LETTERS

Rh-Catalyzed Dehydrogenative Cyclization Leading to Benzosilolothiophene Derivatives via Si-H/C-H Bond Cleavage

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Supporting Information



ABSTRACT: Straightforward syntheses leading to π -extended benzosilolothiophene (BST) derivatives by Rh-catalyzed dehydrogenative cyclization reactions have been developed. Electron-deficient ligands were effective for the reactions, and dppe- F_{20} gave the best result. This method could be applied to the synthesis of highly π -extended ladder-type BST derivatives, which exhibited fluorescence.

B enzosilolothiophene (BST, benzo[4,5]silolo[3,2-*b*]thiophene) derivatives constitute an important skeleton for organic materials.^{1,2} For instance, Ashraf and Chen's group and Jen's group individually reported that π -conjugated polymers containing bis(benzosilolothiophene), a ladder unit including BST skeletons, can be used as active materials in organic solar cells.^{2n,p}

The first synthesis of π -extended BST derivatives was reported by Yamaguchi and co-workers. They synthesized ladder-type BST derivatives by cascade-type anionic double cyclization (Scheme 1(i)).³ Ashraf and Chen synthesized bis(benzosilolothiophene) by the tetra-lithiation of 2,5-bis(3bromo-2-thienyl)-1,4-dibromobenzene and a subsequent reaction with dichlorodi-n-octylsilane (Scheme 1(ii)).^{2p} While this is a typical method for synthesizing silicon-bridged π conjugated compounds, the yield of the product was low. Jen used a similar method with a precursor in which the 5-positions of thienyl groups were protected by trimethylsilyl groups.²ⁿ Though the yield of the protected BST derivative was higher than that of the nonprotected BST derivative, several reaction steps were required to introduce and remove trimethylsilyl groups. Shimizu and Hiyama reported a palladium-catalyzed intramolecular direct arylation via C–O/C–H bond cleavage.⁴ During their investigation of the scope of the reactions, they achieved the synthesis of BST derivatives (Scheme 1(iii)).4 While this is an efficient reaction for constructing a BST skeleton, several steps were required for synthesis of the precursor. Takai and Kuninobu reported a dehydrogenative cyclization of biarylhydrosilanes via Si–H/C–H bond cleavage using Wilkinson's catalyst.⁵ During their study, they found that the cyclization reaction of 2-(3-thienyl)-1-dimethylhydrosilane proceeded regioselectively at the 2-position of thiophene to give a regioisomer of BST (Scheme 1(iv)), but the application of their method for the synthesis of BST derivatives has not been reoprted.^{5d} While several methods for the synthesis of π -extended BST derivatives are available,⁶ there has been no report on an efficient synthesis of π -extended BST derivatives from readily available precursors such as a 2-arylthiophene bearing a silyl group (Scheme 1(v)). This approach should have several advantages, since it should be easy to synthesize the precursors due to the high reactivity of the 2-position of the thiophene unit.

Recently, we have been interested in the efficient synthesis of π -extended heteroaromatics.⁷ In this study, we focused on an efficient synthesis of π -extended BST derivatives and found a novel catalytic system for the synthesis of BST derivatives. We report here a novel Rh-catalyzed dehydrogenative cyclization leading to the synthesis of BST derivatives via cleavage of the Si–H bond and C–H bond at the 3-position of a thiophene ring or 2-position of a phenyl group. This method could also be

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Scheme 1. Synthetic Approaches for BST Derivatives

(i) Cascade-type anionic double-cyclization (Yamaguchi)



(ii) Tetra-lithiation and subsequent reaction with dichlolosilane (Ashraf, Chen & Jen)



(iii) C-O/C-H bond cleavage (Shimizu, Hiyama)

$$\overbrace{\mathsf{OTf}}^{i,\mathsf{Pr}} \xrightarrow{\mathsf{S}}_{\mathsf{OTf}} \xrightarrow{\mathsf{Pr}}_{\mathsf{S}} \xrightarrow{\mathsf{Pd} \text{ catalyst}}_{\mathsf{base}} \xrightarrow{i,\mathsf{Pr}}_{\mathsf{S}} \xrightarrow{i,\mathsf{Pr}}_{\mathsf{S}}$$

(iv) Si-H/C-H bond cleavage leading to a BST isomer (Takai, Kuninobu)



(v) Si-H/C-H bond cleavage (This work)

R-Si-H H	or	H H-Si-R	Rh catalyst	R Si R
s		3		

applied to the synthesis of highly π -extended BST derivatives, and their fundamental physical properties were investigated.

First, we chose 2 - [2 - (diphenylsilyl)phenyl]benzo[b] - benzo[b] - benzo[thiophene (1a) as a model substrate and carried out rhodium-catalyzed dehydrogenative cyclization. Takai and Kuninobu's conditions gave only a trace amount of the desired product.^{5d} We re-examined the reaction conditions as shown in Table 1. When 1a was treated with $[Rh(cod)Cl]_2$ (5 mol %) and PPh3 (30 mol %) at 145 °C for 5 h, an intermolecular reaction proceeded predominantly, and the desired BST 2a was obtained in only 5% yield (entry 1). We tested numerous monodentate ligands, such as an electron-rich ligand (entry 2), an electron-deficient ligand (entry 3), and a trialkylphosphine (entry 4), and all of them were insufficient for the reaction. Further screening revealed that triphenylphosphite $(P(OPh)_3)$ was an efficient monodentate ligand for the reaction (entry 5). The use of $P(OPh)_3$ increased the conversion of 1a and the yield of 2a (98% conversion, 56% yield). We next optimized the reaction with bidentate ligands. Bis(diphenylphosphino)alkanes, such as dppe, dppp, and dppb, were ineffective (entries 6-8). In contrast, when dppf was used as a ligand, 2a was obtained in 46% yield (entry 9). The use of BINAP as a ligand gave a similar result (entry 10, 43% yield). Electron-deficient bidentate ligands gave better results. When 1,2-bis[bis(2,3,5,6tetrafluoro-4-trifluoromethylphenyl)phosphino]ethane (L1) or dppe-F₂₀ was used as a ligand, 2a was obtained in respective yields of 68% and 69% (entries 11 and 12). The amount of $[Rh(cod)Cl]_2$ could be reduced to 1 mol %, and the yield of 2a increased to 83% due to the suppression of the intermolecular side reactions (entry 13). For this reaction, we assumed that the active catalytic species is Rh(dppe-F₂₀)H.⁸ To promote the generation of the active Rh-H species, we next added 15 mol % of (EtO)₃SiH as an additive. As expected, the addition of $(EtO)_3$ SiH increased the yield of 2a (entry 14, NMR yield:

Table 1. Rh-Catalyzed Dehydrogenative Cyclization of 1a^a

Ph Ph~Si	-H H S Igand (2 toluene,	Cl] ₂ (5 mol %) 30 mol % P) 145 °C, 5 h	Ph Ph Si S 2a
entry	ligand	$\operatorname{conv}(\%)^{b}$	yield (%) ^b
1	PPh ₃	70	5
2	$P(p-tol)_3$	54	2
3	$P(C_6H_4-p-CF_3)_3$	85	20
4	$P(t-Bu)_3$	90	10
5	$P(OPh)_3$	98	56
6	dppe	36	2
7	dppp	39	2
8	dppb	48	12
9	dppf	>98	46
10	BINAP	>98	43
11	L1	95	68
12	dppe-F ₂₀	98	69
13 ^c	dppe-F ₂₀	90	83
14 ^{c,d}	dppe-F ₂₀	>98	88 (91) ^e (92) ^{e,f}

^{*a*}Reaction conditions: **1a** (0.20 mmol), $[Rh(cod)Cl]_2$ (5 mol %), ligand (30 mol % of P), toluene (0.2 mL), 145 °C, 5 h. ^{*b*}Determined by GC analysis using 1-methylnaphthalene as an internal standard. ^{*c*}Performed with $[Rh(cod)Cl]_2$ (1 mol %) and dppe-F₂₀ (3 mol %). ^{*d*}15 mol % of (EtO)₃SiH was added. ^{*e*}Isolated yield. ^{*f*}Performed with 1.0 mmol of **1a**.

88%; Isolated yield: 91%). A similar yield of 2a was obtained from 1.0 mmol of 1a (entry 14, 92% yield).

To clarify the scope of the dehydrogenative cyclization, we next synthesized several BST derivatives 2 under the optimized conditions (Scheme 2). The cyclization of a precursor with a dimethylsilyl group also proceeded, and BST 2b was obtained in moderate yield (60%). In this case, the absence of (EtO)₃SiH gave a better result. While a longer reaction time was required, BST 2c and 2d were obtained in respective yields of 81% and 86%. The cyclization reaction of an alkylated precursor gave alkylated BST 2e in 72% yield. Precursors bearing an electron-donating or -withdrawing group can be used in the reaction to afford the cyclized products 2f and 2g in respective yields of 94% and 77%. We next tried the dehydrogenative cyclization of precursors bearing thienothiophene moieties. The cyclization reactions proceeded under the optimized conditions to give 2h and 2i in low yields. In some cases, the addition of (EtO)₃SiH was unnecessary. In particular, using 1 bearing an electron-donating moiety, the yield of 2 decreased drastically with (EtO)₃SiH (2b, 2e, and 2f). While the reason remains unclear, we assume that some side reactions proceed under these conditions.

We next carried out the cyclization reaction of precursors **3** which have a hydrosilyl group on their thiophene skeletons (Scheme 3). While we can assume that the electrochemical properties and steric conditions of the hydrosilyl groups of **3** were different from those of **1**, the cyclization reaction of **3** proceeded smoothly to give the cyclized products under similar conditions. For instance, when **3**-(diphenylsilyl)-2-phenylbenzo[*b*]thiophene (precursor **3a**) was treated under the optimized conditions, dehydrogenative cyclization proceeded smoothly to afford the desired BST **2a** in 96% yield. Similarly, the reaction of **3**-(diphenylsilyl)-2-phenylthiophene (**3b**) gave **2c** in 81% yield. For these reactions, the addition of (EtO)₃SiH was essential.



"Reaction conditions: 1 (0.20 mmol), $[Rh(cod)Cl]_2$ (1 mol %), dppe-F₂₀ (3 mol %), (EtO)₃SiH (15 mol %), toluene (0.2 mL), 145 °C, 5 h. Isolated yield. In parentheses are yields without (EtO)₃SiH. ^bPerformed for 20 h. 'Performed for 48 h.

Scheme 3. Rh-Catalyzed Dehydrogenative Cyclization of 3



To obtain further insight into the reaction mechanism, we carried out a kinetic isotope effect (KIE) experiment using **1a** and **1a**-*d* (Scheme 4) and found that the KIE $(k_{\rm H}/k_{\rm D})$ value was



1.13. This result suggests that cleavage of the C–H bond of thiophene would not be the rate-determining step of this reaction, which is different from the intramolecular direct silylation reported by Takai and Kuninobu.^{5d,8}

A plausible mechanism for dehydrogenative cyclization leading to the synthesis of 2 is illustrated in Figure 1. First, the Rh–Cl bond of the Rh catalyst would be converted to a Rh–H bond by the reaction with hydrosilanes.⁹ Next, (i) oxidative addition of 1 to the generated Rh^I–H species occurs to form Rh^{III} intermediate **A**. (ii) Reductive elimination of hydrogen would give intermediate **B**, and (iii) subsequent oxidative addition of the C–H bond of thiophene would form



Figure 1. A plausible mechanism for dehydrogenative cyclization leading to the synthesis of 2.

intermediate C.¹⁰ (iv) Finally, the subsequent reductive elimination of C forms a new Si–C bond to give the desired product 2 and regenerates active Rh^I–H species. The results of the KIE experiments suggest that step (iii), oxidative addition to generate intermediate C, is not the rate-determining step. We also carried out preliminary DFT calculations regarding the mechanism and found that reductive elimination to generate 2 (step (iv)) had the greatest activation energy among all of the steps (15.8 kcal/mol). This result suggests that step (iv) might be the rate-determining step.¹¹ This is consistent with the fact that electron-deficient ligands are effective in this reaction.¹²

This strategy could also be used for the construction of highly π -extended BST derivatives (Scheme 5). The dehydro-

Scheme 5. Synthesis of Highly π -Extended Ladder-Type BSTs 5 and 7



genative cyclization of precursors **4** and **6** proceeded smoothly to give the corresponding ladder-type BSTs **5** and 7 in the respective yields of 92% and 75%. Solutions of **5** and 7 in CH₂Cl₂ exhibited fluorescence. In particular, 7 exhibited strong fluorescence in both the liquid and solid states (solution: $\lambda_{em} =$ 429, 455 nm, $\Phi = 0.81$; solid: $\lambda_{em} = 502$ nm, $\Phi = 0.65$).¹³

In conclusion, we have developed a Rh/dppe- F_{20} -catalyzed dehydrogenative cyclization leading to BSTs. This catalytic system can be applied to cyclized precursors with a hydrosilyl group on a phenyl or thienyl group. The dehydrogenative cyclization of precursors bearing two hydrosilyl groups also proceeded under the reaction conditions, which demonstrated

that this reaction system could be useful for the construction of π -extended ladder-type BSTs. Further studies on the scope of this reaction system and the application of the obtained BSTs are in progress in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.7b00878.

Experimental details, photophysical and electrochemical properties of **5** and 7, spectral data for all new compounds, data of the KIE experiments, and theoretical calculations (PDF)

Crystallographic data of a precursor of 6 (CIF)

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Notes

The authors declare no competing financial interest.

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