10. The Diyne Reaction of 3,3′-Bis(phenylethynyl)-2,2′-bithiophene Derivatives *via* Rhodium Complexes: A Novel Approach to Condensed Benzo[2,1-*b*:3,4-*b*′]dithiophenes

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Dedicated to Prof. Dr. Dr. h.c. *Dieter Seebach*, Zürich, on the occasion of his 60th birthday on October 31, 1997 with best wishes

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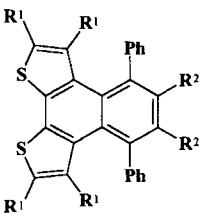
The syntheses of benzo-fused benzo[2,1-*b*:3,4-*b*′]dithiophenes **1** and benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes **2** are described. The treatment of easily available 3,3′-bis(phenylethynyl)-2,2′-bithiophene derivatives **5a** and **6** (*via* Pd^{II}-catalyzed alkynylation of the corresponding 3,3′-dibromo-2,2′-bithiophenes; see *Scheme 1*) with chlorotris-(triphenylphosphine)rhodium(I) yields the corresponding cyclic rhodium complexes **7** (*Scheme 2*) which smoothly react with acetylenes and sulfur to give **1** and **2** in good yields (*Schemes 3–5*).

Introduction. – The development of new strategies for the syntheses of polycondensed thiophenes has recently received much attention because of the unusual aromatic [1] and photophysical [2] properties displayed by these compounds as well as the potential for use of these derivatives as organic conductors and superconductors [3], electron acceptors [4] and donors [5], photosensitive receptors [6], and as materials for nonlinear optics [7].

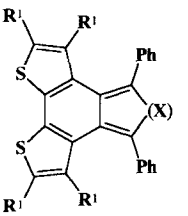
Heteroatoms incorporated into these arene systems serve to increase polarizability, enhance electron density, and promote intermolecular interaction. For this reason, the syntheses of chalcogene-rich arenes, like condensed bi- and trithiophenes, are interesting. As C-rich heterocycles, these arene derivatives should be interesting precursors for the synthesis of heteronuclear polycyclic aromatic hydrocarbons (PAHs).

Benzodithiophene and benzotrithiophene derivatives [1] are synthetically accessible by several routes: by oxidative coupling of *ortho*-dilithiated *cis*-dithienylethenes with copper(II) chloride [8], by photochemically induced cyclization of dithienylethenes [2] [9], by condensation of thiolactones under high pressure [10], and by aromatization of thiophene rings starting from benzo-fused dihydrothiophenes [11].

Prompted by the fundamental observation of *E. Müller* and coworkers [12], which showed the potential of the rhodium(I)-promoted diyne reaction for controlled synthesis of aromatic systems, we previously attempted to transfer this concept to the preparation of analogues of methano[10]annulene [13]. Based on the efficiency of these reactions, we decided to investigate the reactivity of alkynylated 2,2′-bithiophene derivatives as 1,6-diyne to demonstrate a novel, synthetically simple preparation of condensed benzo[2,1-*b*:3,4-*b*′]dithiophenes and benzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes of type **1** and **2**.



1



2

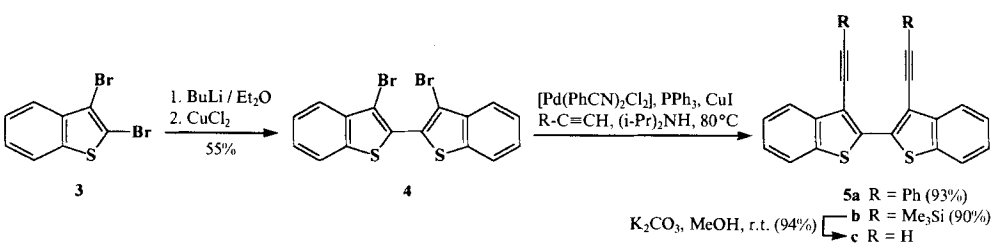
R^1 = H, benzo-fused

R^1 = H, Ph, Si Me_3, COOMe,

X = S, (O)

Results and Discussion. – Presently, the most efficient route to 3,3′-dialkynylated 2,2′-bithiophene derivatives involves the Pd^{II}-catalyzed alkynylation of 3,3′-dibromo-2,2′-bithiophenes according to the methodology of *Hagihara* [14] and *Whitesides* [15]. In a previous publication, we described the synthesis of 3,3′-bis(phenylethynyl)-2,2′-bithiophene **6** [16] using this method. Further investigations showed that this sequence is applicable to the preparation of the benzo-fused analogue 3,3′-bis(phenylethynyl)-2,2′-bi(benzo[*b*]thiophene) (**5a**) starting from the corresponding 3,3′-dibromo-2,2′-bi(benzo[*b*]thiophene) (**4**). Compound **4** was prepared by oxidative coupling of the easily available, regioselectively α-lithiated 3-bromo-benzo[*b*]thien-2-yllithium [17] with copper(II) chloride at −78° in 55% yield according to the strategy for the syntheses of bithiophenes and 3,3′-bi(benzo[*b*]thiophenes) reported by *Gronowitz* [18] and *Wynberg* [19]. By reaction of **4** with phenylacetylene or (trimethylsilyl)acetylene under *Whitesides*'s conditions which employ a catalyst system composed of bis(benzonitrile)dichloropalladium(II), copper(I) iodide, and triphenylphosphine in boiling diisopropylamine, the corresponding 3,3′-dialkynylated 2,2′-bi(benzo[*b*]thiophene) derivatives **5a, b** were obtained in excellent yields as shown in *Scheme 1*. The terminally unprotected 3,3′-diethynyl-2,2′-bi(benzo[*b*]thiophene) (**5c**) could easily be prepared by protodesilylation of the trimethylsilyl-protected derivative **5b** with aqueous K_2CO_3 solution in degassed MeOH at room temperature in very high yield (*Scheme 1*). Compound **5c** is, in contrast to the described benzo-unfused derivatives [16], stable to air.

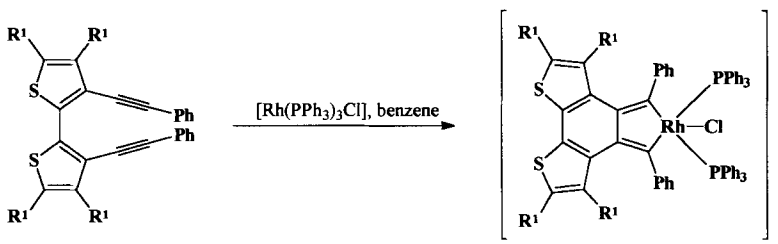
Scheme 1



3 4

As shown above, the easily accessible 3,3′-bis(phenylethynyl)-2,2′-bithiophene derivatives **5a** and **6** provided excellent 1,6-diyne synthones for the preparation of condensed benzo[2,1-*b*:3,4-*b*′]dithiophenes of structure **1** and **2**. Treatment of **6** and **5a** with chlorotris(triphenylphosphine)rhodium(I) in absolute benzene at 80° for *ca.* 4 h (TLC monitoring) gave the corresponding rhodium complexes **7a, b** as dark red (**7a**) or purple (**7b**) intermediates (*Scheme 2*).

Scheme 2



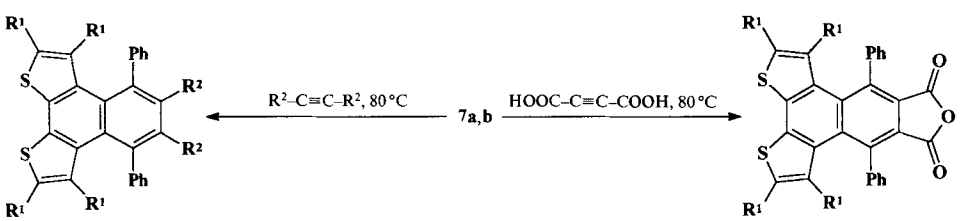
6 R^1 = H
5a R^1 = benzo-fused

7a R^1 = H
b R^1 = benzo-fused

Because of their low stability, the rhodium complexes **7** were not isolated but reacted directly. The displacement of the Rh-atom by an acetylene resulted in substituted naphtho[2,1-*b*:3,4-*b*′]dithiophene derivatives of structure **1** (*Scheme 3*). Using this methodology, the reaction of **7** with gaseous acetylene and dimethyl but-2-ynedioate gave the diphenyl-substituted naphtho[2,1-*b*:3,4-*b*′]dithiophenes **1a, b** and diphenyl-substituted dimethyl naphtho[2,1-*b*:3,4-*b*′]dithiophene-dicarboxylates **1e, f** after short reaction times in high yields. Due to the steric bulk of the Ph substituents, treatment of solutions of **7** with diphenylacetylene (tolane) required longer reaction times (*ca.* 4 h) and gave comparatively low yields of the tetraphenyl-substituted products **1c, d**.

Attempts to synthesize the corresponding dicarboxylic acids *via* Rh-displacement with but-2-ynedioic acid were not successful. Because of the heterogeneous character of the reaction mixtures, a large excess of but-2-ynedioic acid was used, surprisingly

Scheme 3



1a R^1 = H, R^2 = H (87%)
b R^1 = benzo-fused, R^2 = H (85%)
c R^1 = H, R^2 = Ph (56%)
d R^1 = benzo-fused, R^2 = Ph (62%)
e R^1 = H, R^2 = COOMe (81%)
f R^1 = benzo-fused, R^2 = COOMe (75%)

1g R^1 = H (36%)
h R^1 = benzo-fused (53%)

the naphtho[2,1-*b*:3,4-*b'*]dithiophene-dicarboxylic acid anhydrides **1g,h** were obtained (*Scheme 3*). This phenomenon, never reported in the case of diyne reactions, can be explained by the characteristic tendency of aromatic *ortho*-dicarboxylic acids to eliminate H_2O at higher temperature. It cannot be excluded, however, that the dehydration was caused by the presence of the rhodium complex. The NMR spectroscopic characterization of **1h** was not possible, due to its insolubility in common organic solvents.

In the synthesis of the bis(trimethylsilyl)-diphenyl-naphtho[2,1-*b*:3,4-*b'*]dithiophene derivatives **1k,l** under the same reaction conditions as described above, two main products were isolated, inspite of the use of a large excess (15 equiv.) of bis(trimethylsilyl)acetylene (*Scheme 4*). In addition to the major desired products **1k,l**, the monosubstituted trimethylsilyl derivatives **1i,j** were obtained in a ratio of *ca.* 9:1 (determined by ^{1}H-NMR (integration of Me_3Si signals)). The product ratios, not exactly reproducible, are dependent on the reaction conditions such as temperature, reaction time, and most importantly, on the concentration of the acetylene component. Thus, treatment of **7a,b** with 5 equiv. of bis(trimethylsilyl)acetylene furnished the products **1i/1h** and **1j/1l**, respectively, as *ca.* 1:1 mixtures (*Table*). Because of the similarities of the products, their separation by column chromatography was very difficult. Repeated recrystallization of the crude mixtures succeeded only in the case of the isolation of the bis(trimethylsilyl)-substituted derivatives **1k,l**. To obtain the pure mono(trimethylsilylated) derivatives **1i,j** for characterization, they were synthesized by the described method using (trimethylsilyl)acetylene. The formation of compounds **1i,j** can be explained by the *Lewis* acid catalyzed protodesilylation [20] of the bis(trimethylsilyl)-substituted derivatives **1k,l** with the intermediate rhodium species; but this explanation is not conclusive.

Scheme 4

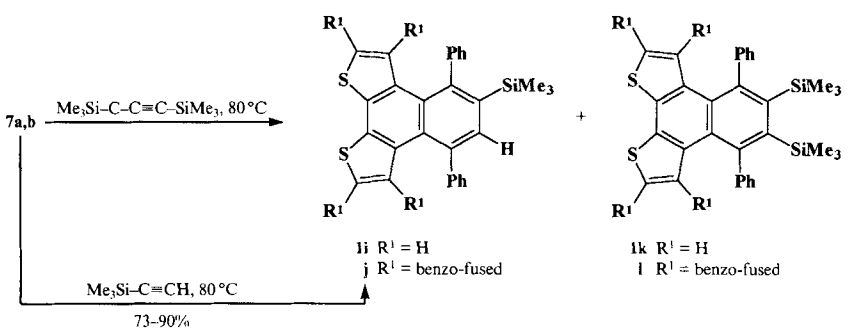


Table. *Diyne Reaction of* **6** *and* **5a**

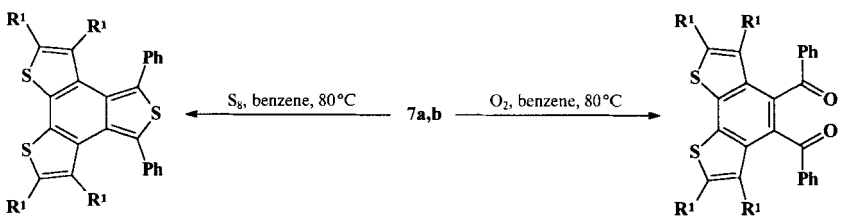
	$Me_3Si–C≡C–SiMe_3$ (equiv.)	Temp.	Product ratio [%][a]			
			1i	**1k**	**1j**	**1l**
6 (R^1 = H)	5	reflux	60	40		
6 (R^1 = H)	15	reflux	15	85		
5a (R^1 = benzo-fused)	5	reflux			50	50
5a (R^1 = benzo-fused)	15	reflux			10	90

[a]) Ratio was determined by ^{1}H-NMR.

In contrast to the other compounds **1** described here, NMR-spectroscopic characterization of the diphenyl-bis(trimethylsilyl)-dibenzonaphthodithiophene **11** showed that free rotation of the Ph groups is prevented by the bulky trimethylsilyl substituents and the annelated benzene rings. Thus, distinct resonance signals appeared for each C-atom of the Ph groups in the ^{13}C-NMR-spectra.

An alternative preparation of heteroaromatic compounds has also been reported by *E. Müller* and coworkers [12] in their investigations of the diyne reaction with chalcogenes. According to this method, the benzo[2,1-*b*:3,4-*b'*:5,6-*c''*]trithiophene derivatives **2a, b** were prepared by treatment of the corresponding rhodium complexes **7a, b** in benzene with sulfur in moderate yields (*Scheme 5*). The introduction of an O-atom to create the corresponding furane derivatives cannot be accomplished using this route. However, this reaction gave the dibenzoyl-substituted benzo[2,1-*b*:3,4-*b'*]dithiophenes **2c, d** as oxidative ring opening products. This finding can be related to already published observations in the syntheses of other furane-fused arenes [12] [21]. Reactions with the higher chalcogenes selenium and tellurium were not performed.

Scheme 5



2a R^1 = H (78%)
b R^1 = benzo-fused (89%)

2c R^1 = H (48%)
d R^1 = benzo-fused (60%)

In conclusion, we have shown that the easily obtained 3,3'-bis(phenylethynyl)-2,2'-bithiophenes **5a** and **6** are excellent precursors for the syntheses of benzo-fused di- and trithiophene derivatives **1** and **2** using the diyne reaction. The generality of this method was demonstrated by the ability to introduce variable substituents R^1, R^2 and to create novel heteroarenes. Unfortunately, attempts to apply this route to 3,3'-bis[(trimethylsilyl)ethynyl]-2,2'-bithiophenes such as, *e.g.*, **5b** failed.

We thank *BASF AG*, *Bayer AG*, and *Hoechst AG*, the *Fonds der Chemischen Industrie*, as well as the *Deutsche Forschungsgemeinschaft* for support of this work. Thanks go to *Hewlett-Packard* for providing UV/VIS spectrometers. We would also like to thank Ms. *U. Hertle* and Dr. *W. Kramer* for NMR spectra and Mr. *H. Rudy* and Mr. *P. Weyrich* for elemental analyses and mass spectra. Dr. *R. Faust* is warmly thanked for many helpful discussions and Ms. *A. Bryant-Friedrich*, M. Sc., for help with the manuscript.

Experimental Part

General. All reactions were carried out under Ar in flame-dried glassware. $(i\text{-Pr})_2NH$ was freshly distilled from KOH, and Et_2O and benzene were distilled from sodium-benzophenone before use. Column chromatography (CC): silica gel (60–200 mesh) from *ICN-Biomedicals*. M.p.: *Reichert* melting-point microscope; uncorrected. UV/VIS Spectra: *Hewlett-Packard-HP-8453-UV/VIS-ChemStation* and *Hewlett-Packard-HP-8452A* diode array

spectrophotometer; CH_2Cl_2 solns.; λ in nm (lg ε). IR Spectra: *Perkin-Elmer-PE-1600-FT-IR* spectrophotometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR Spectra: *Bruker-WM-250* spectrometer (at 250.13 MHz), *Bruker-AM-360* spectrometer (at 360.12 MHz) and *Varian-XL-300* spectrometer (at 299.95 MHz); δ in ppm rel. to Me_4Si, J in Hz. ^{13}C-NMR Spectra: at 62.89, 90.56, and 75.43 MHz on the same spectrometers; the degree of substitution was determined by J-modulated spin-echo experiments. MS: *Varian-MAT-311-A* mass spectrometer at 70 eV; m/z (rel. %). Elemental analyses. *Foss-Heraeus Vario EL*; all compounds gave satisfactory analyses (C,H,S ± 0.3%).

*3,3′-Dibromo-2,2′-bi(benzo[*b*]thiophene)* (**4**). Anh. $CuCl_2$ (4 g, 0.03 mol) was added to a soln. of 3-bromobenzo[*b*]thien-2-yllithium in 200 ml of abs. Et_2O at −78° (3-bromobenzo[*b*]thien-2-yllithium was prepared by treating 5.84 g (0.02 mol) of 2,3-dibromobenzo[*b*]thiophene **3** with 8.4 ml (0.021 mol) of 2.5M BuLi in hexane at −78° for 20 min and then at −20° for 1 h). After stirring at −78° for 2 h, the mixture was allowed to warm to r.t. overnight and then treated with 5N HCl at 0°. The Et_2O phase was diluted with $CHCl_3$, extracted with 5N HCl to remove residual $CuCl_2$, washed with H_2O, dried ($MgSO_4$), and evaporated. Recrystallization from benzene or petroleum ether (100–140) gave pure **4** (2.31 g, 54.5%). Colorless needles. M.p. 178°. IR (KBr): 3056*w*, 1466*w*, 1445*w*, 1401*w*, 1321*w*, 1293*m*, 1245*m*, 1166*w*, 1153*w*, 1138*w*, 1014*w*, 946*w*, 932*w*, 841*w*, 813*m*, 747*s*, 719*s*, 698*s*, 580*w*, 542*w*, 421*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.92–7.87 (*m*, 2 H); 7.85–7.80 (*m*, 2 H); 7.53–7.41 (*m*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 138.89, 137.85, 129.15, 126.11, 125.23, 123.81, 122.04, 110.66. EI-MS: 424 (80, M^+), 264 (100, $[M-2\,Br]^+$), 219 (35, $[M-2\,Br-CHS]^+$), 212 (10, $[M/2]^+$), 132 (30, $[C_6H_4{-}C_2S]^+$). HR-MS: 423.8412 ($C_{16}H_8S_2{}^{79}Br^{81}Br^+$; calc. 423.8414).

*3,3′-Dialkynylated 2,2′-Bi(benzo[*b*]thiophene) Derivatives* **5**: *General Procedure.* To the clear soln. of **4** (0.5 mmol, 212 mg) in 80 ml of freshly distilled $(i\text{-}Pr)_2NH$ were added 0.2 mmol (78 mg) of bis(benzonitrile)dichloropalladium(II), 0.4 mmol (106 mg) of PPh_3 and 0.2 mmol (38 mg) of CuI. The soln. was degassed by passing a rapid stream of Ar through it. An excess of the corresponding acetylene (2 mmol of phenylacetylene or (trimethylsilyl)acetylene) was then added at r.t. After stirring for 30 min, the soln. was heated at 70° for 4 h. During this time, the soln. rapidly turned bright yellow, then yellow brown, and finally dark brown, with the formation of a precipitate. The mixture was allowed to cool to r.t. and then filtered.

*3,3′-Bis(phenylethynyl)-2,2′-bi(benzo[*b*]thiophene)* (**5a**). CC (petroleum ether (40–60)/$CHCl_3$ 5:1) of the yellow brown precipitate and recrystallization from toluene gave pure **5a** (216 mg, 92.7%). Yellow needles. M.p. 235–236° (dec.). UV/VIS (CH_2Cl_2): 236 (4.69), 279 (4.56), 339 (sh, 4.17), 353 (4.27), 401 (4.44), 421 (sh, 4.33). IR (KBr): 3056*w*, 2200*w*, 1595*w*, 1496*w*, 1457*w*, 1441*w*, 1420*w*, 1350*w*, 1322*w*, 1256*w*, 1015*w*, 877*w*, 854*w*, 753*s*, 729*s*, 690*s*, 624*w*, 592*w*, 545*m*, 522*m*, 429*m*. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$ 1:1): 8.04–8.00 (*m*, 2 H); 7.83–7.79 (*m*, 2 H); 7.72–7.67 (*m*, 4 H); 7.49–7.39 (*m*, 10 H). ^{13}C-NMR (75 MHz, $CDCl_3/CS_2$ 1:1): 139.24, 138.37, 138.14, 131.32, 128.43, 128.27, 125.81, 124.83, 123.23, 123.14, 121.71, 116.40, 99.43, 84.45. EI-MS: 466 (100, M^+), 388 (20, $[M-C_6H_6]^+$), 233 (10, $[M/2]^+$). HR-MS: 466.0849 ($C_{32}H_{18}S_2^+$; calc. 466.00850).

*3,3′-Bis[(trimethylsilyl)ethynyl]-2,2′-bi(benzo[*b*]thiophene)* (**5b**). CC (petroleum ether (40–60)/$CHCl_3$ 5:1) of the filtrate and recrystallization from MeCN or EtOH gave pure **5b** (205 mg, 89.5%). Yellow crystals. M.p. 179–180°. UV/VIS (CH_2Cl_2): 236 (4.71), 250 (sh, 4.53), 269 (sh, 4.12), 333 (sh, 4.27), 346 (4.37), 360 (4.43), 382 (4.53), 405 (4.47). IR (KBr): 3067*w*, 2956*w*, 2900*w*, 2136*w*, 1467*w*, 1458*w*, 1335*m*, 1320*w*, 1251*s*, 1159*m*, 1097*s*, 1051*m*, 1014*w*, 879*s*, 843*s*, 760*s*, 733*s*, 656*m*, 588*m*, 438*m*. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$ 1:1): 7.96–7.90 (*m*, 2 H); 7.81–7.76 (*m*, 2 H); 7.48–7.36 (*m*, 4 H); 0.38 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3/CS_2$ 1:1): 139.29, 139.24, 137.96, 125.76, 124.76, 123.20, 121.53, 116.39, 105.88, 99.01, −0.28. EI-MS: 458 (70, M^+), 443 (10, $[M-Me]^+$), 428 (5, $[M-2\,Me]^+$), 385 (15, $[M^+-Me_3Si]^+$), 370 (10, $[M-Me-Me_3SiC{\equiv}C]^+$), 355 (25, $[M-2\,Me-Me_3SiC{\equiv}C]^+$), 73 (100, Me_3Si^+). HR-MS: 458.1017 ($C_{26}H_{26}S_2Si_2^+$; calc. 458.1015).

*3,3′-Diethynyl-2,2′-bi(benzo[*b*]thiophene)* (**5c**). To a suspension of 92 mg (0.2 mmol) of **5b** in deoxygenated MeOH (50 ml) was added at r.t. sat. aq. K_2CO_3 soln. (0.5 ml). The mixture was stirred for 4 h (→soln.). The soln. was diluted with CH_2Cl_2, washed several times with H_2O, dried ($MgSO_4$), and evaporated. Pure **5c** (59 mg, 93.9%) was obtained by recrystallization from MeOH. Light yellow needles. M.p. 125–126° (dec.). UV/VIS (CH_2Cl_2): 233 (4.65), 261 (sh, 4.00), 351 (4.32), 371 (4.37), 392 (4.23). IR (KBr): 3301*s*, 3055*w*, 2089*w*, 1468*w*, 1457*m*, 1412*m*, 1322*w*, 1249*w*, 1162*w*, 1012*w*, 856*w*, 763*s*, 757*s*, 725*s*, 638*s*, 629*s*, 599*s*, 591*s*, 429*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98–7.94 (*m*, 2 H); 7.81–7.78 (*m*, 2 H); 7.47–7.39 (*m*, 4 H); 3.74 (*s*, 2 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 139.90, 139.33, 138.39, 126.13, 125.20, 123.45, 121.91, 115.99, 86.98, 77.97. EI-MS: 314 (100, M^+), 269 (10, $[M-CHS]^+$), 157 (10, $[M/2]^+$). HR-MS: 314.0223 ($C_{20}H_{10}S_2^+$; calc. 314.0224).

*Chloro[3,3′-bis(phenylethynyl)-2,2′-bithiophene- or -2,2′-bi(benzo[*b*]thiophene)]bis(triphenylphosphine)-rhodium(I) Complexes* **7a, b**: *General Procedure.* To a soln. of 0.2 mmol of 3,3′-bis(phenylethynyl)-2,2′-bithiophene derivative (73 mg of **6** or 93 mg of **5a**) in 80 ml of deoxygenated benzene was added chlorotris(triphenylphosphine)rhodium(I) (0.2 mmol, 186 mg). The clear soln. was heated at 80° for *ca.* 4 h (TLC monitoring). During this time, the soln. rapidly turned dark red (**7a**) or purple (**7b**). The soln. of **7a** or **7b**, was used for further reactions. The pure complexes were not isolated.

*Diphenylnaphtho[2,1-*b*:3,4-*b*′]dithiophenes* **1**: *General Procedure.* To a freshly prepared soln. of complex **7a, b** was added an excess of the corresponding acetylene in one portion at 80°. After stirring for *ca.* 4 h at 80°, the soln. turned brown (TLC monitoring). The soln. was allowed to cool to r.t. and evaporated. The residue was chromatographed (silica gel).

*4,7-Diphenylnaphtho[2,1-*b*:3,4-*b*′]dithiophene* (**1a**). Through a soln. of **7a** was passed a slow stream of dry acetylene for 1 h (TLC monitoring). CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from EtOH gave pure **1a** (68 mg, 86.7%). Colorless needles. M.p. 202–203°. UV/VIS (CH_2Cl_2): 254 (sh, 4.49), 268 (4.58), 280 (4.57), 326 (4.16), 336 (4.12). IR (KBr): 3096*w*, 3061*w*, 3023*w*, 1490*w*, 1441*w*, 1300*m*, 1182*w*, 1071*w*, 1021*m*, 947*w*, 914*w*, 879*w*, 833*m*, 809*w*, 778*w*, 758*m*, 734*w*, 723*m*, 701*s*, 690*w*, 671*s*, 624*w*, 605*w*, 556*w*, 531*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.65–7.43 (*m*, 12 H); 7.03 (*d*, ^3J = 5.6, 2 H); 6.51 (*d*, ^3J = 5.6, 2 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 144.19, 139.15, 134.02, 133.35, 129.40, 128.55, 127.55, 127.48, 127.25, 121.18. EI-MS: 392 (100, M^+). HR-MS: 392.0693 ($C_{26}H_{16}S_2^+$; calc. 392.0693).

*5,8-Diphenylnaphtho[2,1-*b*:3,4-*b*′]bis[1]benzothiophene* (**1b**). Through a soln. of **7b** was passed a slow stream of dry acetylene (TLC monitoring). CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from toluene gave pure **1b** (84 mg, 85.4%). Light yellow crystals. M.p. 342–343°. UV/VIS (CH_2Cl_2): 248 (sh, 4.63), 260 (4.66), 292 (4.52), 314 (4.47), 326 (4.49), 376 (4.36), 390 (sh, 4.30). IR (KBr): 3054*w*, 3022*w*, 3021*w*, 1597*w*, 1491*m*, 1442*m*, 1232*m*, 1022*w*, 1008*m*, 917*m*, 831*m*, 803*m*, 766*s*, 757*s*, 734*m*, 726*s*, 703*s*, 662*m*, 592*m*, 557*m*, 499*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.83 (*s*, 2 H); 7.53–7.48 (*m*, 4 H); 7.48–7.43 (*m*, 2 H); 7.29–7.15 (*m*, 10 H); 6.93–6.86 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 143.56, 138.34, 137.54, 136.39, 133.87, 130.08, 129.28, 128.81, 128.42, 128.00, 127.20, 127.01, 124.69, 123.29, 122.18. EI-MS: 492 (100, M^+), 415 (10, $[M - C_6H_6]^+$), 246 (5, $[M/2]^+$). HR-MS: 492.1008 ($C_{34}H_{20}S_2^+$; calc. 2492.1006).

*4,5,6,7-Tetraphenylnaphtho[2,1-*b*:3,4-*b*′]dithiophene* (**1c**). Treatment of **7a** with 1 mmol (178 mg) of diphenylacetylene, CC (petroleum ether (40–60)/$CHCl_3$ 5:1), and recrystallization from benzene gave pure **1c** (61 mg, 56.1%). Colorless crystals. M.p. 318–320° (dec.). UV/VIS (CH_2Cl_2): 248 (sh, 4.50), 274 (sh, 4.72), 284 (4.80), 314 (sh, 4.05), 328 (4.14), 340 (sh, 4.08). IR (KBr): 3134*w*, 3096*w*, 3055*w*, 3022*w*, 1599*w*, 1495*m*, 1441*m*, 1296*m*, 1105*w*, 1070*w*, 1025*m*, 848*w*, 758*s*, 733*m*, 698*s*, 643*m*, 561*m*. ^{1}H-NMR (300 MHz, C_6D_6): 7.21–7.13 (*m*, 6 H); 7.06–6.94 (*m*, 8 H); 6.85–6.78 (*m*, 4 H); 6.73–6.67 (*m*, 2 H); 6.55 (*d*, ^3J = 5.6, 2 H); 6.39 (*d*, ^3J = 5.6, 2 H). ^{13}C-NMR (75 MHz, C_6D_6); 143.34, 141.26, 139.85, 138.42, 135.31, 134.61, 131.87, 131.78, 128.50, 128.32, 128.15, 127.06, 126.99, 125.70, 121.49. EI-MS: 544 (100, M^+), 467 (10, $[M - C_6H_5]^+$), 390 (10, $[M - 2\ C_6H_5]^+$), 77 (20, $C_6H_5^+$). HR-MS: 544.1318 ($C_{38}H_{24}S_2^+$; calc. 544.1319).

*5,6,7,8-Tetraphenylnaphtho[2,1-*b*:3,4-*b*′]bis[1]benzothiophene* (**1d**). Treatment of **7b** with 1 mmol (178 mg) of diphenylacetylene, CC (petroleum ether (40–60)/$CHCl_3$ 5:1), and recrystallization from toluene gave pure **1d** (80 mg, 62.1%). Light yellow crystals. M.p. 342–344°. UV/VIS (CH_2Cl_2): 247 (sh, 4.50), 255 (4.51), 301 (4.50), 314 (4.46), 330 (4.47), 355 (3.87), 367 (sh, 4.08), 376 (4.16), 387 (sh, 4.11). IR (KBr): 3078*w*, 3054*m*, 3021*w*, 1599*w*, 1491*w*, 1442*m*, 1074*w*, 1026*m*, 1015*m*, 810*m*, 754*s*, 729*s*, 699*s*, 683*m*, 668*m*, 561*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.75 (*d*, ^3J = 8.3, 2 H); 7.70 (*d*, ^3J = 8.3, 2 H); 7.17–7.11 (*m*, 2 H); 7.07–6.93 (*m*, 12 H); 6.90–6.81 (*m*, 8 H); 6.80–6.74 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.38, 140.44, 138.03, 137.99, 136.33, 135.34, 133.78, 133.32, 131.80, 130.35, 129.80. 126.96, 126.85, 126.19, 125.58, 125.32, 124.63, 123.03, 122.02. EI-MS: 644 (100, M^+), 566 (5, $[M - C_6H_6]^+$), 488 (5, $[M - 2\ C_6H_6]^+$), 322 (5, $[M/2]^+$). HR-MS: 644.1635 ($C_{46}H_{28}S_2^+$; calc. 644.1632).

*Dimethyl 4,7-Diphenylnaphtho[2,1-*b*:3,4-*b*′]dithiophene-5,6-dicarboxylate* (**1e**). Treatment of **7a** with 1 mmol (142 mg) of dimethyl but-2-ynedioate, CC ($CHCl_3$), and recrystallization from MeCN gave pure **1e** (82 mg, 80.7%). Colorless needles. M.p. 284–285°. UV/VIS (CH_2Cl_2): 254 (sh, 4.48), 272 (sh, 4.68), 268 (4.75), 332 (4.08). IR (KBr): 3102*w*, 3057*w*, 3027*w*, 2970*w*, 2947*w*, 1735*s*, 1436*m*, 1372*m*, 1318*w*, 1301*w*, 1224*s*, 1192*w*, 1171*m*, 1114*w*, 1104*w*, 1077*w*, 1024*m*, 982*w*, 924*w*, 864*w*, 833*w*, 760*m*, 739*w*, 727*m*, 696*m*, 659*w*, 630*w*, 578*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.52–7.49 (*m*, 6 H); 7.43–7.39 (*m*, 4 H); 7.01 (*d*, ^3J = 5.6, 2 H); 6.19 (*d*, ^3J = 5.6, 2 H); 3.49 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 168.63, 140.39, 137.00, 135.85, 133.08, 129.77, 129.53, 128.54, 128.25, 128.09, 127.30, 121.88, 52.18. EI-MS: 508 (100, M^+), 477 (20, $[M - MeO_3]^+$), 436 (10, $[M - 2\ MeO]^+$). HR-MS: 508.0802 ($C_{30}H_{20}S_2O_4^+$; calc. 508.0803).

*Dimethyl 5,8-Diphenylnaphtho[2,1-*b*:3,4-*b*′]bis[1]benzothiophene-6,7-dicarboxylate* (**1f**). Treatment of **7b** with 1 mmol (142 mg) of dimethyl but-2-ynedioate, CC ($CHCl_3$), and recrystallization from MeCN gave pure **1f** (91 mg, 74.8%). Light yellow crystals. M.p. 290–292°. UV/VIS (CH_2Cl_2): 240 (4.73), 256 (4.69), 306 (4.70), 332 (4.61), 376 (4.37), 386 (sh, 4.35). IR (KBr): 3058*w*, 2944*w*, 1745*s*, 1729*s*, 1493*w*, 1452*m*, 1433*m*, 1370*m*, 1292*s*, 1259*w*, 1219*s*, 1182*m*, 1160*m*, 1120*m*, 1072*w*, 1042*w*, 1026*w*, 1009*m*, 985*w*, 947*w*, 871*w*, 846*w*, 781*w*, 759*m*, 730*m*, 706*m*, 681*w*, 569*m*, 502*w*, 433*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.79–7.75 (*m*, 2 H); 7.54–7.50 (*m*, 2 H); 7.41–7.37 (*m*, 4 H); 7.22–7.15 (*m*, 8 H); 6.94–6.88 (*m*, 2 H); 3.70 (*s*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 169.93, 139.97, 137.82, 135.61, 135.55, 134.63, 130.60, 129.82, 129.67, 128.38, 128.21, 127.92, 126.44, 124.92, 123.25, 121.98, 52.50. EI-MS: 608 (100, M^+), 490 (10, $[M - 2\ CO_2Me]^+$), HR-MS: 608.1115 ($C_{38}H_{24}S_2O_4^+$; calc. 608.1116).

*4,7-Diphenylnaphtho[2,1-*b*:3,4-*b*′]dithiophene-5,6-dicarboxylic Acid Anhydride* (= *7,11-Diphenyldithieno[3′,2′:3,4;2″,3″:5,6]benzo[*e*]isobenzofuran-8,10-dione;* **1g**). Treatment of **7a** with 5 mmol (590 mg) of but-2-ynedioic acid and CC ($CHCl_3$) gave pure **1g** (33 mg, 35.7%). Light yellow crystals. M.p. > 350°. UV/VIS (CH_2Cl_2): 296 (4.57), 314 (4.57), 392 (sh, 3.85). IR (KBr): 3110*w*, 3087*m*, 1848*m*, 1817*m*, 1767*s*, 1522*w*, 1443*w*, 1394*w*, 1368*m*, 1296*m*, 1208*s*, 1170*m*, 1097*s*, 1027*s*, 919*s*, 910*s*, 895*m*, 800*s*, 756*s*, 738*m*, 722*m*, 690*s*, 668*m*, 635*w*, 613*w*, 574*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.66–7.62 (*m*, 6 H); 7.48–7.42 (*m*, 4 H); 7.15 (*d*, ^3J = 5.8, 2 H); 6.39 (*d*, ^3J = 5.8, 2 H). ^{13}C-NMR (91 MHz, $CDCl_3$): 161.79, 140.91, 138.37, 137.30, 133.97, 132.56, 129.34, 129.24, 129.12, 127.57, 123.36. EI-MS: 462 (100, M^+), 390 (80, $[M - C_2O_3]^+$), 188 (20, $[M - C_2O_3 - C_4(C_6H_5)_2]^+$). HR-MS: 462.0386 ($C_{28}H_{14}S_2O_3^+$; calc. 462.0384).

*5,8-Diphenylnaphtho[2,1-*b*:3,4-*b*′]bis[1]benzothiophene-6,7-dicarboxylic Acid Anhydride* (= *4,15-Diphenylbis[1]benzothieno[3′,2′:3,4;2″,3″:5,6]benzo[*a*]isobenzofuran-1,3-dione;* **1h**). Treatment of **7b** with 5 mmol (590 mg) of but-2-ynedioic acid, CC ($CHCl_3$), and recrystallization from chlorobenzene gave pure **1h** (60 mg, 53.4%). Intense yellow crystals. M.p. > 350°. UV/VIS (CH_2Cl_2): 240 (4.58), 262 (4.48), 302 (sh, 4.31), 314 (4.44), 366 (4.65), 408 (sh, 4.06). IR (KBr): 3054*w*, 3049*w*, 1840*s*, 1805*m*, 1773*s*, 1499*w*, 1445*w*, 1353*m*, 1343*w*, 1324*w*, 1197*s*, 1014*m*, 916*m*, 756*m*, 729*s*, 699*m*, 643*w*, 601*w*, 562*w*. EI-MS: 562 (100, M^+), 518 (5, $[M - CO_2]^+$), 490 (10, $[M - C_2O_3]^+$), 44 (20, CO_2^+). HR-MS: 562.0699 ($C_{36}H_{18}S_2O_3^+$; calc. 562.0697).

*4,7-Diphenyl-5,6-bis(trimethylsilyl)naphtho[2,1-*b*:3,4-*b*′]dithiophene* (**1k**). Treatment of **7a** with 3 mmol (510 mg) of bis(trimethylsilyl)acetylene gave **1k** as the major product (reaction of **7a** with 1 mmol (170 mg) of bis(trimethylsilyl)acetylene yielded **1i**/**1k** 6:4). CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from MeCN gave pure **1k** (45 mg, 42.0%). Colorless needles. M.p. 258–262°. UV/VIS (CH_2Cl_2): 258 (sh, 4.13), 288 (sh, 4.56), 294 (4.59), 322 (sh, 3.84), 332 (3.90), 342 (sh, 3.84). IR (KBr): 3094*w*, 3049*w*, 3020*w*, 2982*w*, 2953*w*, 2893*w*, 1493*w*, 1442*w*, 1385*w*, 1300*m*, 1282*w*, 1244*s*, 1197*w*, 1155*w*, 1104*w*, 1061*m*, 1023*m*, 926*m*, 860*s*, 842*s*, 815*s*, 796*m*, 763*s*, 724*s*, 704*s*, 684*s*, 662*w*, 630*w*, 573*w*, 535*w*, 487*w*, 410*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.55–7.35 (*m*, 10 H); 6.92 (*d*, ^3J = 5.4, 2 H); 6.04 (*d*, ^3J = 5.4, 2 H); 0.05 (*s*, 18 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 145.82, 144.13, 143.68, 134.34, 134.18, 133.76, 128.28, 127.99, 127.87, 127.67, 120.64, 5.04. EI-MS: 536 (70, M^+), 521 (20, $[M - Me]^+$), 463 (60, $[M - Me_3Si]^+$), 73 (100, Me_3Si^+). HR-MS: 536.1482 ($C_{32}H_{32}S_2Si_2^+$; calc. 536.1484).

*5,8-Diphenyl-6,7-bis(trimethylsilyl)naphtho[2,1-*b*:3,4-*b*′]bis[1]benzothiophene* (**1l**). Treatment of **7b** with 3 mmol (510 mg) of bis(trimethylsilyl)acetylene gave **1l** as the major product (reaction of **7b** with 1 mmol (170 mg) of bis(trimethylsilyl)acetylene yielded **1j**/**1l** 1:1). CC (petroleum ether (40–60)/$CHCl_3$ 5:1) and recrystallization from MeCN gave pure **1l** (45 mg, 35.4%). Light yellow needles. M.p. > 350°. UV/VIS (CH_2Cl_2): 252 (4.62), 294 (sh, 4.48), 310 (4.65), 322 (4.64), 336 (4.68), 366 (4.33), 378 (sh, 4.28). IR (KBr): 3059*w*, 2978*w*, 2946*m*, 2928*m*, 2893*m*, 2851*w*, 1511*w*, 1491*w*, 1457*w*, 1437*w*, 1419*w*, 1319*w*, 1263*w*, 1246*m*, 1162*w*, 1104*w*, 1076*w*, 1024*w*, 1012*m*, 952*w*, 866*m*, 838*s*, 806*m*, 787*m*, 758*s*, 727*s*, 705*m*, 700*w*, 674*w*, 646*w*, 626*w*, 500*w*, 482*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.23 (*d*, ^3J = 7.5, 2 H); 7.77 (*d*, ^3J = 7.8, 2 H); 7.58–7.46 (*m*, 4 H); 7.20–7.12 (*m*, 4 H); 6.94–6.87 (*m*, 2 H); 6.82–6.75 (*m*, 2 H); 6.62 (*d*, ^3J = 7.8, 2 H); 0.05 (*s*, 18 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 144.37, 143.89, 143.76, 137.86, 136.05, 133.99, 133.42, 132.96, 130.24, 129.33, 127.78, 127.71, 127.54, 126.62, 124.50, 122.81, 121.83, 4.42. EI-MS: 636 (40, M^+), 621 (5, $[M - Me]^+$), 563 (10, $[M - Me_3Si]^+$), 548 (10, $[M - Me_3Si - Me]^+$), 533 (5, $[M - Me_3Si - 2\ Me]^+$), 490 (5, $[M - 2\ Me_3Si]^+$), 73 (100, Me_3Si^+). HR-MS: 636.1794 ($C_{40}H_{36}S_2Si_2^+$; calc. 636.1797).

*4,7-Diphenyl-5-(trimethylsilyl)naphtho[2,1-*b*:3,4-*b*′]dithiophene* (**1i**). Treatment of **7a** with 2 mmol (196 mg) of (trimethylsilyl)acetylene, CC (petroleum ether (40–60)/$CHCl_3$ 5:1), and recrystallization from MeCN gave pure **1i** (68 mg, 73.3%). Colorless needles. M.p. 215–216°. UV/VIS (CH_2Cl_2): 248 (sh, 4.50), 272 (4.67), 282 (4.70), 328 (4.18), 340 (sh, 4.13). IR (KBr): 3141*w*, 3105*w*, 3051*w*, 3020*w*, 2950*w*, 2890*w*, 1490*m*, 1440*m*, 1398*w*, 1301*m*, 1261*m*, 1245*s*, 1192*w*, 1159*w*, 1108*w*, 1072*m*, 1063*m*, 1021*m*, 959*m*, 923*m*, 892*w*, 854*s*, 838*s*, 832*s*, 759*s*, 724*s*, 699*s*, 677*s*, 665*m*, 628*m*, 614*m*, 547*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.73 (*s*, 1 H); 7.65–7.62 (*m*, 2 H); 7.56–7.49 (*m*, 8 H); 7.01 (*d*, ^3J = 5.6, 1 H); 6.98 (*d*, ^3J = 5.6, 1 H); 6.52 (*d*, ^3J = 5.6, 1 H); 6.06 (*d*, ^3J = 5.6, 1 H); 0.05 (*s*, 9 H). ^{13}C-NMR (63 MHz, $CDCl_3$): 145.43, 144.93, 144.53, 138.04, 136.52, 134.65, 134.47, 133.71, 133.66, 133.41, 131.22, 129.78, 128.79, 128.64, 127.97, 127.95, 127.94, 127.83, 127.69, 127.36, 121.23, 120.97, 1.05. EI-MS: 464 (100, M^+), 449 (20, $[M - Me]^+$), 434 (10, $[M - 2\ Me]^+$), 419 (10, $[M - 3\ Me]^+$), 391 (10, $[M - Me_3Si]^+$), 73 (100, Me_3Si^+). HR-MS: 464.1089 ($C_{29}H_{24}S_2Si^+$; calc. 464.1089).

*5,8-Diphenyl-6-(trimethylsilyl)naphtho[2,1-*b*:3,4-*b*′]bis[1]benzothiophene* (**1j**). Treatment of **7b** with 2 mmol (196 mg) of (trimethylsilyl)acetylene, CC (petroleum ether (40–60)/$CHCl_3$ 5:1), and recrystallization from MeCN gave pure **1j** (99 mg, 89.5%). Light yellow needles. M.p. 313–315°. UV/VIS (CH_2Cl_2): 256 (4.64), 298 (4.55), 316 (4.52), 376 (4.33). IR (KBr): 3057*m*, 3022*w*, 2947*m*, 2894*w*, 1597*w*, 1491*m*, 1437*m*, 1387*w*, 1326*w*, 1246*m*, 1222*w*, 1158*w*, 1074*w*, 1025*m*, 1012*m*, 954*m*, 859*s*, 839*s*, 803*m*, 780*w*, 759*s*, 727*s*, 706*s*, 649*w*, 626*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.01 (*s*, 1 H); 7.81 (*d*, ^3J = 8.1, 1 H); 7.75 (*d*, ^3J = 8.1, 1 H); 7.62 (*d*, ^3J = 8.4, 1 H); 7.55–7.50 (*m*, 3 H);

7.44–7.40 (*m*, 2 H); 7.29–7.11 (*m*, 8 H); 6.96–6.85 (*m*, 2 H); 0.19 (*s*, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 144.67, 144.28, 143.41, 138.26, 137.59, 136.74, 136.38, 135.93, 134.63, 134.20, 134.02, 133.44, 132.11, 130.36, 129.37, 129.34, 128.94, 128.92, 128.73, 128.23, 127.73, 127.28, 126.94, 126.73, 124.49, 124.36, 123.16, 122.60, 122.03, 121.73, 1.67. EI-MS: 564 (100, M^+), 549 (15, $[M - Me]^+$), 534 (5, $[M - 2\,Me]^+$), 491 (15, $[M - Me_3Si]^+$), 73 (15, Me_3Si^+). HR-MS: 564.1402 ($C_{37}H_{28}S_2Si^+$; calc. 564.1402).

*Diphenylbenzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophenes* **2a**, **b**: *General Procedure.* To a freshly prepared soln. of **7a**, **b** was added an excess (3 mmol, 96 mg) of sulfur in one portion at 80°. After stirring for *ca.* 30 min at 80°, the soln. turned red brown (TLC: complete conversion). The soln. was allowed to cool to r.t., evaporated, and chromatographed (silica gel).

*4,6-Diphenylbenzo[2,1-*b*:3,4-*b*′:5,6-*c*″]trithiophene* (**2a**). Starting from **7a**, CC ($CHCl_3$) and recrystallization from AcOEt gave pure **2a** (62 mg, 77.9%). Yellow needles. M.p. 192°. UV/VIS (CH_2Cl_2): 242 (4.41), 286 (4.09), 297 (4.07), 311 (sh, 3.88), 328 (3.84), 367 (sh, 4.11), 377 (4.13). IR (KBr): 3045*w*, 3011*w*, 1594*w*, 1498*w*, 1486*w*, 1474*w*, 1440*w*, 1309*w*, 1268*w*, 1213*w*, 1177*w*, 1105*w*, 1074*w*, 1020*w*, 934*w*, 921*w*, 881*w*, 866*w*, 830*m*, 755*s*, 732*m*, 715*s*, 700*s*, 652*s*, 623*w*, 519*w*, 502*w*, 466*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.66–7.61 (*m*, 4 H); 7.53–7.47 (*m*, 6 H); 7.12 (*d*, ^3J = 5.4, 2 H); 7.09 (*d*, ^3J = 5.4, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 134.61, 133.40, 131.89, 130.66, 130.26, 129.67, 128.40, 128.24, 124.24, 122.34. EI-MS: 398 (100, M^+). HR-MS: 398.0258 ($C_{24}H_{14}S_3^+$; calc. 398.0258).

*5,7-Diphenyl[2]benzothieno[5,4-*b*:6,7-*b*′]trithiophene* (**2b**). Starting from **7b**, CC ($CHCl_3$) and recrystallization from chlorobenzene or toluene gave pure **2b** (88 mg, 88.7%). Orange needles. M.p. 235–236°. UV/VIS (CH_2Cl_2): 242 (4.72), 285 (4.32), 315 (4.21), 349 (4.04), 369 (4.08), 422 (4.24). IR (KBr): 3056*w*, 1594*m*, 1492*m*, 1443*m*, 1319*w*, 1306*w*, 1235*w*, 1140*w*, 1075*w*, 1025*m*, 1014*m*, 757*s*, 741*m*, 730*s*, 695*s*, 679*m*, 650*m*, 616*w*, 535*w*, 523*w*, 499*m*, 433*w*. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$ 2:1): 7.78–7.74 (*m*, 2 H); 7.48–7.44 (*m*, 4 H); 7.36–7.32 (*m*, 6 H); 7.19–7.13 (*m*, 2 H); 6.84–6.75 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3/CS_2$ 2:1): 138.74, 136.01, 135.18, 135.01, 135.75, 130.35, 129.39, 128.41, 127.62, 126.73, 126.17, 124.37, 123.22, 121.81. EI-MS: 498 (100, M^+), 422 (20, $[M - C_6H_6]^+$). HR-MS: 498.0570 ($C_{32}H_{18}S_3^+$; calc. 498.0571).

Reaction of Rhodium Complexes **7a**, **b** *with Oxygen: General Procedure.* Through a freshly prepared soln. of **7a**, **b** was passed a slow stream of dry O_2 at 80°. After stirring for *ca.* 30 min at 80°, the soln. turned brown (TLC monitoring). The soln. was allowed to cool to r.t., evaporated, and chromatographed (silica gel).

*(Benzo[2,1-*b*:3,4-*b*′]dithiophene-4,5-diyl)bis[phenylmethanone]* (**2c**). Starting from **7a**, CC ($CHCl_3$) and recrystallization from MeOH gave pure **2c** (38 mg, 48.2%). Light yellow crystals. M.p. 196–198°. UV/VIS (CH_2Cl_2): 240 (sh, 4.48), 254 (4.58), 284 (4.45), 334 (3.36). IR (KBr): 3097*w*, 3056*w*, 1646*s*, 1595*m*, 1579*m*, 1506*w*, 1451*m*, 1389*m*, 1317*w*, 1308*w*, 1263*m*, 1250*m*, 1216*w*, 1183*m*, 1168*m*, 1056*w*, 1012*m*, 928*w*, 879*w*, 829*m*, 818*m*, 743*m*, 723*s*, 699*m*, 654*m*, 640*m*, 586*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.65–7.61 (*m*, 4 H); 7.54–7.47 (*m*, 2 H); 7.45 (*d*, ^3J = 5.5, 2 H); 7.35–7.29 (*m*, 4 H); 7.23 (*d*, ^3J = 5.5, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 196.56, 137.85, 135.76, 134.39, 133.27, 131.66, 129.86, 128.19, 125.85, 124.38. EI-MS: 398 (55, M^+), 321 (65, $[M - C_6H_5]^+$), 293 (30, $[M - C_6H_5 - CO]^+$), 105 (80, $[C_6H_5 - CO]^+$), 77 (100, $C_6H_5^+$). HR-MS: 398.0435 ($C_{24}H_{14}S_2O_2^+$; calc. 398.0435).

*(Benzo[2,1-*b*:3,4-*b*′]bis[1]benzothiophene-5,6-diyl)bis[phenylmethanone]* (**2d**). Starting from **7b**, CC ($CHCl_3$) and recrystallization from toluene gave pure **2c** (59 mg, 59.5%). Light yellow needles. M.p. 312–314°. UV/VIS (CH_2Cl_2): 253 (4.64), 263 (4.61), 275 (sh, 4.56), 299 (4.39), 321 (4.20), 357 (3.63). IR (KBr): 3062*w*, 1663*s*, 1596*m*, 1579*m*, 1521*m*, 1452*s*, 1383*w*, 1322*s*, 1294*w*, 1261*s*, 1236*m*, 1202*m*, 1173*m*, 1065*w*, 1025*w*, 991*s*, 973*s*, 854*w*, 812*w*, 756*s*, 735*s*, 724*s*, 708*m*, 686*s*, 668*m*, 600*m*, 505*w*, 421*w*. ^{1}H-NMR (250 MHz, 323 K, $CDCl_3$): 7.90–7.85 (*m*, 2 H); 7.82–7.75 (br. *m*, 4 H); 7.70–7.65 (*m*, 2 H); 7.52–7.42 (br. *m*, 2 H); 7-41–7.33 (*m*, 2 H); 7.33–7.25 (br. *m*, 4 H); 7.23–7.12 (*m*, 2 H). ^{13}C-NMR (75 MHz, 323 K, $CDCl_3$): 197.38, 139.58, 137.69, 134.97, 134.34, 134.08, 131.49, 130.27, 130.05, 128.69, 127.11, 125.18, 125.03, 123.27. EI-MS: 498 (100, M^+), 421 (40, $[M - C_6H_5]^+$), 393 (25, $[M - C_6H_5 - CO]^+$), 364 (45), 105 (85, $[C_6H_5 - CO]^+$), 77 (65, $C_6H_5^+$). HR-MS: 498.0749 ($C_{32}H_{18}S_2O_2^+$; calc. 498.0748).

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