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Facile synthetic procedure for and
electrochemical properties of
hexa(2-thienyl)benzenes directed toward
electroactive materials

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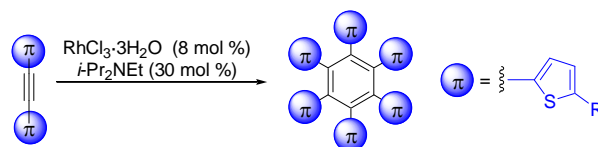
Graphical Abstract

Facile synthetic procedure for and electrochemical properties of hexa(2-thienyl)benzenes directed towards electroactive materials

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Facile synthetic procedure for and electrochemical properties of hexa(2-thienyl)benzenes directed towards electroactive materials

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Abstract— In the presence of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and *i*-Pr₂NEt, the cyclotrimerization of di(2-thienyl)acetylenes proceeded smoothly to afford hexa(2-thienyl)benzenes. CV analysis of the hexa(2-thienyl)benzenes showed that they may be useful as electroactive materials.

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Keywords: Rh/amine catalyst; Cyclotrimerization; Hexa(2-thienyl)benzene; Electroactive material.

Over the past decade, extended π -conjugated compounds¹ have been studied for use as materials in organic electroluminescent devices^{2,3} and energy storage devices.^{4,5} Recently, two-dimensional aromatic cores, such as starburst hexaarylbenzene derivatives, have been synthesized, and their electrochemical and photochemical properties have been intensively studied.⁶ However, there have been only a few reports on the construction of hexaheteroarylbenzenes, such as hexa(2-thienyl)benzene derivatives, because they are difficult to synthesize. One way to construct hexathienylbenzene derivatives is Stille-type coupling of hexabromobenzene and thienylstannane, wherein the reaction should use a large amount of toxic stannanes.⁷ Another way is transition metals-catalyzed cyclotrimerization of dithienylacetylenes.⁸ However, the trimerization of internal alkynes bearing heteroaryl groups is inhibited by the steric hindrance of products and the coordination of hetero-atoms to the central metal of the catalyst. For instance, Weber and co-workers reported that the reaction of di-2-thienylacetylene catalyzed by $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ gave a dimerized product, a benzothiophene derivative, as the major product (63%) and hexa(2-thienyl)benzene was obtained in only 5% yield.^{8a} One approach to solving this problem is to introduce large substituents at the 5-position of thiophene moieties. Müllen and co-workers reported that $\text{Co}_2(\text{CO})_8$ catalyzed the cyclization of di(5-*n*-C₁₂H₂₅-thiophen-2-yl)acetylene to give hexathienylbenzene derivatives in 61% yield.^{8b} To our knowledge, there are no other reports on the efficient construction of hexathienylbenzene derivatives, although

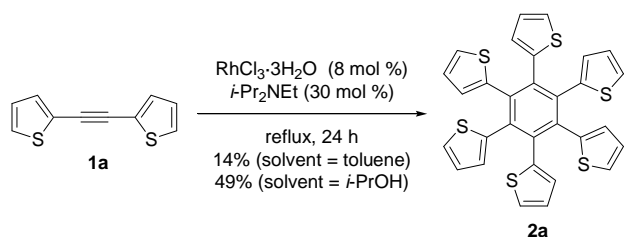
they should be novel, intriguing building blocks for not only electroactive materials but also photo-materials.

Recently, we found that the cyclotrimerization of internal alkynes proceeds efficiently in the presence of the RhCl_3/i -Pr₂NEt catalyst.⁹ These successful results prompted us to investigate the application of our methods to the synthesis of hexathienylbenzene derivatives. We report here the RhCl_3/i -Pr₂NEt-catalyzed cyclotrimerization of di(2-thienyl)acetylenes, and the electrochemical properties of the resulting starburst-type benzene derivatives.

First, we performed the trimerization of di(2-thienyl)acetylene **1a** (Scheme 1). In the presence of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (8 mol %) and *i*-Pr₂NEt (30 mol %), a solution of di(2-thienyl)acetylene (**1a**) in toluene was heated to reflux for 24 h to afford hexa(2-thienyl)benzene (**2a**)¹⁰ in 14% yield and 44% of **1a** was recovered. Although the dimerization did not take place, as we expected, the yield of **2a** was unsatisfactory. The low reactivity might be attributable to the coordination of a thienyl group to the Rh center. To suppress this coordination, we next used *i*-PrOH as a solvent, and the yield of **2a** increased to 49%.

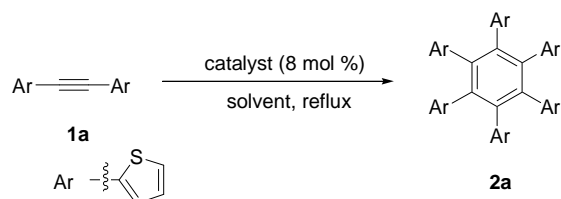
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Scheme 1. $\text{RhCl}_3/i\text{-Pr}_2\text{NEt}$ -catalyzed cyclotrimerization of **1a**.

To evaluate the catalytic activity of $\text{RhCl}_3/i\text{-Pr}_2\text{NEt}$, the cyclotrimerization of **1a** was carried out using several catalysts (Table 1). Notably, the reaction using $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ in *i*-PrOH showed higher reactivity than with other catalysts which are frequently used for the trimerization reaction of acetylene derivatives (entry 1). With toluene or 1,4-dioxane as a solvent, the yield of **2a** decreased (entries 2 and 3). When the reaction was carried out using $\text{RhCl}(\text{PPh}_3)_3$ (Wilkinson's catalyst) in *i*-PrOH or toluene, **2a** was obtained in respective yields of only 5% and 26% (entries 4 and 5). $[\text{Rh}(\text{cod})_2][\text{BF}_4]$ (cationic catalyst) was ineffective, and starting material **1a** was recovered (entries 6 and 7). When $\text{Co}_2(\text{CO})_8$ was used in *i*-PrOH, the corresponding product was not obtained at all (entry 8). With 1,4-dioxane as a solvent, the corresponding product was obtained in 37% yield (entry 9). It is likely that $\text{RhCl}_3/i\text{-Pr}_2\text{NEt}$ catalyst might be electron-rich due to the coordination of *i*-Pr₂NEt, and could promote the efficient formation of metallacycle intermediates.

Table 1

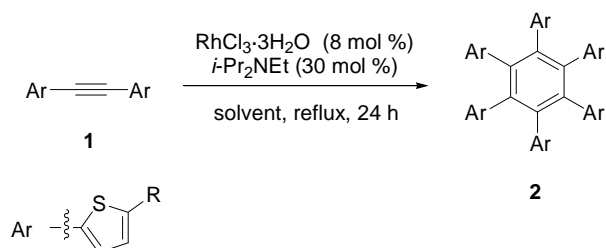
Cyclotrimerization of **1a** using several catalysts

Entry	Catalyst	Solvent	Time (h)	Yield (%) ^a	Recov. 1a (%) ^a
1	$\text{RhCl}_3\cdot 3\text{H}_2\text{O}/i\text{-Pr}_2\text{NEt}$	<i>i</i> -PrOH	24	49	49
2	$\text{RhCl}_3\cdot 3\text{H}_2\text{O}/i\text{-Pr}_2\text{NEt}$	Toluene	24	14	44
3	$\text{RhCl}_3\cdot 3\text{H}_2\text{O}/i\text{-Pr}_2\text{NEt}$	Dioxane	24	11	87
4	$\text{RhCl}(\text{PPh}_3)_3$	<i>i</i> -PrOH	24	5	73
5	$\text{RhCl}(\text{PPh}_3)_3$	Toluene	48	26	54
6	$[\text{Rh}(\text{cod})_2][\text{BF}_4]$	<i>i</i> -PrOH	24	-	68
7	$[\text{Rh}(\text{cod})_2][\text{BF}_4]$	Toluene	48	-	71
8	$\text{Co}_2(\text{CO})_8$	<i>i</i> -PrOH	24	-	-
9	$\text{Co}_2(\text{CO})_8$	Dioxane	24	37	-

^a Isolated yield.

In a similar manner, we performed the cyclotrimerization of di(2-thienyl)acetylenes bearing substituents on the 5-position of their thienyl groups (Table 2). In toluene and *i*-PrOH, the cyclotrimerization of alkyne **1b**, bearing a 5-methylthienyl group, gave the cycloadduct in respective yields of 63% and 50% (entries 1 and 2).¹¹ Notably, the reactivity of **1b** in toluene was similar to that in *i*-PrOH, which is different from that of **1a**, probably because the methyl group on α -position of thienyl group might reduce the coordination ability of the thienyl group. Indeed, in toluene, the cyclotrimerization of alkyne **1c**, bearing a 5-acetylthienyl group which also can coordinate to the Rh center, gave cycloadduct **2c**¹² in only 4% yield and **1c** was recovered in 20% yield (entry 3). With *i*-PrOH as a solvent, the yield of **2c** dramatically increased to 50% (entry 4). These results suggest that $\text{RhCl}_3/i\text{-Pr}_2\text{NEt}$ catalyst might be more active in toluene than *i*-PrOH, but *i*-PrOH would suppress the coordination of a thienyl group to the Rh center.

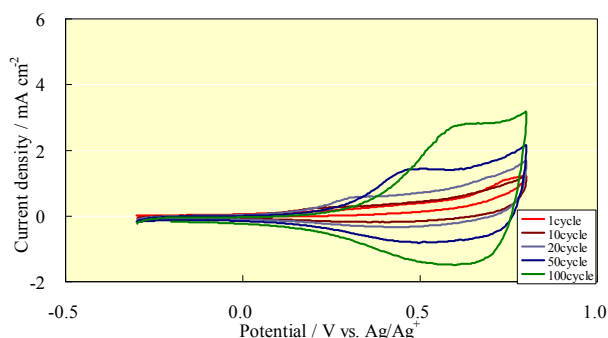
Table 2

RhCl₃/*i*-Pr₂NEt-catalyzed cyclotrimerization of **1**

Entry	1	R	Solvent	2	Yield (%) ^a	Recov. 1 (%) ^a
1	1b	Me	Toluene	2b	63	-
2	1b	Me	<i>i</i> -PrOH	2b	50	18
3	1c	Ac	Toluene	2c	4	20
4	1c	Ac	<i>i</i> -PrOH	2c	50	-

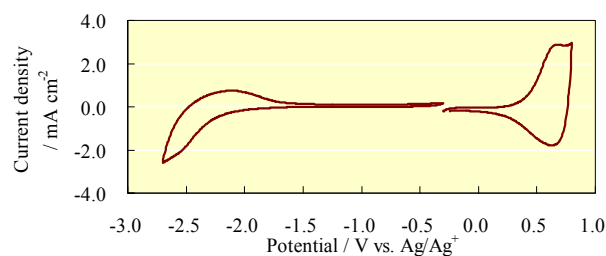
^a Isolated yield.

Next, we subjected **2a** to cyclic voltammetry (CV) measurements (Fig. 1). The growth of redox waves was observed in the potential range from 0.2 to 0.8 V during the sequential potential cycling ($\times 100$), which suggested the formation of an electroactive film on the surface of the working electrode. In fact, a film was observed on the surface of the electrode. This suggests that the extension of π -conjugation of **2a** might occur during the electrooxidation. Next, to investigate the main coupling position of a **2a**-based film, we measured the CV of **2b** bearing a methyl group at the 5-position of the thienyl groups. In CV, no significant increase in redox waves was observed, which suggests that electrooligomerization might occur at the 5-position of the thienyl groups. No film was observed on the working electrode during the electrooxidation of **2b**.

Fig. 1. Cyclic voltammograms of **2a** (10 mM) in TEABF₄/PC (1 M) solution. Scan rate: 100 mVs⁻¹.

The generated film was then subjected to CV analysis (Fig. 2). CV of the film showed two distinct redox responses: one in the potential range from 0.2 to 0.8 V (*p*-doping), and the other from -1.5 V to -2.8 V (*n*-doping), which are similar to those of frequently used polythiophene

derivatives reported by Ferraris.¹³ The maximum potential difference between redox waves of *n*- and *p*-doping were 3.5 V, which indicated a 3.5-eV band gap.

Fig. 2. CVs of **2a**-based film formed after CVs in Fig. 1. Electrolyte: **2a** (10 mM) in TEABF₄/PC (1 M) solution. Scan rate: 100 mVs⁻¹. Number of cycling: 5th cycle.

In summary, a simple method for constructing hexathienylbenzenes has been developed, and their fundamental electrochemical properties have been clarified. We found that hexa(2-thienyl)benzene (**2a**) generated films by sequential potential cycling (CV). Though the exact structure of the film has not been clear yet, it should be a novel type polymer or oligomer containing thiophene linked at 2 and 5 positions. In addition, these **2a**-based films may be a candidate for the electroactive materials in energy storage devices. Further studies on hexaheteroarylbenzenes are underway in our laboratory.

Acknowledgments

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11. Hexakis(5-methyl-2-thienyl)benzene (**2b**): Yellow solids; $R_f = 0.23$ (hexane/toluene 5:1); ¹H NMR (600 MHz, CDCl₃) δ 6.33 (s, 12H), 2.30 (s, 18H); ¹³C NMR (150 MHz, CDCl₃) δ 15.2, 123.9, 128.7, 137.0, 138.8, 140.2; IR (KBr) 3068, 2912, 2855, 2357, 1747, 1442, 1219, 800 cm⁻¹; Anal. Calcd for C₃₆H₃₀S₆: C, 66.01; H, 4.62. Found: C, 66.09; H, 4.53.
12. Hexakis(5-acetyl-2-thienyl)benzene (**2c**): Colorless solids; $R_f = 0.07$ (hexane/EtOAc 3:1); ¹H NMR (600 MHz, CDCl₃) δ 7.27 (d, $J = 3.6$ Hz, 6H), 6.67 (d, $J = 3.6$ Hz, 6H), 2.43 (s, 18H); ¹³C NMR (150 MHz, CDCl₃) δ 26.7, 130.9, 131.8, 136.5, 145.8, 146.7, 190.7; IR (KBr) 3080, 1658, 1471, 1381, 1274 cm⁻¹.
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Supplementary Material