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OMe. CF₃, SiMe₃

9 examples

7–81% vield

Palladium-Catalyzed Double Borylation of Diaryl Sulfoxides with Diboron

Α

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Abstract Borylation of the C–S bond of diaryl sulfoxides with bis(pinacolato)diboron (B_2pin_2) is accomplished by means of a phosphine-ligated palladium catalyst and LiN(SiMe₃)₂ as a base. Both of the aryl rings of the diaryl sulfoxides are converted into borylated products.

Key words borylation, diaryl sulfoxide, C–S cleavage, palladium, diboron

In modern organic chemistry organoboron compounds play various crucial roles, not only as synthetic intermediates, but also as functional materials and pharmaceuticals in their own right.¹ With the increasing attention devoted to organoboron compounds, a number of new C–B bond formations have been developed. Among these synthetic strategies, Miyaura-type *ipso*-borylation of aryl (pseudo)halides has occupied a privileged position.^{2,3} Although highly reactive aryl iodides, bromides, or sulfonates have been employed as the substrates conventionally, borylations of inert bonds such as C–Cl.⁴ C–F,⁵ C–O,⁶ C–N⁷ and C– C⁸ have been achieved with the aid of coordinatively unsaturated and electron-rich transition-metal catalysts.

Aryl sulfides are regarded as potentially attractive electrophiles in the cross-coupling arena, and transformations of their C–S bonds have long been investigated.^{9,10} Nevertheless, one is often faced with difficulties in transitionmetal-catalyzed C–S bond cleavage because of the robustness of the C–S bonds as well as the high affinity of the sulfur fragments toward metal catalysts.¹¹ Despite these challenges, a series of C–S bond transformations have been emerging with the aid of sturdy transition-metal catalysts such as N-heterocyclic carbene (NHC)-ligated metal complexes.^{10g} Recently, Hosoya and we independently reported the borylation of aryl sulfides by means of rhodium and palladium catalysts, respectively.¹² As a part of our interest in C– S bond transformations,^{10g,12b,13} we focused on *ipso*-borylation of aryl sulfoxides. Although there is only one example of the borylation of methyl phenyl sulfoxide, the yield of the product was insufficient.^{12a} Here we report double borylation of diaryl sulfoxides with bis(pinacolato)diboron (B₂pin₂) by employing a phosphine-ligated palladium catalyst.

LiN(SiMe₃)₂

We started our investigation by applying our previous palladium-catalyzed borylation system^{12b} to diphenyl sulfoxide (1a) as a model substrate (Table 1). In the presence of 6 equivalents of LiN(SiMe₃)₂ and 5 mol% of Pd-PEPPSI-IPr¹⁴ (Figure 1), **1a** was treated with 4 equivalents of B₂pin₂ in THF at 80 °C. As a result, borylated product 2a was observed but the yield was low. (Table 1, entry 1). We then tested other NHC-ligated palladium complexes as catalysts (entries 2 and 3). When SingaCycle-A3¹⁵ was used, both of the phenyl rings of **1a** were involved in the borylation to furnish 2a in 81% yield, which was calculated based on the molar amount of the phenyl rings of **1a** (entry 3). Monodentate or bidentate trialkylphosphines were inferior to the IPr ligand (entries 4-6). On the other hand, Buchwald-type dialkylphosphinobiphenyl ligands afforded 2a in good yields (entries 7–9). Eventually, an SPhos-ligated complex, SPhos Pd G2,¹⁶ was found to be the best, furnishing 2a in 87% yield (entry 10). As a by-product, 10% of biphenyl was observed, which could be generated through the reaction of 1a with borylated species 2a. An excess amount of LiN(SiMe₃)₂ was indispensable, and a trace amount of 2a was formed with a catalytic amount of LiN(SiMe₃)₂. NaN(SiMe₃)₂, KN(SiMe₃)₂, and other inorganic lithium bases did not work well (entries 11-15).

With the optimum reaction conditions, we investigated the scope of diaryl sulfoxides (Table 2). Methyl- and phenyl-



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substituted diaryl sulfoxides **1b** and **1c** underwent the double borylation to afford **2b** and **2c**, respectively (entries 2 and 3). A trimethylsilyl moiety survived even under the strongly basic reaction conditions (entry 4). Electron-deficient trifluoromethyl-substituted diaryl sulfoxide **1e** gave **2e** in moderate NMR yield (entry 5). Unfortunately, the isolated yield of **2e** was only 7% owing to the difficulty in separation from by-products. *p*-Methoxy-substituted diaryl sulfoxide **1f** was reluctant to undergo the borylation, and a

Table 1 Optimization of the Reaction Conditions



Entry	Catalyst	Base	Yield (%)
1	Pd-PEPPSI-IPr	LiN(SiMe ₃) ₂	27
2	SingaCycle-A1	LiN(SiMe ₃) ₂	32
3	SingaCycle-A3	$LiN(SiMe_3)_2$	81
4	Pd(PtBu ₃) ₂	$LiN(SiMe_3)_2$	63
5	2.5 mol% Pd ₂ (dba) ₃ + 10 mol% PCy ₃	$LiN(SiMe_3)_2$	18
6	2.5 mol% Pd ₂ (dba) ₃ + 5 mol% dcype	$LiN(SiMe_3)_2$	0
7	2.5 mol% Pd ₂ (dba) ₃ + 5 mol% XPhos	$LiN(SiMe_3)_2$	73
8	2.5 mol% Pd ₂ (dba) ₃ + 5 mol% DavePhos	$LiN(SiMe_3)_2$	74
9	2.5 mol% Pd ₂ (dba) ₃ + 5 mol% SPhos	$LiN(SiMe_3)_2$	77
10	SPhos Pd G2	$LiN(SiMe_3)_2$	87
11	SPhos Pd G2	NaN(SiMe ₃) ₂	20
12	SPhos Pd G2	KN(SiMe ₃) ₂	49
13	SPhos Pd G2	LiOtBu	<5
14	SPhos Pd G2	Li ₂ CO ₃	<5
15	SPhos Pd G2	LiF	0

 $^{\rm a}$ NMR yield was calculated based on the molar amount of the phenyl rings of ${\rm 1a.}$



larger catalyst loading and a longer reaction time were necessary to achieve full conversion (entry 6). A methyl moiety at the *ortho*-position did not affect the efficiency of the reaction (entry 7). Naphthyl sulfoxides **1h** and **1i** also gave the products **2h** and **2i**, respectively, although the borylation of the bulkier **1i** required a 10 mol% catalyst loading and a longer reaction time (entries 8 and 9). Unfortunately, benzofuryl sulfoxide **1j** did not afford the borylated product and a complex mixture was obtained (entry 10). Instead of diaryl sulfoxides, methyl phenyl sulfoxide (**1k**) gave **2a** in low yield although **1k** was fully consumed (entry 11). Benzenethiol was obtained in ca. 30% NMR yield as a major byproduct. As a diboron reagent, bis(neopentyl glycolato)diboron (B₂nep₂) was inferior to B₂pin₂; **2a'** was formed in 25% NMR yield (entry 12).

When the borylation of electronically biased unsymmetrical diaryl sulfoxide **11** was conducted at 40 °C, the borylation occurred preferentially on the electron-deficient $F_3CC_6H_4$ side to provide **2e** as the major product (Scheme 1).

Our previous borylation of aryl sulfides also proceeded under similar palladium catalysis.^{12b} Therefore, we examined the chemoselectivity between an aryl sulfide and a sulfoxide under the SPhos-palladium catalysis. Methylsulfanyl-substituted diaryl sulfoxide **1m** was treated with B_2pin_2 under the standard reaction conditions. As a consequence, product **2m** via borylation at the sulfinylated carbon was obtained as the major product accompanied by a small amount of 1,4-diborylated benzene **3** (Scheme 2). In this case, reduction of the sulfinyl moiety of **1m** also occurred to form the corresponding diaryl sulfide as a dominant by-product.¹⁷







Scheme 2 Borylation of a diaryl sulfoxide having a sulfanyl moiety

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In place of diaryl sulfoxides, diphenyl sulfone (**4a**) gave borylated product **2a** in 46% yield, which was calculated based on the molar amount of the phenyl rings of **4a** (Scheme 3).

A plausible reaction mechanism is shown in Scheme 4. Diaryl sulfoxide **1** would undergo oxidative addition to the palladium(0) species to form arylpalladium(II) intermediate **A**.¹⁸ Although the arylsulfenate anion on **A** would tightly



followed by reductive elimination. The resulting borate species **D** can dissociate into the boryl sulfenate **E** and $\text{LiN}(\text{SiMe}_3)_2$. The former species would subsequently undergo the second catalytic borylation with $B_2\text{pin}_2$ because $\text{pinB}-S(=O)^-$ would be a good leaving group. Further investigations will be necessary to clarify the fate of the pinB-S(=O) unit. Since an excess amount of $\text{LiN}(\text{SiMe}_3)_2$ was necessary for the borylation, we assumed that boron-containing fragments would react with the amide anion and that $\text{LiN}(\text{SiMe}_3)_2$ would be thus consumed.

coordinate to the palladium center, highly reactive borate

complex **C** would promote the boryl transfer to generate **B**

 Table 2
 Scope of Diaryl Sulfoxides in Double Borylation with B2pin2



^a Yield of isolated product. The yield was calculated based on the molar amount of the aryl rings of 1. The NMR yield is shown in parentheses.

^b 10 mol% of catalyst.

^c 15 mol% of catalyst.

^d Reaction time: 40 h.

^e Bis(neopentyl glycolato)diboron (B₂nep₂) was used.



Scheme 4 A plausible reaction mechanism

In conclusion, we have developed a process for the C–S bond borylation of diaryl sulfoxides in which both of the aryl rings of the substrates were converted into the borylated products. The reaction was promoted by the SPhos-ligated palladium catalyst and LiN(SiMe₃)₂ as a base.

All reactions were performed under a nitrogen atmosphere. Dehydrated THF was purchased from KANTO CHEMICAL CO., INC. and stored under a nitrogen atmosphere. Diarvl sulfoxides 1c.¹⁹ 1f.²⁰ and 1h²⁰ were prepared according to the literature. Diaryl sulfoxides 1d,²¹ 1e,²⁰ 1g,²⁰ 1i,²¹ 1j¹⁹, and 1m²¹ were synthesized by similar procedures described in previous reports. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel 60F₂₅₄. Preparative TLC was performed on silica gel (Merck 60PF₂₅₄). Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-9260 II NEXT system with CHCl₃ as the eluent. ¹H NMR (600 MHz) and ¹³C NMR (151 MHz) spectra were recorded on a JEOL ECA-600 spectrometer and were recorded in CDCl₃ (for ¹H, δ = 7.26; for ¹³C, δ = 77.0). Carbons bearing boron atoms were not observed due to the quadrupolar relaxation mechanism of the ¹¹B nucleus and consequently are not reported here.

4-Methoxyphenyl 4-(Trifluoromethyl)phenyl Sulfoxide (11)

A round-bottom flask was charged with 4-nitrobenzotrifluoride (1.9 g, 10 mmol), 4-methoxybenzenethiol (1.7 g, 12 mmol), Cs_2CO_3 (3.9 g, 12 mmol), and DMSO (60 mL). The resulting mixture was stirred at r.t. for 75 h. After the reaction was complete, H_2O (50 mL) was added and the resulting mixture was extracted with Et_2O (3 × 30 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (hexane/EtOAc = 25:1) to give the corresponding diaryl sulfide (2.1 g, 7.4 mmol, 74%). The resulting diaryl sulfide (0.57 g, 2.0 mmol) was dissolved in CH_2Cl_2 (10 mL), and *m*CPBA (containing ca. 30% H_2O , 0.49 g, 2.0 mmol) was added to the solution. The resulting mixture was allowed to warm to r.t. and stirred for 4 h. After completion of the reaction, saturated aqueous K_2CO_3 was added to the reaction mixture and the resulting solution was extracted with EtOAc

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 $(3 \times 20 \text{ mL})$. The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane/EtOAc = 5:1) to give **11** (0.40 g, 1.3 mmol, 67%) as a white solid. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.²²

Double Borylation of Diaryl Sulfoxides 1 (Table 2); Typical Procedure

A Schlenk tube was charged with diphenyl sulfoxide (**1a**) (41 mg, 0.20 mmol), SPhos Pd G2 (7.2 mg, 0.010 mmol), B₂pin₂ (0.20 g, 0.80 mmol), and LiN(SiMe₃)₂ (0.20 g, 1.2 mmol). THF (0.80 mL) was added to the tube and the resulting mixture was stirred at 80 °C for 20 h. After the reaction was complete, saturated aqueous NH₄Cl (2 mL) was added and the resulting biphasic mixture was extracted with Et₂O (5 × 5 mL). The combined organic layer was dried over Na₂SO₄, passed through a pad of silica gel, and concentrated under reduced pressure. The residue was purified by preparative TLC (hexane/EtOAc = 10:1) to provide (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**2a**) (54 mg, 0.26 mmol, 66%) as a colorless oil. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.^{12a}

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (2b)

The crude product was purified by preparative TLC (hexane/EtOAc = 10:1) to afford **2b** (66 mg, 0.30 mmol, 76%) as a colorless oil. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.^{12a}

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (2c)^{11a}

The crude product was purified by preparative TLC (toluene/EtOAc = 200:1) and preparative recycling GPC to afford **2c** (48 mg, 0.17 mmol, 43%) as a colorless oil. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.^{12a}

Trimethyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phe-nyl]silane (2d)

The crude product was purified by preparative TLC (hexane/EtOAc = 10:1) to afford **2d** (89 mg, 0.32 mmol, 81%) as a white solid. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.²³

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrifluoride (2e)

The crude product was purified by preparative TLC (hexane/EtOAc = 10:1) and preparative recycling GPC to afford **2e** (7.3 mg, 0.027 mmol, 7%) as a white solid. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.²⁴

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (2f)

The crude product was purified by preparative TLC (toluene/EtOAc = 20:1) and preparative recycling GPC to afford **2f** (38 mg, 0.16 mmol, 40%) as a colorless oil. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.^{12a}

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (2g)

The crude product was purified by preparative TLC (hexane/EtOAc = 20:3) to afford **2g** (54 mg, 0.25 mmol, 61%) as a colorless oil. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.^{5d}

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2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (2h)

The crude product was purified by preparative TLC (hexane/EtOAc = 10:1) to afford **2h** (66 mg, 0.26 mmol, 65%) as a white solid. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.^{12a}

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene (2i)

The crude product was purified by preparative TLC (toluene/EtOAc = 50:1) and preparative recycling GPC to afford **2i** (62 mg, 0.25 mmol, 61%) as a white solid. All the resonances in the ¹H and ¹³C NMR spectra were consistent with the reported data.^{12a}

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Supporting Information

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