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

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Abstract

In the presence of $RhCl_3 \cdot 3H_2O$ and i-Pr_2NEt, 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.

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

Over the past decade, extended π-conjugated compounds[1] have been studied for the 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 $RuH_2(CO)(PPh_3)_3$ 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 $Co_2(CO)_8$ catalyzed the cyclization of di(5-n-$C_{12}H_{25}$-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-Pr_2NEt 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-Pr_2NEt-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 $RhCl_3 \cdot 3H_2O$ (8 mol %) and i-Pr_2NEt (30 mol %), a solution of di(2-thienyl)acetylene (**1a**) in toluene was heated to reflux

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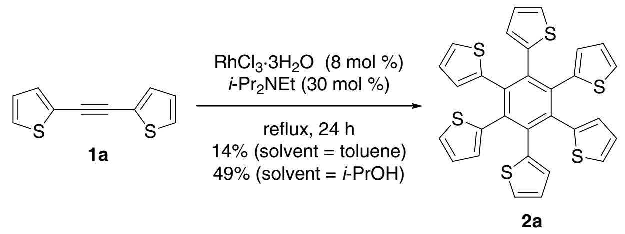
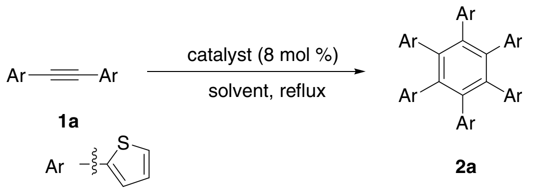


Scheme 1. $RhCl_3$/*i*-Pr_2NEt-catalyzed cyclotrimerization of **1a**.

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%.

To evaluate the catalytic activity of $RhCl_3$/*i*-Pr_2NEt, the cyclotrimerization of **1a** was carried out using several catalysts (Table 1). Notably, the reaction using $RhCl_3·3H_2O$ 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 $RhCl(PPh_3)_3$ (Wilkinson's catalyst) in *i*-PrOH or toluene, **2a** was obtained in respective yields of only 5% and 26% (entries 4 and 5). $[Rh(cod)_2][BF_4]$ (cationic catalyst) was ineffective, and starting material **1a** was recovered (entries 6 and 7). When $Co_2(CO)_8$ 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 $RhCl_3$/*i*-Pr_2NEt catalyst might be electron-rich due to the coordination of *i*-Pr_2NEt, and could promote the efficient formation of metallacycle intermediates.

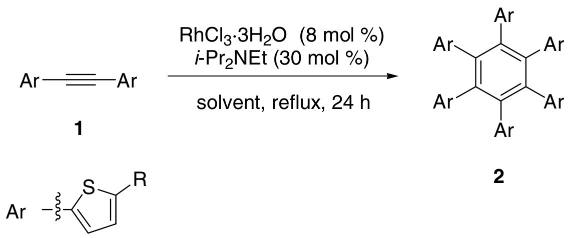
Table 1
Cyclotrimerization of **1a** using several catalysts



Entry	Catalyst	Solvent	Time (h)	Yield[a] (%)	Recov. **1a**[a] (%)
1	$RhCl_3·3H_2O$/*i*-Pr_2NEt	*i*-PrOH	24	49	49
2	$RhCl_3·3H_2O$/*i*-Pr_2NEt	Toluene	24	14	44
3	$RhCl_3·3H_2O$/*i*-Pr_2NEt	Dioxane	24	11	87
4	$RhCl(PPh_3)_3$	*i*-PrOH	24	5	73
5	$RhCl(PPh_3)_3$	Toluene	48	26	54
6	$[Rh(cod)_2][BF_4]$	*i*-PrOH	24	—	68
7	$[Rh(cod)_2][BF_4]$	Toluene	48	—	71
8	$Co_2(CO)_8$	*i*-PrOH	24	—	—
9	$Co_2(CO)_8$	Dioxane	24	37	—

[a] Isolated yield.

Table 2
$RhCl_3$/*i*-Pr_2NEt-catalyzed cyclotrimerization of **1**



Entry	1	R	Solvent	2	Yield[a] (%)	Recov. 1[a] (%)
1	**1b**	Me	Toluene	**2b**	63	—
2	**1b**	Me	*i*-PrOH	**2b**	50	18
3	**1c**	Ac	Toluene	**2c**	4	20
4	**1c**	Ac	*i*-PrOH	**2c**	50	—

[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 $RhCl_3$/*i*-Pr_2NEt 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.

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 (×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

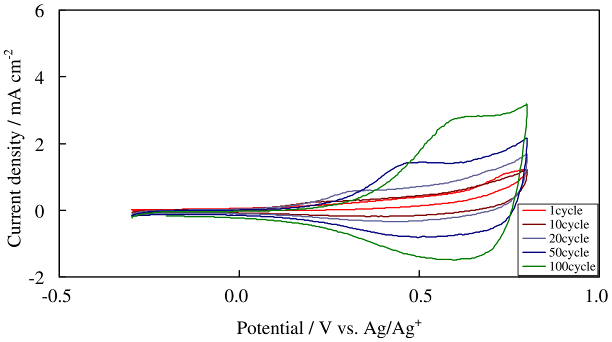


Fig. 1. Cyclic voltammograms of **2a** (10 mM) in $TEABF_4$/PC (1 M) solution. Scan rate: 100 mV s^{-1}.

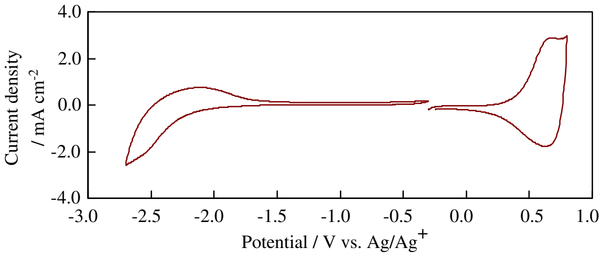


Fig. 2. CVs of **2a**-based film formed after CVs in Fig. 1. Electrolyte: **2a** (10 mM) in TEABF$_4$/PC (1 M) solution. Scan rate: 100 mV s^{-1}. Number of cycling: 5th cycle.

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**.

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 and co-workers.[13] The maximum potential difference between redox waves of n- and p-doping was 3.5 V, which indicated a 3.5 eV band gap.

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.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.069.

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10. *General procedure for Rh/amine-catalyzed cyclotrimerization of alkyne* **1**: To a solution of RhCl$_3$·3H$_2$O (11 mg, 0.04 mmol) in *i*-PrOH (3.0 mL) were added *i*-Pr$_2$NEt (26 μL, 0.15 mmol) and di(2-thienyl)acetylene **1a** (96 mg, 0.50 mmol). The mixture was stirred at reflux for 24 h. After being cooled to room temperature, the reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/toluene 5:1) to afford hexa(2-thienyl)benzene **2a** (47 mg, 49%) as yellow solids: $R_f = 0.27$ (hexane/toluene 5:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.59 (dd, $J = 3.6$, 1.2 Hz, 6H), 6.68 (dd, $J = 5.4$, 3.6 Hz, 6H), 7.08 (dd, $J = 5.4$, 1.2 Hz, 6H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 125.8, 126.2, 129.1, 137.0, 140.7; IR (KBr) 3068, 2923, 2360, 1647, 1381, 694 cm^{-1}; Anal. Calcd for C$_{30}$H$_{18}$S$_6$: C, 63.12; H, 3.18. Found: C, 63.08; H, 3.36.
11. *Hexakis(5-methyl-2-thienyl)benzene* (**2b**): Yellow solids; $R_f = 0.23$ (hexane/toluene 5:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.33 (s, 12H), 2.30 (s, 18H); ^{13}C NMR (150 MHz, CDCl$_3$) 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 C$_{36}$H$_{30}$S$_6$: 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), ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.27 (d, $J = 3.6$ Hz, 6H), 6.67 (d, $J = 3.6$ Hz, 6H), 2.43 (s, 18H); ^{13}C NMR (150 MHz, CDCl$_3$) 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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