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Notes

Reactions of Fused Polycyclic 1,2-Dithiins with Transition Metals: Synthesis of Heteroacenes via Desulfurization

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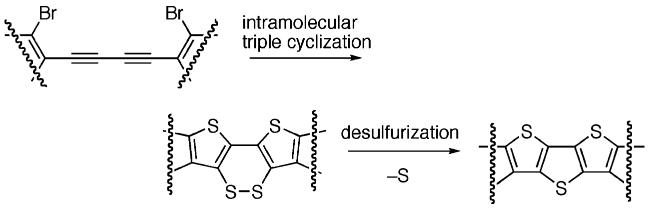
Summary: Bis(thieno[3,2-b]thiophene)-fused 1,2-dithiin reacts with a stoichiometric amount of Ni(cod)$_2$/2PPh$_3$ to produce a dimeric Ni(II) complex via the oxidative addition of the disulfide bond in the 1,2-dithiin skeleton to the Ni(0) center. An X-ray crystal structure analysis revealed that this complex has a dimeric structure in which one sulfur atom derived from the disulfide bond bridges two metal centers. The resultant Ni complex undergoes desulfurization at elevated temperature to produce a fully fused thiophene-based heteroacene.

Introduction

Linearly fused polyacenes, exemplified by pentacene, are attractive fundamental materials for electronic applications,[1] including organic thin film transistors.[2] Their rigid flat π-conjugated frameworks are a decisive advantage leading to unique properties, such as a high carrier mobility.[3] Considerable efforts have recently been devoted to explore new polyacene compounds.[4] In this context, thiophene-based heteroacenes are alternative promising candidates, since the heteroatom would affect not only the electronic structures but also the solid-state structures, thus making them more attractive. However, only a limited number of this class of molecules have been reported to date,[5−10] probably due to the lack of useful synthetic methodology. Under this circumstance, we recently developed a new synthetic route to the heteroacenes, as shown in Scheme 1.[11] The intramolecular triple cyclization of bis(*o*-haloaryl)-diacetylenes with sulfur produces the thiophene-fused 1,2-dithiins, which subsequently undergo desulfurization in the presence of copper to produce the target heteroacenes.[7] Whereas this route is facile and versatile, one drawback is that the fused 1,2-dithiin skeleton is rather robust and the desulfurization requires drastic conditions such as heating at 250−350 °C. This harsh condition sometimes causes a serious problem for the synthesis of substituted heteroacenes. Therefore, the exploration of a new desulfurization reaction that proceeds under milder conditions is our current objective. We now report a new desulfurization of the fused 1,2-dithiins promoted by transition metal complexes with phosphine ligands.[12]

Scheme 1



Results and Discussion

To study the reactivity of the fused 1,2-dithiins toward transition metal complexes, we employed bis(thieno[3,2-*b*]-thiophene)-fused 1,2-dithiin **1a** bearing *t*-BuMe$_2$Si groups on

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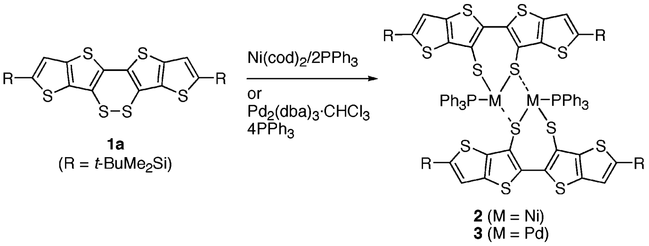
10.1021/om051000g CCC: $33.50

Scheme 2



1a (R = *t*-BuMe$_2$Si)

2 (M = Ni)
3 (M = Pd)

the terminal thiophene rings as the starting material. The reactions of **1a** with a stoichiometric amount of Ni(cod)$_2$/2PPh$_3$ or Pd$_2$(dba)$_3$·CHCl$_3$/4PPh$_3$ in toluene were first carried out at room temperature, as shown in Scheme 2. In each case, the oxidative addition of the disulfide bond to the metal center smoothly proceeded, as proven by the NMR spectra of the reaction mixture. While the resultant Ni(II) complex was decomposed during the column chromatography, the recrystallization from a dichloromethane/hexane mixed solvent produced pure complex **2** as dark orange crystals. In contrast, the analogous Pd(II) complex **3** was rather stable and could be isolated in 89% yield by preparative gel permeation chromatography. An X-ray structure analysis[13] revealed that both metal complexes **2** and **3** have dimeric structures similar to each other, in which one sulfur atom derived from the disulfide bond bridges two metal centers, resulting in formation of a four-membered cyclic structure. As an example, the ORTEP drawing of **2** is shown in Figure 1. In these structures, the bis(thieno[3,2-*b*]thiophene) π-conjugated frameworks have highly twisted structures, in which the dihedral angles between the thieno[3,2-*b*]thiophene mean planes are 45.3° for **2** and 59.4° for **3**. This difference is probably due to the different sizes of the central metals.

To realize the desulfurization from the oxidative addition products, we carried out the reactions of dithiin **1a** with transition metal complexes at higher temperature. Table 1 shows the results obtained under several conditions in which the reactions were conducted in one pot without isolation of the intermediate metal complexes. While the in-situ-produced Pd complex **3** in entry 1 remained unchanged even upon refluxing its toluene solution for 20 h, the reaction of **1a** with Ni(cod)$_2$/2PPh$_3$ under the same conditions successfully gave the desulfurized product **4a** in 60% yield (entry 2). Noteworthy is that Ph$_3$P═S was obtained as a byproduct in an amount (ca. 60%) comparable to that of **4a**, indicative of the important role of PPh$_3$ as a sulfur-trapping agent. Therefore, the effect of the amount of the phosphine was next studied (entries 3−6). While the reactions with 2 or 3 mol amounts of PPh$_3$ produced the heteroacene **4a** in yields comparable to each other, the use of an excess phosphine ligand (6 mol amounts) decreased the yield (entry 5). More importantly, the reaction without PPh$_3$ resulted in the formation of **4a** only in a trace amount (entry 6). This result demonstrated that the phosphine ligand is essential for promoting this reaction. In entries 7−10, several other phosphine ligands were also examined. As a trend, the use of a bulkier ligand, such as P(*o*-tolyl)$_3$ or PCy$_3$, tends to decrease the yield. In entry 11, a Ni(acac)$_2$/2DIBAH (diisobutylaluminum hydride) system, which generates a Ni(0) species in situ, was also employed as an alternative to Ni(cod)$_2$. Beneficially, this procedure worked well to give the product in a yield comparable to that in the case of Ni(cod)$_2$. Finally, the solvent effect was investigated in entries 12−14. The use of THF, 1,2-dichloroethane, or DMF, instead of toluene, resulted in the decreased yield of the heteroacene, indicating that the aromatic hydrocarbon solvent is a better choice for this reaction.

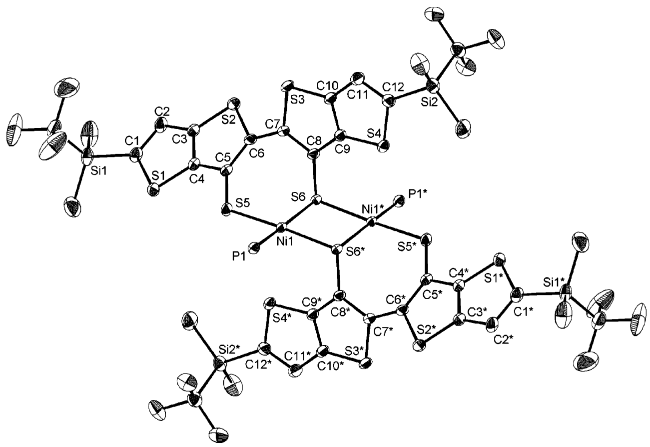
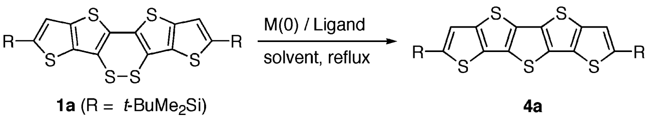


Figure 1. ORTEP drawing of Ni complex **2** (50% probability thermal ellipsoids). Phenyl groups of PPh$_3$ are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Ni1−S5, 2.1903(9); Ni1−S6, 2.2086(8); Ni1−P1, 2.2111(8); S5−C5, 1.752(3); C5−C6, 1.383(4); C6−C7, 1.438(4); C7−C8, 1.374(4); C8−S6, 1.770(3); S5−Ni1−S6, 96.07(3); S5−Ni1−P1, 90.53(3); Ni1−S5−C5, 117.20(9); S5−C5−C6, 131.0(2); C5−C6−C7, 129.3(2); C6−C7−C8, 128.5(2); C7−C8−S6, 120.0(2); Ni1−S6−C8, 95.91(9).

Table 1. Desulfurization of Fused 1,2-Dithiin 1a[a]



1a (R = *t*-BuMe$_2$Si)

4a

entry	metal	ligand	solvent	% yield
1	0.5Pd$_2$(dba)$_3$·CHCl$_3$	2PPh$_3$	toluene	<1
2	Ni(cod)$_2$	2PPh$_3$	toluene	60
3	Ni(cod)$_2$	1PPh$_3$	toluene	45
4	Ni(cod)$_2$	3PPh$_3$	toluene	53
5	Ni(cod)$_2$	6PPh$_3$	toluene	40
6	Ni(cod)$_2$	none	toluene	3
7	Ni(cod)$_2$	3P(*o*-tolyl)$_3$	toluene	23
8	Ni(cod)$_2$	3PCy$_3$	toluene	10
9	Ni(cod)$_2$	3PMePh$_2$	toluene	45
10	Ni(cod)$_2$	1.5dppf	toluene	38
11	Ni(acac)$_2$/2DIBAH	3PPh$_3$	toluene	52
12	Ni(acac)$_2$/2DIBAH	3PPh$_3$	THF	28
13	Ni(cod)$_2$	3PPh$_3$	1,2-dichloroethane	4
14	Ni(cod)$_2$	2PPh$_3$	DMF	41

[a] The reactions were conducted in a 0.09 mmol scale with a stoichiometric amount of the metal complex in 35 mM concentration. The reaction mixtures were stirred at room temperature for 1 h, then refluxed for 20 h.

On the basis of these results, we next applied this reaction to the synthesis of long alkyl group-bound heteroacene **4b**, as shown in Scheme 3. It is noted that the transformation from **1b** to **4b** under the conventional reaction conditions (Cu powder, neat, 320 °C) resulted only in the formation of a complex

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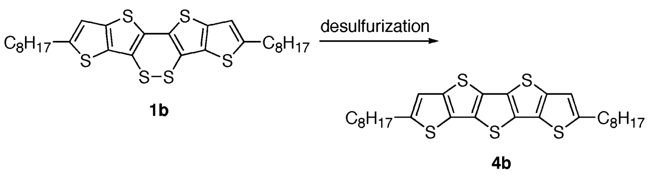
[13] Crystallographic data: **2**: C$_{43}$H$_{49}$Cl$_2$NiPS$_6$Si$_2$, fw = 974.94, crystal dimensions 0.25 × 0.15 × 0.05 mm^3, monoclinic, space group $P2_1/a$, a = 13.722(4) Å, b = 21.866(6) Å, c = 16.436(5) Å, β = 101.8198(15)°, V = 4827(2) Å^3, Z = 4, D_c = 1.342 g cm^{-3}, μ(Mo Kα) = 0.884 mm^{-1}, T = 173(2) K, F(000) = 2032, $2\theta_{max}$ = 55°; 38 184 reflections measured, of which 10 889 were unique. Final R_1 = 0.0535 with wR_2 = 0.1203 for 10 889 observed reflections with $I > 2\sigma(I)$; **3**·CH$_2$Cl$_2$·CH$_3$CN: C$_{45}$H$_{52}$Cl$_2$NPPdS$_6$Si$_2$, fw = 1063.69, crystal dimensions 0.20 × 0.10 × 0.02 mm^3, triclinic, space group $P\bar{1}$, a = 10.886(4) Å, b = 12.357(5) Å, c = 19.233(7) Å, α = 90.384(3)°, β = 96.225(5)°, γ = 106.675(7)°, V = 2461.7(16) Å^3, Z = 2, D_c = 1.435 g cm^{-3}, μ(Mo Kα) = 0.854 mm^{-1}, T = 173(2) K, F(000) = 1096, $2\theta_{max}$ = 50°; 15 468 reflections measured, of which 8292 were unique. Final R_1 = 0.0549 with wR_2 = 0.1498 for 8292 observed reflections with $I > 2\sigma(I)$.

Scheme 3



Cu, neat, 320 °C: complex mixture
Ni(cod)$_2$, 2PPh$_3$, toluene, 110 °C: **4b** 17% yield

mixture, probably due to undesirable reactions that occurred at the methylene moiety next to the thiophene rings under such harsh conditions. In contrast, the present homogeneous desulfurization using Ni(cod)$_2$/2PPh$_3$ in refluxing toluene produced **4b** in 17% yield. This result demonstrates the advantage of the present reaction over the conventional method, although it still needs improvement in terms of the efficiency. The product heteroacene **4b** is an attractive compound, which may be suitable for the formation of a self-assembled monolayer with a high carrier mobility. Further study of the solid-state properties of the heteroacene compounds is currently in progress in our laboratory.

Experimental Section

General Comments. ^{1}H and ^{13}C NMR spectra were measured with a JEOL AL-400 spectrometer or a JEOL GSX-270 spectrometer. Thin-layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using a Fuji Silysia silica gel PSQ60B (60 μm). Recycling preparative gel permeation chromatography was performed by a JAI LC918 with two polystyrene gel columns (JAIGEL 1H and 2H) using chloroform as an eluent. Bis(1,5-cyclooctadiene)nickel(0), Ni(cod)$_2$, was purchased from Strem Chemical Inc. and directly used as received. All the following reactions were carried out under an argon atmosphere.

1,4-Bis(3-bromo-5-*tert*-butyldimethylsilyl-2-thienyl)-1,3-butadiyne. To a solution of diisopropylamine (8.1 mL, 61.5 mmol) in THF (25 mL) was added a hexane solution of *n*-BuLi (1.60 M, 34.9 mL, 55.9 mmol) dropwise at −78 °C. After stirring for 15 min, the solution was allowed to warm to 0 °C over 20 min. The produced lithium diisopropylamide solution was then added to a solution of 1,4-bis(3-bromo-2-thienyl)-1,3-butadiyne (9.45 g, 25.4 mmol) and *tert*-butyldimethylsilyl chloride (8.42 g, 55.9 mmol) in THF (250 mL) at −78 °C. After stirring for 1 h, the mixture was gradually warmed to room temperature and stirred for 24 h. After quenching with 1 M NH$_4$Cl aqueous solution (75 mL), the mixture was extracted with ether. The organic layer was washed with water and brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to column chromatography on alumina (10/1 hexane/toluene, $R_f = 0.85$) to give 11.2 g (18.6 mmol) of the title compound in 73% yield as a yellow solid. Mp: 152−153 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.29 (s, 12H), 0.92 (s, 18H), 7.06 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ −5.31, 16.88, 26.14, 76.34, 82.12, 119.33, 124.22, 137.12, 143.61. MS (EI): *m/z* 598 [M$^+$]. HRMS (EI): 597.9842, calcd for $C_{24}H_{32}Br_2S_2Si_2$ 597.9851.

(3-Bromo-5-octyl-2-thienyl)trimethylsilylacetylene. To a solution of 3-bromo-5-octyl-2-iodothiophene (12.0 g, 29.9 mmol), PdCl$_2$(PPh$_3$)$_2$ (210 mg, 0.299 mmol), and CuI (113.9 mg, 0.598 mmol) in diisopropylamine (40 mL) was added a solution of trimethylsilylacetylene (3.53 g, 35.9 mmol) in diisopropylamine (20 mL) dropwise at room temperature. The mixture was stirred for 17 h at the same temperature. Insoluble salts were removed by filtration with Celite and washed with ether. The filtrate was concentrated under reduced pressure and subjected to silica gel column chromatography (hexane, $R_f = 0.39$) to give 9.15 g (24.6 mmol) of the title compound in 82% yield as a pale yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.25 (s, 9H), 0.88 (t, $J = 6.8$ Hz, 3H), 1.20−1.38 (m, 10H), 1.62 (tt, $J = 6.8$, 7.6 Hz, 2H), 2.72 (t, $J = 7.6$ Hz, 2H), 6.62 (s, 1H). ^{13}C NMR (68 MHz, CDCl$_3$): δ −0.019, 14.20, 22.73, 28.96, 29.24, 29.31, 30.30, 31.18, 31.89, 96.00, 102.25, 115.78, 117.83, 126.79, 147.58. MS (EI): *m/z* 370 [M$^+$]. HRMS (EI): 370.0791, calcd for $C_{17}H_{27}BrSSi$ 370.0786.

(3-Bromo-5-octyl-2-thienyl)acetylene. A mixture of (3-bromo-5-octyl-2-thienyl)trimethylsilylacetylene (7.10 g, 19.1 mmol) and potassium carbonate (264 mg, 1.91 mmol) in a 1/1 THF/methanol mixed solvent (24 mL) was stirred at room temperature for 1 h. After concentration under reduced pressure, a 1N HCl aqueous solution (3 mL) was added and the mixture was extracted with ether. The organic layer was washed with water and brine, dried over MgSO$_4$, filtered, and concentrated to give 5.35 g (17.9 mmol) of the title compound in 94% yield as a pale orange oil. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.20−1.38 (m, 10H), 1.63 (tt, $J = 6.8$, 7.6 Hz, 2H), 2.73 (t, $J = 7.6$ Hz, 2H, 7.6 Hz), 6.64 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.07, 22.61, 28.88, 29.12, 29.18, 30.17, 31.05, 31.77, 75.63, 84.23, 116.06, 116.67, 126.84, 148.20. MS (EI): *m/z* 298 [M$^+$]. HRMS (EI): 298.0403, calcd for $C_{17}H_{27}BrSSi$ 298.0391.

1,4-Bis(3-bromo-5-octyl-2-thienyl)-1,3-butadiyne. A mixture of (3-bromo-5-octyl-2-thienyl)acetylene (5.35 g, 17.9 mmol), CuI (170 mg, 0.894 mmol), and *N,N,N′,N′*-tetramethylethylenediamine (208 mg, 1.79 mmol) in acetone (58 mL) was stirred at room temperature for 3 h under oxygen. After concentration under reduced pressure, a 1 N HCl aqueous solution was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with a saturated Na$_2$S$_2$O$_3$ aqueous solution, water, and brine and dried over MgSO$_4$. After filtration, the filtrate was concentrated under reduced pressure and purified by silica gel column chromatography (hexane, $R_f = 0.39$) to give 4.69 g (7.86 mmol) of the title compound in 88% yield as a yellow solid. Mp: 35−36 °C. ^{1}H NMR (270 MHz, CDCl$_3$): δ 0.89 (t, $J = 6.2$ Hz, 6H), 1.20−1.43 (m, 20H), 1.65 (tt, $J = 6.2$, 7.6 Hz, 4H), 2.75 (t, $J = 7.6$ Hz, 4H,), 6.68 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.09, 22.63, 28.93, 29.14, 29.19, 30.43, 31.04, 31.79, 76.30, 80.72, 116.83, 118.02, 127.34, 149.98. MS (EI): *m/z* 594 [M$^+$]. HRMS (EI): 594.0632, calcd for $C_{28}H_{36}Br_2S_2$ 594.0625.

Synthesis of Fused 1,2-Dithiins. 2,7-Bis(*tert*-butyldimethylsilyl)bis(thieno[3,2-*b*]thieno)[3,2-*c*;2′,3′-*e*][1,2]dithiin (1a). To a solution of 1,4-bis(3-bromo-5-*tert*-butyldimethylsilyl-2-thienyl)-1,3-butadiyne (5.0 g, 8.32 mmol) in THF (83 mL) was added a pentane solution of *t*-BuLi (1.49 M, 22.3 mL, 33.3 mmol) dropwise at −78 °C. After stirring for 1 h, sulfur crystals (1.07 g, 33.3 mmol) were added at the same temperature. After stirring for 5 min, the mixture was gradually warmed to room temperature with stirring over 2 h. Potassium hexacyanoferrate(III) (11.0 g, 33.3 mmol) in 1 M NaOH aqueous solution (100 mL) was added, and the mixture was extracted with ether. The organic layer was washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The mixture was passed through a silica gel column with hexane as an eluent ($R_f = 0.49$) and was recrystallized from hexane to give 1.81 g (3.17 mmol) of **1a** in 38% yield as red crystals. Mp: 205−208 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.35 (s, 12H), 0.97 (s, 18H), 7.34 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ −5.04, 17.01, 26.32, 115.76, 126.66, 136.91, 138.28, 142.63, 143.44. MS (EI): *m/z* 568 [M$^+$], 536 [(M − S)$^+$]. Anal. Calcd for $C_{24}H_{32}S_6Si_2$: C, 50.65; H, 5.67. Found: C, 50.40; H, 5.60.

2,7-Dioctylbis(thieno[3,2-*b*]thieno)[3,2-*c*;2′,3′-*e*][1,2]dithiin (1b). This compound was synthesized in 35% yield as red crystals from 1,4-bis(3-bromo-5-octyl-2-thienyl)-1,3-butadiyne essentially in the same manner as described for **1a**: Mp: 134 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.89 (t, $J = 7.2$ Hz, 6H), 1.28−1.39 (m, 20H), 1.72 (tt, $J = 7.6$, 8.0 Hz, 4H), 2.89 (t, $J = 7.6$ Hz. 4H), 6.93 (s, 2H). ^{13}C NMR (68 MHz, CDCl$_3$): δ 14.21, 22.75, 29.09, 29.28, 29.39, 31.39, 31.59, 31.92, 115.56, 116.51, 134.51, 135.72, 136.38, 149.80. MS (EI): *m*/*z* 564 [M$^+$], 532 [(M − S)$^+$]. Anal. Calcd for $C_{28}H_{36}S_6$: C, 59.52; H, 6.42. Found: C, 59.59; H, 6.40.

Isolation of Nickel Complex 2. To a toluene solution (1.0 mL) of Ni(cod)$_2$ (26.6 mg, 0.097 mmol) and triphenylphosphine (50.7 mg, 0.193 mmol) was added compound **1a** (50 mg, 0.088 mmol) at room temperature. The mixture was stirred for 18 h at the same temperature. A 10 mL portion of acetonitrile was added to the mixture, and an insoluble material was collected by filtration to give 52.2 mg (0.046 mmol) of **2** in 67% yield. Further recrystallization using a slow diffusion technique with CH_2Cl_2 and hexane gave red single crystals suitable for X-ray analysis. Mp: 267−268 (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.30 (s, 3H), 0.33 (s, 3H), 0.57 (s, 3H), 0.62 (s, 3H), 0.96 (s, 9H), 1.22 (s, 9H), 7.05 (br, 6H), 7.23 (br, 4H), 7.43 (br, 1H), 7.61 (br, 6H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.56.

Isolation of Palladium Complex 3. This complex was also prepared essentially in the same manner as described for **2**, using **1a** (50 mg, 0.088 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (50 mg, 0.048 mmol), and triphenylphosphine (50.7 mg, 0.193 mmol). The obtained reaction mixture was passed through a silica gel column (1/1 CH_2Cl_2/EtOAc), followed by purification using gel permeation chromatography (chloroform as an eluent) to obtain 73 mg (0.078 mmol) of **3** in 89% yield as a brown solid. Further recrystallization using a slow diffusion technique with CH_2Cl_2 and acetonitrile gave single crystals suitable for X-ray structural analysis. Mp: 290 °C (dec). ^{1}H NMR (400 MHz, dichloroethane-*d*$_4$, 120 °C): δ 0.33 (s, 6H), 0.39 (s, 6H), 0.98 (s, 9H), 1.06 (s, 9H), 7.13 (br, 1H), 7.19 (m, 6H), 7.31 (m, 3H), 7.37 (s, 1H), 7.55 (m, 6H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.61.

General Procedure of Nickel-Promoted Desulfurization. 2,7-Bis(*tert*-butyldimethylsilyl)bis(thieno[3,2-*b*]thieno)[3,2-*b*;2′,3′-*d*]thiophene (4a). To a solution of Ni(cod)$_2$ (26.6 mg, 0.097 mmol) and triphenylphosphine (50.7 mg, 0.19 mmol) in toluene (1.0 mL) at room temperature was added a toluene solution of **1a** (50 mg, 0.088 mmol, 1.5 mL). The mixture was stirred at room temperature for 1 h and then stirred at 110 °C for 20 h. The insoluble solid was removed by filtration with Celite, and the filtrate was concentrated under reduced pressure. The mixture was passed through a silica gel column (1/1 dichloromethane/EtOAc) and further purified by recycling preparative gel permeation chromatography ($CHCl_3$ as an eluent) to give 28.3 mg (0.053 mmol) of **4a** in 60% yield as a white solid. Mp: 257−259 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.37 (s, 12H), 0.99 (s, 18H), 7.40 (s, 2H). ^{13}C NMR (68 MHz, $CDCl_3$): δ −4.84, 17.14, 26.45, 127.68, 130.95, 134.12, 136.79, 139.77, 142.08. MS (EI): *m*/*z* 536 [M$^+$]. Anal. Calced for $C_{24}H_{32}S_5Si_2$: C, 53.68; H, 6.01. Found: C, 53.55; H, 5.92.

2,7-Dioctylbis(thieno[3,2-*b*]thieno)[3,2-*b*;2′,3′-*d*]thiophene (4b). This compound was synthesized in 17% yield as a white solid from **1b** essentially in the same manner as described for **4a**. Mp: >300 °C. ^{1}H NMR (400 MHz, dichloroethane-*d*$_4$): δ 0.88 (t, *J* = 6.8 Hz, 6H), 1.27 (m, 20H), 1.73 (tt, *J* = 6.8, 7.6 Hz, 4H), 2.90 (t, *J* = 7.6 Hz, 4H), 7.02 (s, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 14.15, 22.60, 28.98, 29.10, 29.23, 31.09, 31,46, 31.75, 117.54, 129.46, 130.89, 131.97, 139.07, 147.61. MS (EI): *m*/*z* 532 [M$^+$]. HRMS (EI): 532.1401, calcd for $C_{28}H_{36}S_5$ 532.1421.

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Supporting Information Available: Crystallographic data for **2** and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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