Synthesis and Properties of a Superphane with One Thiophene and One CpCo-Stabilized Cyclobutadiene Ring

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A superphane consisting of one thiophene ring and one CpCo-stabilized cyclobutadiene ring, **8**, was prepared in an eight-step synthesis from 5-cyclodecynol protected with *tert*-butyldimethylsilyl, **13**. The first key step in this sequence was the reaction of **13** with zirconocene and subsequently with S_2Cl_2 to yield the tricyclic thiophene derivative **12**. The second key step was the ring closure of **11** with CpCo(COD) to give **8**. X-ray structural investigations of **11** and **8** confirmed the structural assignments. Evidence for the close proximity of the CpCo-stabilized cyclobutadiene and the thiophene rings is also given by the electronic absorption spectrum of **8** and the oxidation potential (−0.07 V).

Introduction

Since the first synthesis of [2$_6$](1,2,3,4,5,6)cyclophane (**1**),[1] the "superphane", a series of congeners, such as **2**−**5**, were reported (Chart 1).[2−6] All of them are "symmetric" with respect to the π-systems. Although superphanes with different π-systems are less frequent, they are of considerable interest as models for low barriers of electron transfer[7] in the neutral and radical cationic state.[8] Examples of "non-symmetric" superphanes, in which both π-systems are different, are **6**[9] and **7** (Chart 2).[5,10] The first compound was observed as a side product in a single-pot reaction,[9] whereas the second species was synthesized from a tricyclic diyne.[5,10] In this paper we report a stepwise synthesis of **8**, which can be considered as a hybrid of **3** and **4**.

Chart 1

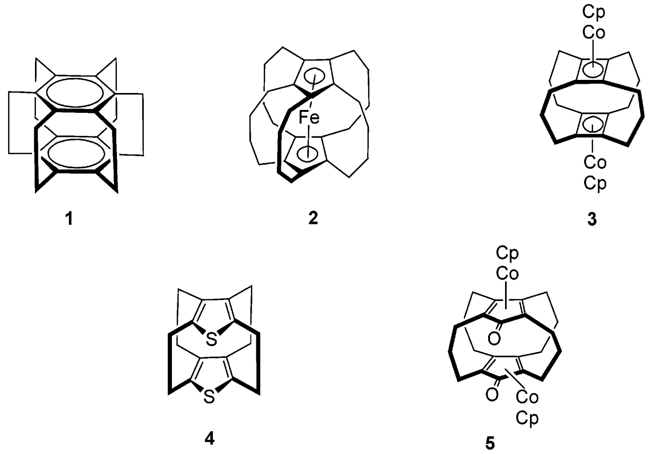
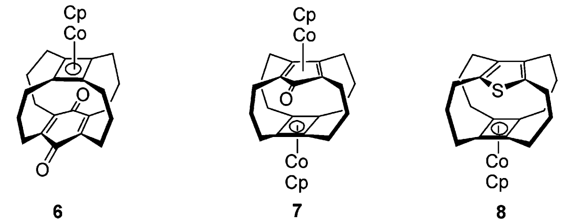


Chart 2



Results and Discussion

Synthesis. We approached the synthesis of **8** in two different ways; each is outlined in a retrosynthetic way in Scheme 1. As the first route, we favored the well-known reaction between 5-cyclodecynol (**10**) and CpCo(COD) to yield the tricyclic diyne **9** in five steps.[11] For the ring closure of the diyne **9** to **8**, we tried a protocol published by Negishi et al.[12] and Nugent et al.[13] by using in situ prepared zirconocene. This path was chosen because we knew from previous studies[11] that

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[1] Sekine, Y.; Brown, M.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 3126−3127. Sekine, Y.; Boekelheide, V. *J. Am. Chem. Soc.* **1981**, *103*, 1777−1785.

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[4] Takeshita, M.; Koike, M.; Tsuzuki, H.; Tashiro, M. *J. Org. Chem.* **1992**, *57*, 4654−4658.

[5] Roers, R.; Rominger, F.; Nuber, B.; Gleiter, R. *Organometallics* **2000**, *19*, 1578−1588.

[6] Gleiter, R.; Kratz, D. *Acc. Chem. Res.* **1993**, *26*, 311−318.

[7] Nelsen, S. F. *Chem. Eur. J.* **2000**, *6*, 581−588 and references therein.

[8] (a) Schaller, R. J.; Haberhauer, G.; Gleiter, R.; Rominger, F. *Eur. J. Inorg. Chem.* **2002**, 2296−2304. (b) Stoll, M. E.; Lovelace, S. R.; Geiger, W. E.; Schimanke, H.; Hyla-Kryspin, I.; Gleiter, R. *J. Am. Chem. Soc.* **1999**, *121*, 9343−9351. (c) Gleiter, R.; Roers, R.; Classen, J.; Jacobi, A.; Huttner, G.; Oeser, T. *Organometallics* **2000**, *19*, 147−151.

[9] Gleiter, R.; Kratz, D. *Tetrahedron Lett.* **1990**, *31*, 5893−5896,

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[11] Gleiter, R.; Langer, H.; Schehlmann, V.; Nuber, B. *Organometallics* **1995**, *14*, 975−986.

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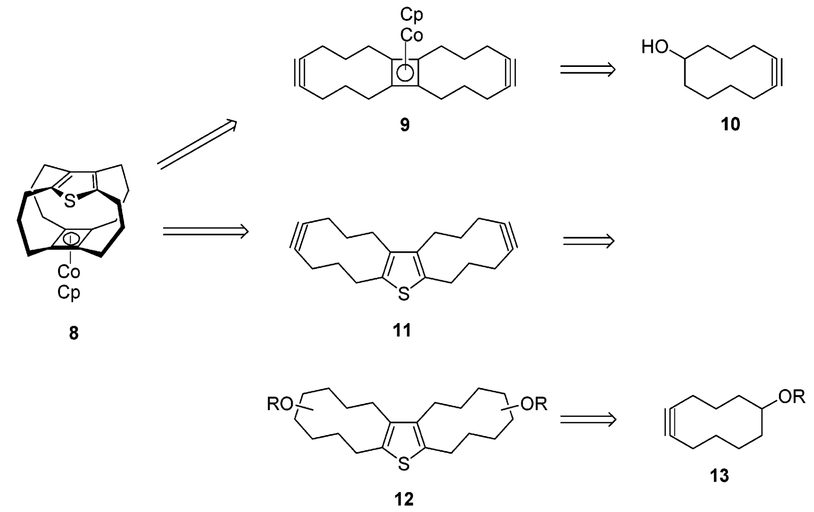
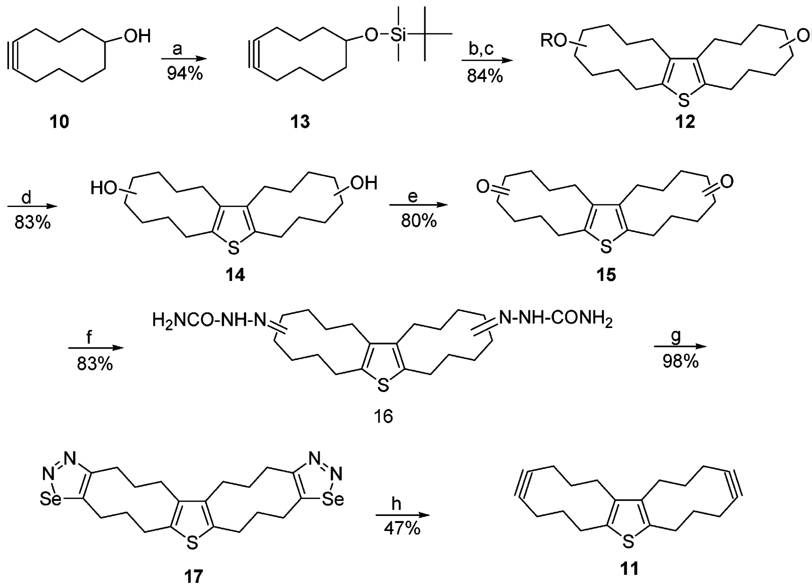
[13] Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312.

10.1021/om030619k CCC: $27.50

Scheme 1



Scheme 2[a]



[a] Conditions: (a) (TBDMS)Cl/imidazole/CH_2Cl_2; (b) Cp_2ZrCl_2/*n*-BuLi/THF, −78 °C; (c) S_2Cl_2; (d) HF(aq)/CH_3CN; (e) PCC/CH_2Cl_2; (f) $H_3N_2CONH_2$·HCl/NaOAc/EtOH; (g) SeO_2/CH_3CO_2H; (h) 180−200 °C/Cu.

in **9** both alkyne units are situated close to each other and, hence, are ideally positioned for the eventually planned ring closure. However, this endeavor failed.

As a second possibility we envisaged the preparation of the thiophene ring first by reacting a protected 5-cyclodecynol, **13**, following the Negishi-Nugent protocol[12,13] (Scheme 1). We reasoned that the tricyclic diyne **11** should be available from the resulting tricyclic thiophene derivative **12**. The diyne **11** is a candidate for ring closure with $CpCoL_2$ to give **8**. This path was our second choice because we assumed that the two triple bonds in **11** are far removed from each other and they are, therefore, in a less favorable position for ring closure as compared to **9**.

After the ring closure of **9** had failed, we started to prepare the thiophene system **11**. This synthesis commenced with 5-cyclodecynol (**10**), which can be obtained from decalin.[11,14] In **10** the protection of the alcohol group with the *tert*-butyldimethylsilyl group (TBDMS) was achieved by reacting **10** with TBDMSCl to yield **13**. In a one-pot reaction (Scheme 2) **13** was transferred to an isomeric mixture of the tricyclic thiophene derivatives **12** by reacting the in situ prepared zirconocene with **13** and subsequently the intermediate with S_2Cl_2.[13] The further reactions, i.e. the removal of the protecting groups with aqueous HF and the oxidation of the resulting mixture of diols **14** to the mixture of isomeric diketones **15** with pyridinium chlorochromate (PCC), worked very well. For the transformation of **15** into **11** we followed a procedure first published by Lalezari et al.[15] In this protocol the bis-semicarbazone of **15**, **16**, was heated together with SeO_2 to yield the bis-selenadiazole **17**. The latter was mixed with copper powder and heated under vacuum to 180−200 °C to yield the tricyclic diyne **11** as colorless crystals. The structure of **11** was confirmed by X-ray analysis using a single crystal.

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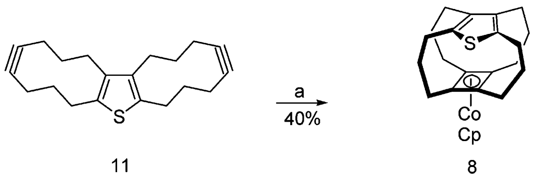
(15) Lalezari, I.; Shafiee, A.; Yalpani, M. *Tetrahedron Lett.* **1969**, 5105−5106. Lalezari, I.; Shafiee, A.; Yalpani, M. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 464.

Scheme 3[a]



[a] Conditions: (a) CpCo(COD)/mesitylene/165 °C.

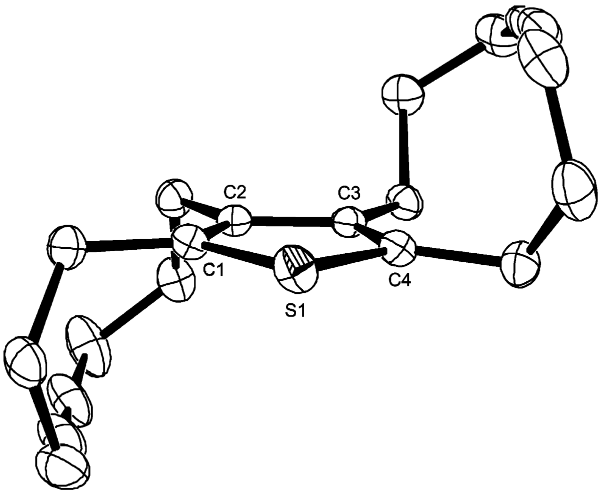
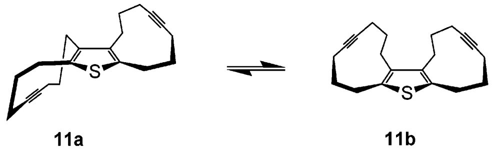


Figure 1. Molecular structure of **11**. The hydrogen atoms are omitted for the sake of clarity. The plot is represented at 50% probability of the thermal ellipsoids.

Scheme 4



Finally, the ring closure of **11** to **8** was achieved by heating **11** in mesitylene at 165 °C with (η^2-cyclooctadiene)(η^5-cyclopentadienyl)cobalt (CpCo(COD)) (Scheme 3). The superphane **8** proved to be very sensitive to silica gel and neutral alumina. A purification was only possible with basic Alox III.

Structural Investigations. We were able to grow single crystals of **8** and **11** which provided their molecular structures in the solid state. In Figure 1 we show the molecular structure of **11**. It is seen that the tricyclic system adopts a chairlike conformation (**11a**) in which both triple bonds are far removed (Scheme 4). To find out if there are other conformations available at room temperature in solution, we have carried out AM1 calculations[16] on **11**. It is found that the boatlike conformation **11b** is less favored than **11a** by 3 kcal/mol. In this local minimum the centers of both triple bonds are 6.2 Å apart. A similar situation was encountered for **9**.[11] The conformation of lowest energy showed a distance of 6.3 Å between the triple bonds. AM1 calculations revealed, however, that there were further conformations with distances between the triple bonds of 4.6 and 3.9 Å at 8.6 and 10.0 kcal/mol, respectively, above the minimum. Taking into account that the ring closure of **11** to **8** needed 165 °C, we can estimate that **11b** and other conformations in which the triple bonds are even closer are also present in solution.

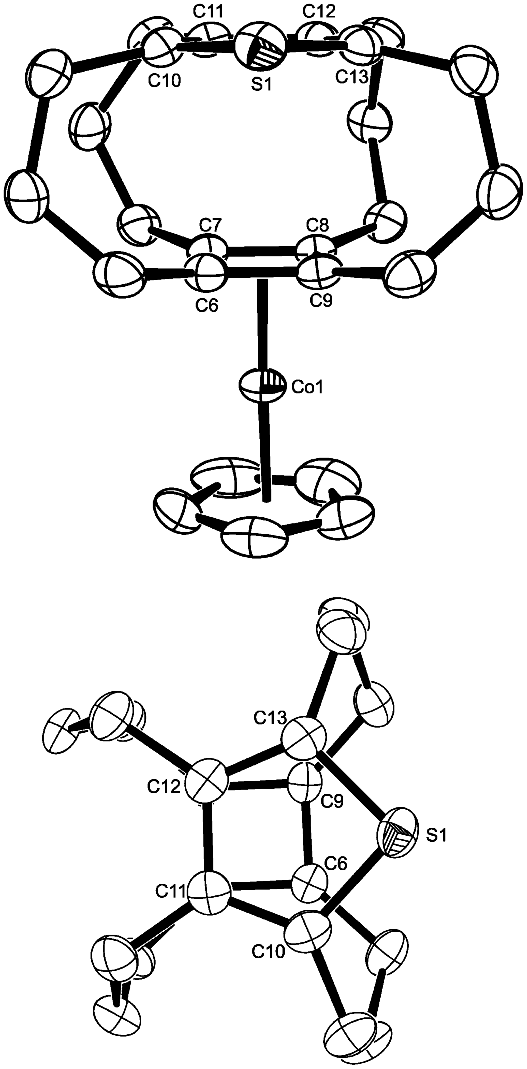


Figure 2. (a) Molecular structure of **8** and (b) top view of the cage part of **8**, with the CpCo fragment omitted. The hydrogen atoms are omitted for the sake of clarity. The plots are represented at 50% probability of the thermal ellipsoids.

In Figure 2a we show the molecular structure of **8** in the solid state. From this diagram it is seen that the carbon atoms bound to the former sp centers are slightly bent toward the inside of the cage. The averaged deviations from planarity amount to 7.1° for those carbons attached to the cyclobutadiene ring. The carbon atoms bound to the α-positions of the thiophene ring deviate by 11.2° and those at the β-positions by 7.6°. The sulfur atom is bent out of the plane spanned by the thiophene carbons by 4.1° toward the outside of the cage. In Figure 2b a top view is given, omitting the CpCo unit. From this picture the conformations of the four propane tethers can be seen. The distances C6−C10 and C9−C13 amount to 2.91 Å, whereas C7−C11 and C8−C12 are found to be 2.89 Å. As a consequence, the plane of the cyclobutadiene ring is inclined by 0.9° toward that of the plane spanned by the four carbon atoms of the thiophene ring.

The UV/vis spectrum of **8** reveals three bands above 250 nm, a very strong band (log $\epsilon = 4.60$) at 282 nm,

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(16) Dewar, M, J. S.; Zoebisch, E. G.; Healy, E. F. Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

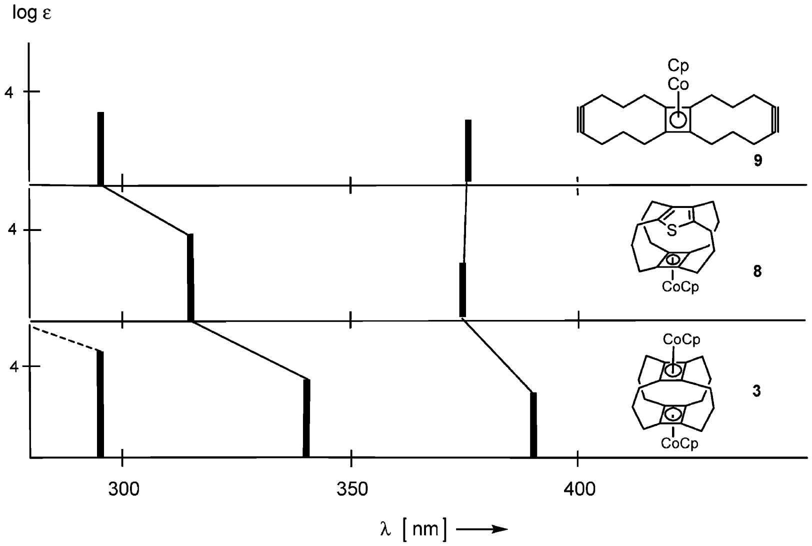

Figure 3. Correlation between the first absorption bands of the electronic spectra of **3**, **8**, and **9**.

and two weaker bands at 361 and 376 nm. A comparison with the UV data of **9** (Figure 3) shows that the two bands at longer wavelength are of similar energy and intensity as those of **8**, suggesting that these transitions arise from the CpCoCb fragment in both species. In Figure 3 we included in our correlation also the data of **3**.[3] This comparison shows a relatively strong shift of band 2 toward lower energy in the series **9**, **8**, **3**. We ascribe this shift to electron donation from the second π-system. The assumption of an interaction between the thiophene and CpCoCb ring systems is corroborated by the observation that the first oxidation potential of **8** (−0.07 eV) is the same as that reported for **3**.[8b,17]

Conclusion

We were successful in synthesizing a superphane, **8**, consisting of a thiophene ring and a CpCo-stabilized cyclobutadiene ring tethered with four propano bridges. This new species was prepared in eight steps, starting from 5-cyclodecynol, by using in situ prepared zirconocene to build up the thiophene ring and a (η^5-cyclopentadienyl)cobalt-supported [2 + 2] addition of two triple bonds to form the cyclobutadiene unit. The close proximity of the two π-systems was shown by means of X-ray investigations of **8**. This proximity is also indicated by the low oxidation potential and in the electronic absorption spectrum of **8**.

Experimental Section

General Methods. All reactions were conducted with oven-dried glassware under an argon atmosphere with magnetic stirring. THF was dried with sodium/benzophenone and distilled under argon. Dichloromethane was distilled over calcium hydride under argon before use. Melting points are uncorrected. Materials for column chromatography: silica gel 60 (Macherey-Nagel), Alox III (Merck). NMR spectra were recorded at 300 or 500 MHz (^{1}H) and 75.5 or 125.8 MHz (^{13}C), respectively, using the solvent as internal standard. The IR spectra were recorded with a FT-IR instrument. The UV/vis absorption spectra were recorded using a Hewlett-Packard 8452 A spectrometer. The high-resolution mass spectra (HRMS) were recorded in the FAB+ or EI (70 eV) mode. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg.

Preparation of 1-(*tert*-Butyldimethylsiloxy)-5-cyclodecyne (13). To a solution of 7.6 g (50 mmol) of 5-cyclodecynol (**10**) in 300 mL of dry dichloromethane was added at room temperature 5.1 g (75 mmol) of imidazole and 8.3 g (55 mmol) of *tert*-butyldimethylsilyl chloride in one portion. The mixture was stirred for 1 day and then hydrolyzed with 60 mL of water. A 300 mL portion of petroleum ether was then poured into the solution. The organic phase was washed with water. After drying the solvent was removed and the raw material was purified by column chromatography on silica gel using a mixture of petroleum ether and ether (15:1). This procedure yielded 12.5 g (94%) of a colorless oil. ^{1}H NMR (500 MHz/CDCl$_3$): δ 4.26 (m, 1H, CH), 2.19 (m, 2H, CH$_2$), 2.17 (m, 2H, CH$_2$), 1.74 (m, 2H, CH$_2$), 1.67 (m, 2H, CH$_2$), 1.60 (m, 2H, CH$_2$), 1.52 (m, 2H, CH$_2$), 1.36 (m, 2H, CH$_2$), 0.88 (s, 9H, C(CH$_3$)$_3$), 0.07 (s, 6H, Si(CH$_3$)$_2$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 85.0 (C(sp)), 84.6 (C(sp)), 70.6 (CH), 36.7 (CH$_2$), 34.3 (CH$_2$), 26.1 (CH$_3$ (*t*-Bu)), 25.0 (CH$_2$), 24.3 (CH$_2$), 24.2 (CH$_2$), 19.1 (CH$_2$), 18.9 (CH$_2$), 18.2 (C), −4.0 (SiCH$_3$), −4.3 (SiCH$_3$), HRMS (FAB+): calcd for $C_{16}H_{24}OSi$ [(M − H)$^+$] 265.1987, found 265.1963. Anal. Calcd for $C_{16}H_{24}OSi$ (265.20): C, 72.11; H, 11.35. Found: C, 71.84; H, 11.30.

Preparation of 2,3,4,5,6,7,8,10,11,12,13,15,16-Hexadecahydro-4,12-bis(*tert*-butyldimethylsiloxy)-1*H*,9*H*-dicyclodeca[*b*,*d*]thiophene (12). To a solution of 146 mg of Cp$_2$ZrCl$_2$ (0.5 mmol) in 20 mL of dry THF was added 0.7 mL (1.0 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. After the mixture was stirred for 90 min, a solution of 266 mg (1.0 mmol) of **13** in 20 mL of dry THF was added at −70 °C over 2 h. When the temperature was raised to 25 °C, the color of the solution changed from yellow to red. At 0 °C 40 μL (0.5 mmol) of S$_2$Cl$_2$ was added with a syringe. After this mixture was stirred for 15 h, the solvent was removed and the raw material was purified by column chromatography on silica gel (petroleum ether/ether 10:1) to yield 237 mg (84%) of a white crystalline material, mp 126 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.75 (m, 2H, CH), 2.82 (m, 4H, CH$_2$), 2.65 (m, 4H, CH$_2$), 1.65 (m, 4H, CH$_2$), 1.56 (m, 4H, CH$_2$), 1.49 (m, 4H, CH$_2$), 1.42 (m, 4H, CH$_2$), 1.25 (m, 4H, CH$_2$), 0.87 (s, 18H, C(CH$_3$)$_3$), 0.06 (t, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 136.6 (C, th), 135.5 (C, th), 71.0 (CH), 35.4 (CH$_2$), 33.9 (CH$_2$), 25.7 (CH$_3$), 24.8 (CH$_2$), 24.0 (CH$_2$), 23.8 (CH$_2$), 20.3 (CH$_2$), 19.9 (CH$_2$), 18.1 (C), −4.6 (Si(CH$_3$)$_2$). HRMS (EI): calcd for $C_{32}H_{60}O_2SSi_2$ [M]$^+$

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[17] Gleiter, R.; Röckel, H.; Pflästerer, G.; Treptow, B.; Kratz, D. *Tetrahedron Lett.* **1993**, 8075−8078.

564.3853, found 564.3851. Anal. Calcd for $C_{32}H_{60}O_2SSi_2$ (564.39): C, 68.02; H, 10.70; S, 5.67. Found: C, 68.05; H, 10.80; S, 5.73.

Preparation of 2,3,4,5,6,7,8,10,11,12,13,14,15,16-Hexadecahydro-4,12-bis(hydroxy)-1*H*,9*H*-dicyclodeca[*b*,*d*]thiophene (14). To a solution of 11.3 g (20 mmol) of **12** in 300 mL of ethyl acetate was added 2.75 mL of a mixture of HF (48% in water) and acetonitrile (1:10) in a plastic vessel. The solution was stirred at room temperature for 2 h. The solution was neutralized with saturated $NaHCO_3$ solution and extracted with ethyl acetate. The organic phase was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography using diethyl ether as eluent. This procedure afforded 5.6 g (83%) of **14** as colorless crystals, mp 165 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 3.95 (m, 2H, CH), 2.83 (m, 4H, CH_2), 2.67 (m, 4H, CH_2), 1.85−1.54 (m, 16H, CH_2), 1.29 (m, 4H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1 (C, th), 135.9 (C, th), 70.2 (CH), 30.4 (CH_2), 30.2 (CH_2), 29.8 (CH_2), 26.6 (CH_2), 26.0 (CH_2), 24.4 (CH_2), 20.2 (CH_2), 20.1 (CH_2). HRMS (EI): calcd for $C_{20}H_{32}O_2S$ [M^+] 336.2123, found 336.2123. Anal. Calcd for $C_{20}H_{32}O_2S$ (336.21): C, 71.38; H, 9.58; S, 9.53. Found: C, 71.12; H, 9.57; S, 9.62.

Preparation of 2,3,4,5,6,7,8,10,11,12,13,14,15,16-Hexadecahydro-4,12-bis(oxy)-1*H*,9*H*-dicyclodeca[*b*,*d*]thiophene (15). To a suspension of 14.6 g (67.5 mmol) of pyridinium chlorochromate in 100 mL of dry dichloromethane was slowly added a solution of 757 mg (2.25 mmol) of **14** in 200 mL of dry dichloromethane. After 3 h 300 mL of diethyl ether was added to the solution. The ethereal solution was purified by column chromatography on silica gel to yield 600 mg (80%) of **15** as a colorless powder, mp 166 °C. ^1H NMR (500 MHz, C_6D_6): δ 2.90 (m, 4H, CH_2), 2.68 (m, 4H, CH_2), 2.47 (m, 4H, CH_2), 2.07 (m, 4H, CH_2), 1.92 (m, 4H, CH_2), 1.70−1.62 (m, 4H, CH_2), 1.47−1.35 (m, 4H, CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ 212.1 (CO), 137.9 (C (Th)), 136.5 (C (Th)), 45.9 (CH_2), 45.6 (CH_2), 35.7 (CH_2), 31.2 (CH_2), 27.4 (CH_2), 25.3 (CH_2), 24.4 $(CH)_2$. UV/vis (CH_2Cl_2, λ_{max}, nm (log ϵ)): 248 (3.91), 302 (1.81). HRMS (EI): calcd for $C_{20}H_{28}O_2S$ (M^+) 332.1810, found 332.1787. Anal. Calcd for $C_{20}H_{28}O_2S$ (332.18); C, 72.25; H, 8.49; S, 9.64. Found: C, 71.99; H, 8.33; S, 9.77.

Preparation of 2,3,4,5,6,7,8,10,11,12,13,14,15,16-Hexadecahydro-4,12-bis(semicarbazone)-1*H*,9*H*-dicyclodeca[*b*,*d*]thiophene (16). To a freshly prepared solution of 228 mg of semicarbazide hydrochloride (2.1 mmol) and 288 mg of sodium acetate (3.5 mmol) in 18 mL of dry ethanol was added 229 mg (0.7 mmol) of **15**. During heating under reflux a precipitate was formed. The precipitate was filtered off and purified by heating it twice with ethanol. This procedure yielded 257 mg (83%) of **16**, which was used without further purification.

Preparation of 2,3,4,5,6,7,8,10,11,12,13,14,15,16-Hexadecahydro-4,12-bis(selenadiazolyl)-1*H*,9*H*-dicyclodeca[*b*,*d*]thiophene (17). A suspension of 73 mg (0.16 mmol) of **16** and 635 mg (0.6 mmol) of selenium dioxide was heated in 4 mL of acetic acid at 45 °C for 9 h. After removal of the solvent under reduced pressure, the residue was dissolved in chloroform and the solution washed with water and a solution of 5% sodium carbonate in water. Removal of the solvent yielded a red solid material (82 mg, 98%), which was used without further purification.

Preparation of 2,3,4,5,6,7,8,10,11,12,13,14,15,16-Hexadecahydro-4,12-bis(alkynyl)-1*H*,9*H*-dicyclodeca[*b*,*d*]thiophene (11). To a solution of 159 mg (0.3 mmol) of the bis-selenadiazole **17** in 8 mL of chloroform was added 1590 mg (25 mmol) of copper powder. The resulting suspension was dried under vacuum. The residue was pyrolyzed at 180 °C within 20 min under vacuum. The product was suspended in methylene chloride and filtered, followed by column chromatography on silica gel with petroleum ether/chloroform (2:1) to yield 42 mg (47%) of colorless crystals, mp 158 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 3.01 (m, 4H, CH_2), 2.76 (m, 4H, CH_2), 2.23 (m, 4H, CH_2), 2.16 (m, 4H, CH_2), 1.90 (m, 4H, CH_2), 1.83 (m, 4H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2 (C (Th)), 137.0 (C (Th)), 83.2 (C(sp)), 82.0 (C(sp)), 26.9 (CH_2), 26.1 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 19.3 (CH_2), 17.5 (CH_2). IR (KBr): 2957−2833 (s), 2291(w), 2226 (w), 1631 (br), 1446 (m), 1428 (m) cm^{-1}. UV/vis (CH_2Cl_2, λ_{max}, nm (log ϵ)): 250 (3.68). HRMS (EI): calcd for $C_{20}H_{24}S$ (M^+) 296.1598, found 296.1585. Anal. Calcd for $C_{20}H_{24}S$ (296.16): C, 81.03; H, 8.16; S, 10.82. Found: C, 80.83; H, 8.19; S, 10.83.

Table 1. Crystal Data and Structure Refinement Details for 8 and 11

	8	11
empirical formula	$C_{25}H_{29}CoS$	$C_{20}H_{24}S$
fw	420.47	296.45
temp (K)	293(2)	200(2)
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1$
unit cell dimens		
a (Å)	8.4755(1)	8.4042(1)
b (Å)	14.9067(1)	11.8333(1)
c (Å)	15.3692(1)	8.8118(1)
α (deg)	90	90
β (deg)	90	114.329(1)
γ (deg)	90	90
Z	4	2
V (Å^3)	1941.77(4)	798.506(15)
D_{calcd} (g/cm^3)	1.438	1.233
abs coeff	0.999	0.195
max/min transmn	0.90/0.70	0.97/0.80
θ range for data coll (deg)	1.90−27.48	2.54−27.47
index ranges	$-11 \le h \le 11$ $-19 \le k \le 19$ $-19 \le l \le 19$	$-10 \le h \le 10$ $-15 \le k \le 15$ $-11 \le l \le 11$
no. of rflns collected	20 190	8203
no. of indep rflns	4445	3610
no. of obsd rflns	4079	3347
goodness of fit on F^2	1.09	1.05
$R(F)$	0.025	0.030
$R_w(F^2)$	0.062	0.075
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.35, −0.21	0.21, −0.15

Preparation of Superphane 8. To a heated (165 °C) solution of 232 mg (1.0 mmol) of CpCo(COD) in 40 mL of mesitylene was added a solution of 119 mg (0.4 mmol) of **11** in 80 mL of mesitylene within 2 h. The progress of the reaction was controlled by TLC. After all **11** had disappeared (12 h), the solvent was removed under vacuum. The residue was dissolved in petroleum ether and purified on basic Alox III. After removal of the solvent, 67 mg (40%) of a brown crystalline material was recovered, mp 170 °C dec. ^1H NMR (300 MHz, C_6D_6): δ 4.46 (s, 5H, Cp), 2.91−2.83 (m, 2H, CH_2), 2.58−2.46 (m, 6H, CH_2), 2.42−2.31 (m, 2H, CH_2), 2.20−1.97 (m, 6H, CH_2), 1.87−1.71 (m, 6H, CH_2), 1.58−1.53 (m, 2H, CH_2). ^{13}C NMR (75 MHz, C_6D_6): δ 138.6 (Th), 132.5 (Th), 81.1 (CH, Cp), 79.2 (Cb), 76.6 (Cb), 27.3 (CH_2), 27.2 (CH_2), 26.9 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 24.9 (CH_2). IR (KBr): 3087 (w), 2964−2854 (s), 1631 (br), 1461 (m), 1430 (m). CV: −0.07 V (referenced to the ferrocene/ferrocenium couple). UV/vis (CH_2Cl_2, λ_{max}, nm, log ϵ): 282 (4.60), 316 (3.38), 374 (2.84). HRMS (FAB+): calcd for $C_{25}H_{29}CoS$ 420.1322, found 420.1312. Anal. Calcd for $C_{25}H_{29}CoS$ (420.13): C, 71.41; H, 6.95; S, 7.63. Found: C, 71.41, H, 6.90; S, 7.89.

X-ray Diffraction Analyses. The reflections were collected with a Bruker Smart CCD diffractometer (Mo Kα radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS[18] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen

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[18] Sheldrick, G. M. Bruker Analytical X-ray Division, Madison, WI, 1997.

atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects. Structure solution and refinement were carried out with the SHELXTL (5.10) software package.[18] ORTEP drawings were obtained using the ORTEP-3 for Windows program by Farrugia.[19] Table 1 contains the crystallographic data and details of the data collection and refinement procedure. CCDC 218564 and 218565 contains the supplementary crystallographic data for **8** and **11**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html/ or from the CCDC, 12 Union Road Cambridge CB2 1EZ, U.K. (fax (internat.), +44-1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

Cyclic Voltammetry. The electrochemical measurements were performed with the METROHM PGSTAT 20 potentiostat system. For the working electrode a METROHM disk electrode was used (radius ~0.3 cm, glassy carbon). The Ag/AgCl reference electrode was separated from the solution by a fine grid and a Luggin capillary. A 0.1 M solution of n-Bu_4NPF_6 in CH_2Cl_2 was used as electrolyte. The potential of ferrocene/ferrocenium was recorded at 495 ± 10 mV. The measurements were recorded at a scan rate of 200 mV s^{-1} at room temperature using a concentration of 919 mmol L^{-1} in CH_2Cl_2. Oxygen was removed from the solution by purging argon through the cell.

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Supporting Information Available: Tables giving crystal data for compounds **8** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.