NEt_2)$	0
8	$(4\text{-}MeC_6H_4)_2SiCl_2$	91[a]
9	$MeSiCl_3$	57
10	$PhSiCl_3$	67

[a] NMR yield. 4,4'-Dimethylbiphenyl (**2c**) was also obtained in 11% yield.

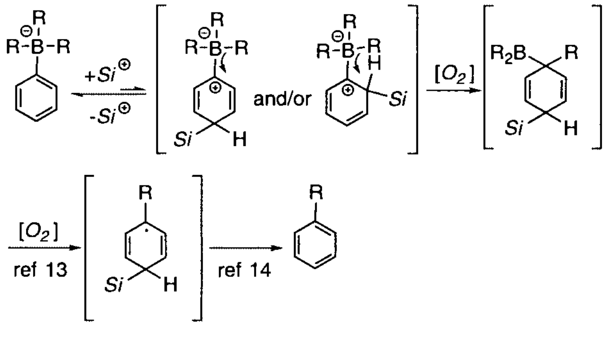
Table 2 demonstrates the results starting from various kinds of organoborate compounds.[8] As shown in entry 4, ligand coupling of tetramethylammonium salt (**1a'**) also proceeded in 83% yield. $Me_4NB(3\text{-}MeC_6H_4)_4$ (**1b**) was similarly converted to 3,3'-dimethylbiphenyl (**2b**) without formation of any regioisomer, indicating that the coupling occurs at the ipso position of the borate. Only a trace amount of B–Si cross-coupling product **3b** was detected by GC (entries 5 and 6). From $Me_4NB(4\text{-}MeC_6H_4)_4$ (**1c**), **2c** was obtained exclusively (entries 7 and 8). In the reaction of unsymmetrical borates, the more nucleophilic aryl group was susceptible to ligand coupling, giving an unsymmetrical biaryl compound as a major product (entries 9–12). For example, the reaction of $Me_4NBPh_3(4\text{-}MeC_6H_4)$ (**1d**) with Ph_2SiCl_2 afforded **2d** in 65% yield, while **2a** was produced only in 9% yield (entry 9).

Although the precise reaction mechanism has not been established, one possible reaction pathway may be explained by a combination of each reported step as illustrated in Scheme 1. When borate and chlorosilane are mixed, a silylium ion equivalent (R_3Si^+) is considered to be generated as reported.[9] The silylium ion is known to react with an aromatic compound to form a silylated cyclohexadienyl cation (Wheland intermediate or σ-complex).[10] Since electrophilic attack of the silylium ion to an aromatic ring is reversible, no further reaction would proceed under an argon atmosphere. The reaction of alkynyltri-

Table 2. The reaction of various organoborate compounds

Entry	Organoborate	Silicon reagent	Products (Yields / %)
1	$NaBPh_4$ (**1a**)	Ph_2SiCl_2	Ph–Ph **2a** (76)
2		$PhSiCl_3$	**2a** (67)
3	Me_4NBPh_4 (**1a'**)	Ph_2SiCl_2	**2a** (54)
4		$PhSiCl_3$	**2a** (83)
5	 **1b**	Ph_2SiCl_2	 **2b** (77)  **3b** (trace)
6		$PhSiCl_3$	**2b** (75), **3b** (trace)
7	 **1c**	Ph_2SiCl_2	 **2c** (96)
8		$PhSiCl_3$	**2c** (92)
9	 **1d**	Ph_2SiCl_2	 **2d** (65) **2a** (9), **2c** (1)
10		$PhSiCl_3$	**2d** (68), **2a** (13), **2c** (1)
11	 **1e**	Ph_2SiCl_2	 **2e** (67) **2a** (10)
12		$PhSiCl_3$	**2e** (56), **2a** (8)

alkylborate with chlorosilane has been reported to afford the β-silylated alkene accompanied with 1,2-migration.[11] Molecular oxygen might promote the 1,2-migration of a nucleophilic ligand on boron to the ipso position on the aromatic ring.[12] Finally, deboration[13]/desilylation[14] via a radical process is promoted by molecular oxygen, giving the corresponding ligand coupling product. Alternative mechanisms such as an electron transfer process via a peroxo species derived from a silylium ion and molecular oxygen cannot be ruled out.



Scheme 1. A possible reaction pathway.

As described above, the present reaction provides a novel oxidative ligand coupling of organoborates promoted by a combination of chlorosilane and molecular oxygen. It is noteworthy that unsymmetrical biaryls can be selectively obtained from the corresponding unsymmetrical borate compounds. Further application and mechanistic studies are now under investigation.

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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

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8 General procedure: To an acetonitrile (5 mL) solution of the borate **1** (0.25 mmol) was added Ph_2SiCl_2 or $PhSiCl_3$ (0.25 mmol) via a syringe at room temperature under an oxygen atmosphere and the mixture was stirred for 5–10 h. The reaction was quenched with 1 M HCl solution, and the mixture was extracted with ether. The combined organic layer was washed with brine, and dried over $MgSO_4$. The organic solvent was evaporated and the resulting crude product was purified by PTLC to give **2** as listed in Table 2.

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