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Donor-substituted CpCo-stabilized cyclobutadienes and superphanes

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Abstract

$RCpCoL_2$ complexes ($L_2 = (CO)_2$ or COD, R = H, CO_2Me, TMS) were reacted with various alkynes substituted with chalcogen atoms adjacent to the triple bonds. These reactions yielded hetero-substituted CpCo-capped cyclobutadienes and superphanes dependent on the ring size of the corresponding cyclic diene used as starting material. Reactions in decaline afforded not only CpCo-capped cyclobutadieno superphanes, but also mixed cyclobutadieno cyclopentadienono superphanes. X-ray analyses do not indicate a significant amount of conjugation between the π systems and the lone pairs of the heteroatoms whereas cyclic voltammetry reveals an easier oxidation when increasing the number of electron-donating heteroatoms.
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Keywords: Cyclobutadiene complexes; Alkynes; Cobalt; Superphanes

1. Introduction

Dicarbonyl(η^5-cyclopentadienyl)cobalt [$CpCo(CO)_2$] has played a major role in organometallic chemistry for the last 50 years [1,2]. Especially, its reactions with alkynes [3] yielded several useful and theoretically attractive molecules such as CpCo-stabilized cyclobutadienes [4], cyclopentadienones [5,6] as well as benzene derivatives [7]. As one possible mechanism for the generation of these species a sequential replacement of the CO units by acetylene fragments was proposed, yielding first a monoacetylene complex **A**, then a diacetylene complex **B**, which is thereafter converted by an oxidative coupling into a 16-electron metallacycle **C** (Scheme 1) [7,8]. The latter species, the so-called cobaltol **C**, has the ability to react either with a further acetylene fragment to afford the benzene derivative **G**, or to form the cyclobutadiene complex **E** by a reductive elimination process, or to insert CO to afford a cyclopentadienone complex **F**. This mechanism was first suggested by Rausch et al. [8] and is shown in Scheme 1. To get a deeper insight into the mechanism several intermediates were isolated and characterized crystallographically. Mono(alkyne)cobalt complexes could be obtained as stable compounds by using either a highly strained [9] or a very electron-deficient alkyne such as bis(*tert*-butylsulfonyl)acetylene (BTSA) [10]. Cobaltols of type **D** with a further ligand L could also be characterized by means of X-ray analyses [11].

In the course of our in-depth study of electron-rich alkynes [12–14] and their reactions with electrophilic complex fragments [15] we elucidated the reaction of RCpCo(COD) (**1**, R = CO_2Me) and $RCpCo(CO)_2$ (**2a**–**2c**, R = H, CO_2Me, TMS) with several electron-rich alkynes [12,16]. In continuation of this work we thought it of general interest to test the reactivity of sulfur-, selenium-, and tellurium-substituted alkynes towards electrophilic cobalt reagents. Several questions were in the focus of these investigations: Which heteroelements are tolerated by this reaction? In which way do cyclic dienes react (formation of tricyclic cyclobutadiene complexes versus formation of CpCo-capped superphanes [17])?

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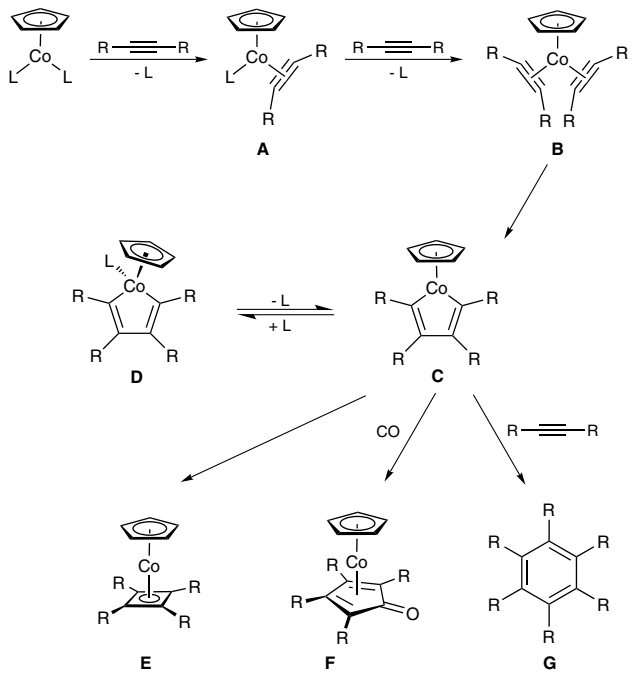


Scheme 1.

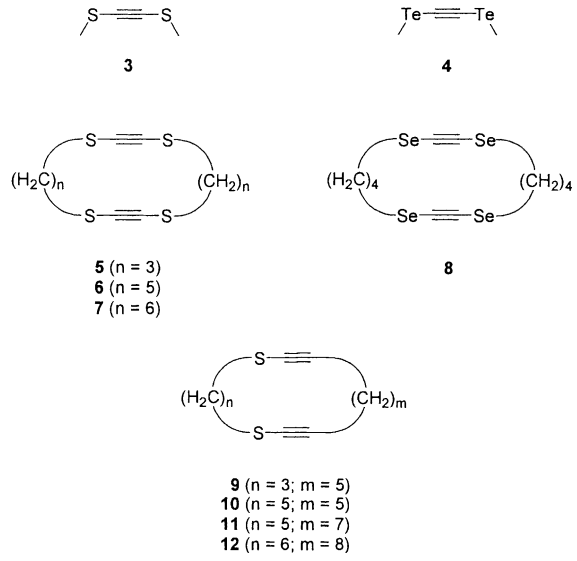


Chart 1.

Furthermore, α,α′-heterosubstituted alkynes would lead to π systems that are completely surrounded by heteroatoms [18]. How do these heteroatoms influence electronic and structural properties?

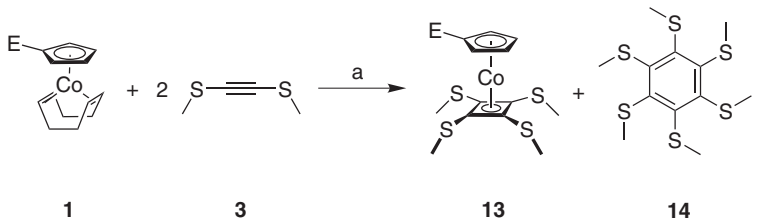
2. Results

We used a variety of recently prepared acyclic and cyclic, symmetrical and asymmetrical alkynes, substituted by chalcogen atoms in the α- and α,α′-positions [12,16] (Chart 1).

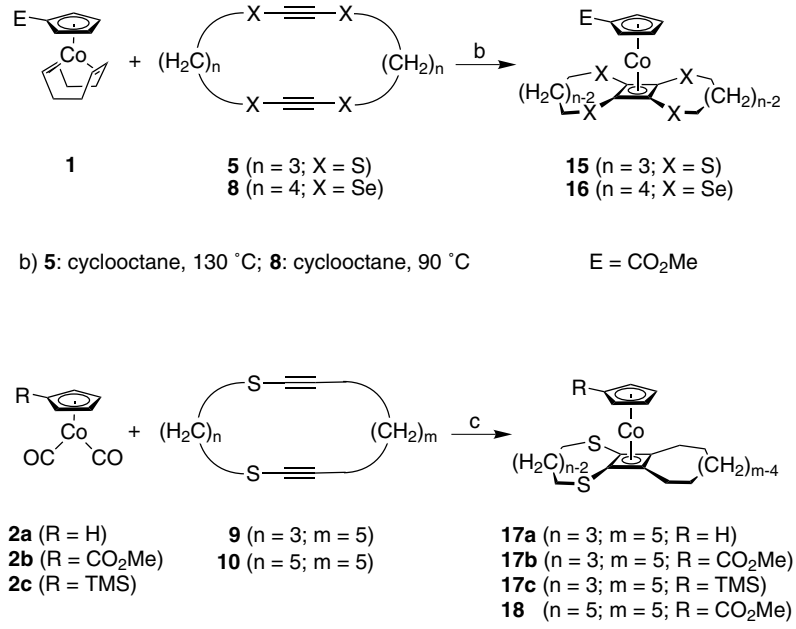
The reactions were carried out in cyclooctane or decaline, mostly under reflux. In the case of the selenium-containing compound **8**, the reaction was carried out at 90 °C, because at higher temperatures decomposition was observed. All these temperatures proved to be too high for the α,α′-tellurium-substituted alkyne **4**. The Te–C bond is so weak that all attempts to synthesize the hitherto unknown π systems totally surrounded by tellurium atoms were in vain. In all other cases mostly [2 + 2] cycloadducts were formed in moderate yields. When using the acyclic dithiaacetylene **3**, besides the CpCo-complexed [2 + 2] cycloadduct **13** we also observed the [2 + 2 + 2] cycloadduct **14** as the main product (Scheme 2). This hexa(methylthio)-substituted benzene **14** was previously synthesized by nucleophilic aromatic substitution of hexachlorobenzene [19].

In the case of the cyclic dienes **5**–**12** we found for **5**, **8**, **9**, and **10** tricyclic cyclobutadiene (Cbd) complexes (Scheme 3).

For larger cycles (e.g., **6**, **7**, **11** and **12**) at higher temperatures the CpCo-capped cyclobutadieno as well as the CpCo-capped mixed cyclobutadieno cyclopentadienono superphanes **19–24** resulted (Schemes 4 and 5). At lower temperature these larger cycles did not react. When the unsymmetrical cycles **11** and **12** were reacted with $RCpCo(CO)_2$ two different cyclobutadieno superphanes were possible, either the 1,2-isomer with adjacent hetero-substituents or the 1,3-isomer with nonadjacent hetero-substituents (Scheme 5). In all cases we found only the 1,2-isomers of the cyclobutadieno superphanes



Scheme 2.

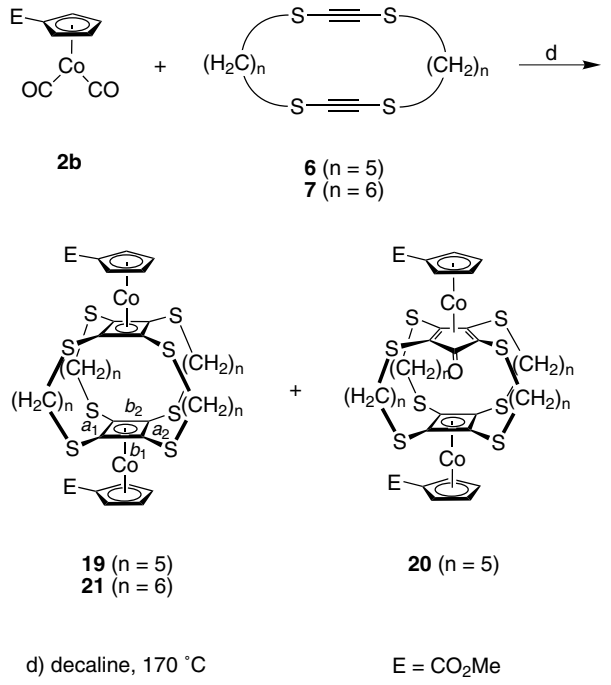


Scheme 3.

22 and **23**. Note, that in Scheme 5 the 1,3-isomers are also shown for the sake of clarity.

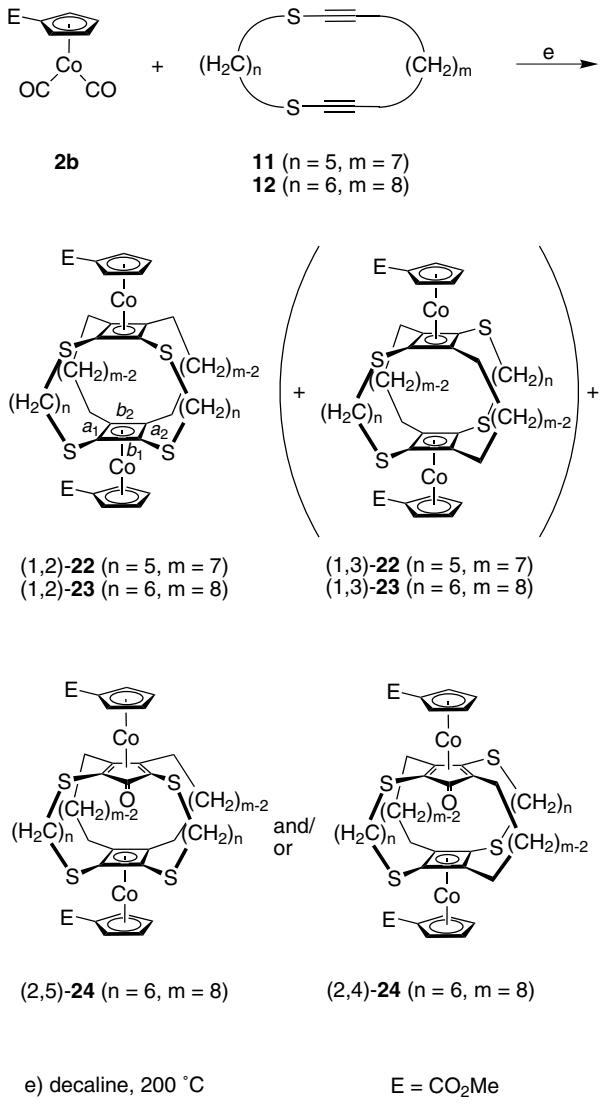
To explain the preference of the 1,2-isomers (1,2)-**22** and (1,2)-**23** we use a qualitative model. Assuming that the reaction sequence follows the path illustrated in Scheme 1, the most important step that decides the regiochemistry is the formation of the cobaltol **C** from the diacetylene complex **B**.

Taking into account Hückel-type calculations on simple α-thiosubstituted alkynes, a strong polarization of the alkyne unit results giving rise to large coefficients of the HOMO at the sulfur center and the carbon center in β-position of the sulfur. One may assume that such a polarization still exists in the diacetylene complex **B** where two regioisomers are equilibrating with each other. Of three possible regioisomeric cobaltols **C** ($R \neq R'$) the head to head isomer is found preferentially in which the large AO coefficients at the β-carbon atoms form the new bond [20]. This effect leads to the (1,2)-regioisomer. A similar argument has been put forward to explain the formation of the C_{2v} symmetric superphanes, when cyclic dienes, substituted at one α-position with $SiMe_2$ groups, were reacted with $CpCoL_2$ [21].



Scheme 4.

All the obtained π complexes **13** and **15**–**24** are remarkably stable. They are inert towards moisture and air. Investigations of the ^{13}C NMR spectra reveal chemical shifts of the carbon signals of the cyclobutadiene ring totally surrounded by sulfur in the range between $\delta = 80$–82. In the case of selenium, this value is shifted to higher field ($\delta = 74$). By means of ^{1}H NMR experiments it is possible to differentiate the regioisomers of the tetrathia-superphanes **22** and **23**. In the case of the (1,2)-regioisomers the CH_2 groups adjacent to the cyclobutadiene rings provide diastereotopic protons whereas in the case of the (1,3)-regioisomers homotopic protons result. The observed splitting in the ^{1}H NMR spectra of **22** and **23** clearly shows that only the (1,2)-



Scheme 5.

regioisomers were found. Due to the rather complicated spectrum of **24** such a clear-cut decision in favour of the (1,2)-regioisomer was not possible. In principle, in the case of **24** three isomers are conceivable (2,4-, 2,5-, and 3,4-), none of which has homotopic protons in the CH_2 groups. Thus our earlier criterion of homotopicity is no longer applicable.

3. Structural investigations and cyclic voltammetry

Of the 14 products obtained from the aforementioned reactions, the products **13**–**15**, **17b**, **19**, **21**, (1,2)-**22** and (1,2)-**23** yielded single crystals which could be investigated by means of X-ray diffraction to study their molecular structures in more detail. The X-ray structures of all π complexes reveal two nearly parallel planes (of the Cbd and the Cp units). In Table 1 we have compared the most relevant distances and interplanar angles. The C–C bond lengths in the Cbd rings are slightly longer than those in the unsubstituted CpCo cyclobutadiene complex (144 pm) [22]. We ascribe this behavior to a combination of steric and electronic effects due to the donor substitution of the Cbd units. There is no significant indication of bond alternation in the four-membered rings, neither in the symmetrically nor in the asymmetrically substituted ones. Nevertheless, the values of the asymmetrically substituted complexes have to be taken with care because S and CH_2 moieties are too similar in their spatial demand and therefore in most cases disorder between these two groups was observed.

In the cyclobutadiene complex **13** we encountered two independent molecules differing from each other in the conformation of the SMe groups. In Fig. 1, we show as an example the tricyclic cyclobutadiene complex with two seven-membered rings which are fused to the cyclobutadiene complex.

The molecular structure of hexa(methylthio)-benzene (**14**) shows a center of inversion. Three adjacent SMe groups point up, three point down. Another conformation of this compound was reported previously [23]. Due to the donor-substitution the π* orbitals of the benzene skeleton are populated. Thus, as a result the bond distances in the six-membered ring are slightly enlarged (1.5–2.0 pm compared with unsubstituted benzene).

In Fig. 2 we compare the two octathia-superphanes **19** and **21**. Both of them crystallize in the triclinic space group $P\bar{1}$ showing a center of inversion. As a result, the Cbd planes are parallel to each other. **19** contains two independent half molecules and three molecules of partly disordered $CHCl_3$ in the asymmetric unit. The bridging alkane chains reveal a strain-free zig-zag conformation. Thus, the distance between the two π systems becomes as large as possible. In the case of **19** this distance is 818 pm (and 820 pm, respectively), whereas in **21** due to one further CH_2 unit the distance amounts to 960 pm. To the best of our knowledge, these are the largest CpCo-stabilized superphanes reported so far [24]. In the case of **19** the two Cbd moieties are situated on top of each other. In contrast, in the structure of **21** they are shifted by 256 pm against each other. As a result, the Co–Co axis in **21** is inclined by 11.6°. This observation is shown in Fig. 3. A similar shifting is observed for the tetrathia-superphane (1,2)-**23** compared to the smaller tetrathia-superphane (1,2)-**22**. In the superphane resulting from cyclooctadeca-1,10-diene and CpCo(COD) with heptamethylene chains between the cyclobutadiene units two conformations were also reported in the solid state: in the first the centers of the parallel cyclobutadiene rings are situated on top of each other, in the second the centers

Table 1
Relevant geometric parameters of the compounds **13**, **15**, **17b**, **19**, **21**, (1,2)-**22** and (1,2)-**23**

Compound	*d*(Co–Cp)	*d*(Co–Cbd)	*ϕ*(Cp–Cbd)	*d*(Cbd–Cbd)	a_1, a_2[f]	b_1, b_2[f]
13[a]	168.3(2)	168.4(2)	4.1(1)	–	146.2(3)	146.1(3)
					146.6(3)	146.7(3)
	167.9(2)	167.8(2)	2.9(1)	–	146.6(3)	145.9(3)
					146.8(3)	146.1(3)
15	169.5(4)	169.4(4)	2.6(3)	–	145.5(6)	145.4(6)
					147.1(6)	146.0(6)
17b[b]	168.6(2)	169.3(2)	2.9(2)	–	144.8(3)	145.8(3)
					144.5(3)	145.0(3)
19[a,d]	166.6(7)	167.0(7)	0.6(6)	818.1(7)	145.3(9)	146.2(9)
					147.3(9)	146.3(9)
	167.8(7)	166.6(7)	2.2(6)	820.1(7)	144.9(9)	144.8(9)
					146.9(9)	148.0(9)
21	166.7(2)	167.0(2)	3.2(2)	925.2(2)	146.4(3)	147.1(3)
					147.5(3)	147.5(3)
(1,2)-**22**[e]	167.3(2)	167.4(2)	3.0(2)	797.9(2)[c]	146.2(3)	146.7(3)
					147.1(3)	147.2(3)
(1,2)-**23**[b,d]	167.5(3)	168.0(2)	0.7(2)	834.4(2)	146.5(3)	145.8(4)
					147.1(3)	146.4(4)

[a] Two independent molecules exist in the asymmetric unit.
[b] Disorder between the S and the CH_2 moieties, the values have to be taken with a grain of salt.
[c] Mean value.
[d] Special position with inversion symmetry.
[e] Special position on mirror plane.
[f] A definition of a_1, a_2, b_1 and b_2 is given in Schemes 4 and 5.

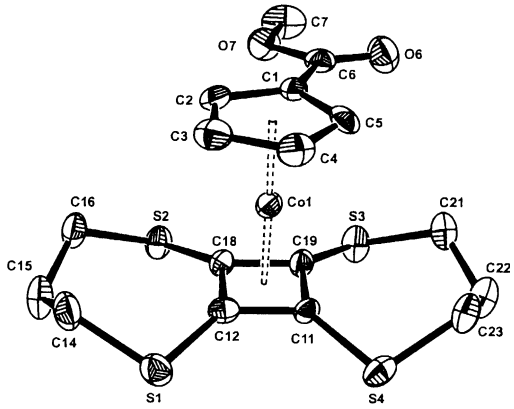


Fig. 1. ORTEP plot (50% ellipsoid probability) of the molecular structure of **15**. Hydrogen atoms are omitted for the sake of clarity.

of the parallel cyclobutadiene units are displaced by 102 pm [24].

To probe further effects of the donor-substitution, we have carried out studies by means of cyclic voltammetry (CV). In general, an oxidation potential measured by CV can be correlated with the HOMO energy of the corresponding complex [25]. Donors should raise the orbital energy, whereas acceptors should lower it. All recorded oxidation potentials are listed in Table 2. A comparison of **17a**–**17c** differing only by the substituent at the Cp ring reveals a slightly electron-donating effect of the TMS group (**17c**) and a slightly electron-withdrawing effect of the ester moiety (**17b**) versus the unsubstituted complex **17a**. The effect of the sulfur substituents at the Cbd ring can be seen by comparing **15** with **17b**: The complex with four donors (**15**) is easier to oxidize than the one with only two donors (**17b**). Furthermore, selenium (**16**) seems to be a worse donor than sulfur which can be rationalized by its smaller overlap with the Cbd unit. A potential splitting of the CV of superphanes was not observed. The distance between the π systems is too large for any significant interaction. The latter result is in line with studies on superphanes where the distance between the π systems was varied between 300 and 700 pm [17a].

4. Conclusion

In this paper, we have shown that sulfur- and selenium-substituted alkynes are able to react with $RCpCoL_2$ to afford donor-substituted π complexes or benzene derivatives. Dependent on the ring size of cyclic dienes which served as starting materials tricyclic cyclobutadiene complexes and CpCo-capped superphanes, respectively, are formed. Asymmetrically substituted alkynes yield only one regioisomer with the heteroatoms adjacent to each other. All donor-substituted complexes are stable at room temperature and resistant to water and oxygen. The X-ray analyses indicate that conjugation between the π system and the adjacent lone pairs of the sulfur substituents does not play a major role. CV reveals an easier oxidation when the number of sulfur substituents is increased.

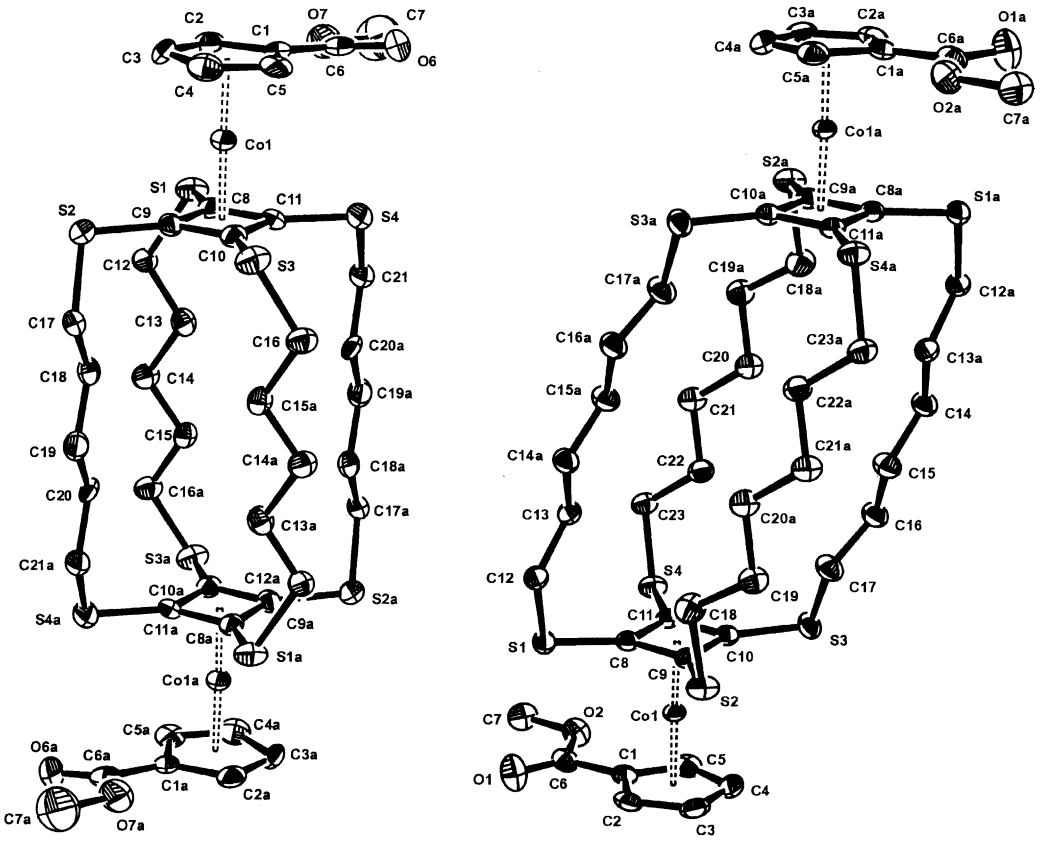


Fig. 2. ORTEP plots (50% ellipsoid probability) of the molecular structures of **19** (left) and **21** (right). Hydrogen atoms are omitted for the sake of clarity.

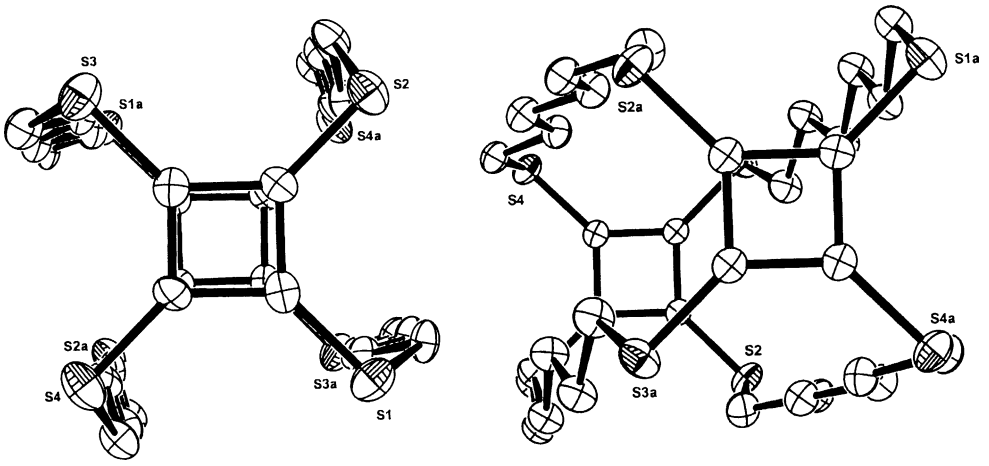


Fig. 3. Top view of the Cbd planes of **19** (left) and **21** (right). The CpCo fragments and the hydrogen atoms are omitted for the sake of clarity.

5. Experimental

5.1. General remarks

Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under argon using dried solvents. Cyclooctane and decaline were dried with sodium-benzophenone and distilled before use; m.p. are uncorrected. Materials used for column chromatography: neutral alumina (Merck), silica gel 60 (Machery-Nagel), Celite (Fluka). ^{1}H NMR and ^{13}C NMR: Bruker Avance 300 (^{1}H at 300 MHz and ^{13}C at 75 MHz), Bruker Avance 500 (^{1}H at 500 MHz and ^{13}C at 125 MHz) using the solvent as internal standard. IR: Bruker Vector 22 FT-IR. UV/Vis: Hewlett–Packard 8452 A spectrometer. MS (FAB^{+}): High resolution: Jeol JMS-700. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. The

Table 2
Comparison of oxidation potentials E of several donor-substituted cyclobutadiene complexes

Compound	E (mV)
13	410
15	190
16	410
17a	200
17b	330
17c	160
18	420
19	450[a]
(1,2)-**22**	530

[a] Irreversible.

starting materials were prepared according to literature methods [12,16,26].

5.2. General procedure for the formation of heterosubstituted cyclobutadiene complexes and superphanes

The appropriate cobalt complex (ECpCo(COD) or RCpCo(CO)$_2$) is dissolved in cyclooctane or decaline and the heterosubstituted alkyne is added in one portion. The reaction mixture is stirred for several days under heating. After completion of the reaction, the crude mixture is purified twice by column chromatography (SiO_2 or alumina and a gradient of *n*-hexane/diethylether 1:0 → 1:1 or a gradient of *n*-hexane/dichloromethane/methanol as eluent).

5.2.1. Cyclobutadiene complex **13**

Starting materials: 177 mg (0.61 mmol) of CpECo(COD) (**1**) and 132 mg (1.12 mmol) of 2,5-dithiahex-3-yne (**3**) in 80 ml of cyclooctane. The mixture is stirred for 5 d at 120 °C. Yield: 87 mg (34%) of **13** and 46 mg (35%) of **14**. Analytical data of **13**: Yellow solid.; m.p. 58 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35 (s, 12H, SCH_3), 2.82 (s, 3H, OCH_3), 5.04 (ps, 2H, CpH), 5.49 (m, 2H, CpH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.1 (SCH$_3$), 51.6 (OCH$_3$), 82.1 (C(Cbd)), 83.4 (C(Cp)H), 85.1 (C(Cp)H), 87.6 (C(Cp)), 166.9 (CO). IR (KBr): 2921, 2054, 1715, 1639, 1510, 1467, 1282. UV–vis (CH_2Cl_2, 0.099 mg ml^{-1}) λ [nm] (log ε): 234 (4.38), 318 (4.22), 358 (3.51). HRMS (FAB$^+$) $C_{15}H_{19}O_2S_4Co$: Calc.: 417.9600. Found: 417.9542. Elemental Anal. Calc.: C, 43.05; H, 4.58; S, 30.65. Found: C, 43.31; H, 4.64; S, 30.58%.

5.2.2. Cyclobutadiene complex **15**

Starting materials: 56 mg (0.19 mmol) of CpECo(COD) (**1**) and 50 mg (0.19 mmol) of 1,4,8,11-tetrathiacyclotetradeca-2,9-diene (**5**) in 50 ml of cyclooctane. The mixture is stirred for 8 d at 130 °C. Yield: 44 mg (52%). Yellow-orange solid; m.p. 165 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 1.55 (m, 2H, CH_2CHHCH_2), 1.90 (m, 2H, CH_2CHHCH_2), 2.61 (m, 8H, SCHH), 3.72 (s, 3H, OCH_3), 4.96 (m, 2H, CpH), 5.78 (m, 2H, CpH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.1 (CH$_2$), 37.0 (CH$_2$), 51.1 (OCH$_3$), 81.8 (C(Cbd)), 84.2 (C(Cp)H), 85.1 (C(Cp)H), 88.0 (C(Cp)), 166.8 (CO). IR (KBr): 2945, 2916, 2054, 1708, 1637, 1466, 1400, 1282. UV–vis (CH_2Cl_2, 0.062 mg ml^{-1}) λ [nm] (log ε): 238 (4.28), 276 (4.12), 320 (3.44), 372 (3.33). HRMS (FAB$^+$) $C_{17}H_{19}O_2S_4Co$: Calc.: 441.9600. Found: 441.9587. Elemental Anal. Calc.: C, 46.14; H, 4.33; S, 28.98. Found: C, 46.21; H, 4.39; S, 28.76%.

5.2.3. Cyclobutadiene complex **16**

Starting materials: 140 mg (0.48 mmol) of CpECo(COD) (**1**) and 230 mg (0.48 mmol) of 1,4,9,12-tetraselenacyclohexadeca-2,10-diene (**8**) in 50 ml of cyclooctane. The mixture is stirred for 12 d at 90 °C. Yield: 95 mg (30%). Yellow-orange solid; m.p. 65 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.93 (m, 4H, $CH_2CHHCHHCH_2$), 2.08 (m, 4H, CH_2CHHCH-HCH_2), 2.88 (m, 4H, SeCHH), 2.96 (m, 4H, SeCHH), 3.84 (s, 3H, OCH_3), 4.95 (m, 2H, CpH), 5.36 (m, 2H, CpH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.0 (CH$_2$), 28.4 (CH$_2$), 51.6 (OCH$_3$), 74.4 (C(Cbd)), 84.4 (C(Cp)H), 86.2 (C(Cp)H), 87.7 (C(Cp)), 166.6 (CO). IR (KBr): 2945, 2850, 1715, 1671, 1466, 1433, 1364, 1280, 1212, 1141. UV–vis (CH_2Cl_2, 0.052 mg ml^{-1}) λ [nm] (log ε): 234 (4.54), 318 (4.16), 356 (3.54). HRMS (FAB$^+$) $C_{19}H_{23}O_2{}^{78}Se^{80}Se_3Co$: Calc.: 659.7699. Found: 659.7666.

5.2.4. Cyclobutadiene complex **17a**

Starting materials: 180 mg (1.0 mmol) of CpCo(CO)$_2$ (**2a**) and 224 mg (1.0 mmol) of 1,5-dithiacyclotetradeca-6,13-diene (**9**) in 60 ml of decaline. The mixture is stirred for 2 d at 200 °C. Yield: 205 mg (59%). Orange solid; m.p. 83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29–2.22 (m, 10H, CH_2), 2.60–3.11 (m, 6H, CH_2), 4.81 (m, 5H, CpH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.6 (CH$_2$), 30.1 (CH$_2$), 30.4 (CH$_2$), 35.2 (CH$_2$), 38.4 (CH$_2$), 79.2 (C(Cp)H), 80.2 (C(Cbd)), 81.5 (C(Cbd)). IR (KBr): 2922, 2845, 2820, 1627, 1418, 806. UV–vis (CH_2Cl_2, 0.137 mg ml^{-1}) λ [nm] (log ε): 378 (3.24), 326 (3.37), 294 (4.40). HRMS (FAB$^+$) $C_{17}H_{21}S_2Co$: Calc.: 348.0417. Found: 348.0388.

5.2.5. Cyclobutadiene complex **17b**

Starting materials: 239 mg (1.0 mmol) of CpECo(CO)$_2$ (**2b**) and 224 mg (1.0 mmol) of 1,5-dithiacyclotetradeca-6,13-diene (**9**) in 60 ml of decaline. The mixture is stirred for 2 d at 200 °C. Yield: 330 mg (80%). Yellow solid; m.p. 130 °C (recrystallized from CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.90 (m, 2H, CH_2), 1.61 (m, 4H, CH_2), 1.93 (m, 2H, CH_2), 2.61 (m, 4H, CH_2), 2.90 (m, 4H, CH_2), 2.91 (s, 3H, CH_3), 4.93 (s, 2H, CpH), 5.59 (s, 2H, CpH). ^{13}C NMR (75 MHz,

$CDCl_3$): δ 26.9 (CH_2), 29.5 (CH_2), 29.8 (CH_2), 34.1 (CH_2), 37.4 (CH_2), 51.0 (OCH_3), 80.1 (*C*(Cbd)), 81.9 (*C*(Cp)H), 82.4 (*C*(Cbd)), 83.5 (*C*(Cp)H), 88.9 (*C*(Cp)), 156.1 (*C*O). IR (KBr): 2920, 2857, 1710, 1637, 1466, 1365, 1282, 1142, 773. UV–vis (CH_2 Cl_2, 0.043 mg ml^{-1}) λ [nm] (log ε): 370 (2.94), 332 (3.25), 300 (4.32). HRMS (FAB^+) $C_{19}H_{23}S_2O_2Co$: Calc.: 406.0472. Found: 406.0466. Elemental Anal. Calc. $C_{19}H_{23}S_2O_2Co \cdot 0.1CH_2Cl_2$: C, 55.29; H, 5.64. Found: C, 55.31; H, 5.60%.

*5.2.6. Cyclobutadiene complex **17c***

Starting materials: 252 mg (1.0 mmol) of CpTMSCo$(CO)_2$ (**2c**) and 224 mg (1.0 mmol) of 1,5-dithiacyclotetradeca-6,13-diene (**9**) in 60 ml of decaline. The mixture is stirred for 2 d at 200 °C. Yield: 196 mg (47%). Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.12 (s, 9H, CH_3), 1.01 (m, 2H, CH_2), 1.52 (m, 4H, CH_2), 1.95 (m, 4H, CH_2), 2.51 (m, 2H, CH_2), 2.89 (m, 4H, CH_2), 4.81 (s, 2H, Cp*H*), 5.08 (s, 2H, Cp*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.1 (CH_3), 26.7 (CH_2), 30.0 (CH_2), 30.4 (CH_2), 34.2 (CH_2), 38.2 (CH_2), 79.2 (*C*(Cbd)), 81.2 (*C*(Cbd)), 84.48 (*C*(Cp)), 84.53 (*C*(Cp)), 85.8 (*C*(Cp)). IR (KBr): 2961, 1414, 1261, 1034, 801, 740. UV–vis (CH_2Cl_2, 0.252 mg ml^{-1}) λ [nm] (log ε): 388 (3.14), 334 (3.28), 298 (4.29). HRMS (FAB^+) $C_{20}H_{29}S_2$ SiCo: Calc.: 420.0812. Found: 420.0784.

*5.2.7. Cyclobutadiene complex **18***

Starting materials: 239 mg (1.0 mmol) of CpECo$(CO)_2$ (**2b**) and 252 mg (1.0 mmol) of 1,7-dithiacyclohexadeca-8,15-diene (**10**) in 60 ml of decaline. The mixture is stirred for 2 d at 200 °C. Yield: 93 mg (21%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80–1.03 (m, 2H, CH_2), 1.12–1.73 (m, 10H, CH_2), 1.88–2.19 (m, 4H, CH_2), 2.39–2.87 (m, 4H, CH_2), 3.75 (s, 3H, OCH_3), 4.02 (s, 2H, Cp*H*), 5.40 (s, 2H, Cp*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.5 (CH_2), 24.5 (CH_2), 26.0 (CH_2), 29.4 (CH_2), 29.9 (CH_2), 34.4 (CH_2), 51.2 (OCH_3), 74.1 (*C*(Cbd)), 82.4 (*C*(Cp)H), 83.7 (*C*(Cp)H), 84.9 (*C*(Cbd)), 91.3 (*C*(Cp)), 167.5 (*C*O). IR (KBr): 2920, 2858, 1716, 1466, 1281, 1141, 821, 736. UV–vis (CH_2Cl_2, 0.159 mg ml^{-1}) λ [nm] (log ε): 370 (2.95), 338 (3.21), 320 (3.34), 284 (4.20), 262 (4.09). HRMS (FAB^+) $C_{21}H_{27}S_2O_2Co$: Calc.: 434.0784. Found: 434.0816.

*5.2.8. Cyclobutadieno superphane **19** and cyclobutadieno cyclopentadienono superphane **20***

Starting materials: 287 mg (1.20 mmol) of CpECo$(CO)_2$ (**2b**) and 382 mg (1.20 mmol) of 1,4,10,13-tetrathiacyclooctadeca-2,11-diene (**6**) in 50 ml of decaline. The mixture is stirred for 2 d at 160–170 °C. Yield: 140 mg (23%) of **19** and 71 mg (12%) of **20**. Analytical data of **19**: Yellow solid; m.p. > 250 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.18 (m, 8H, SCH_2CH_2 CH_2), 1.52 (m, 16H, SCH_2CH_2), 2.67 (m, 16H, SCH_2), 3.77 (s, 6H, OCH_3), 4.81 (m, 4H, Cp*H*), 5.15 (m, 4H, Cp*H*). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 29.7 (CH_2), 32.5 (CH_2), 33.5 (CH_2), 51.8 (OCH_3), 80.1 (*C*(Cbd)), 85.4 (*C*(Cp)H), 87.4 (*C*(Cp)H), 87.9 (*C*(Cp)), 166.8 (*C*O). IR (KBr): 2947, 2925, 2854, 1718, 1627, 1466, 1282, 1144. UV–vis (CH_2Cl_2, 0.073 mg ml^{-1}) λ [nm] (log ε): 242 (4.64), 318 (4.58), 352 (3.63). HRMS (FAB^+) $C_{42}H_{54}O_4S_8Co_2$: Calc.: 996.0452. Found: 996.0400. Elemental Anal. Calc.: C, 50.58; H, 5.46; S, 25.72. Found: C, 50.80; H, 5.58; S, 25.25%. Analytical data of **20**: Red solid; m.p. > 250 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.10–1.54 (m, 18H, CH_2), 2.23 (m, 2H, C*H*H), 2.40 (pt, 4H, SC*HH*), 2.54 (pt, 4H, SC*HH*), 2.56–2.83 (m, 8H, CH_2), 3.12 (m, 4H, SCH*H*), 3.71 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 4.18 (m, 2H, SC*H* H), 4.75 (m, 2H, Cp*H*), 4.79 (m, 2H, Cp*H*), 5.00 (m, 2H, Cp*H*), 5.09 (m, 2H, Cp*H*). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 28.9 (CH_2), 29.0 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 31.8 (CH_2), 31.9 (CH_2), 31.9 (CH_2), 32.2 (CH_2), 34.0 (CH_2), 36.0 (CH_2), 51.7 (OCH_3), 52.3 (OCH_3), 81.9 (*C*), 82.2 (*C*), 85.0 (*C*(Cp)H), 85.0 (*C*), 86.9 (*C*(Cp)H), 88.0 (*C*(Cp)H), 88.1 (*C*), 88.2 (*C*), 89.3 (*C*), 90.2 (*C*(Cp)H), 155.8 (*C*O), 163.8 (*C*OO), 166.0 (*C*OO). IR (KBr): 2927, 2854, 1720, 1600, 1469, 1366, 1282, 1145. UV–vis (CH_2Cl_2, 0.026 mg ml^{-1}) λ [nm] (log ε): 240 (4.58), 314 (4.30), 366 (4.23). HRMS (FAB^+) $C_{43}H_{54}O_5S_8Co_2$: Calc.: 1025.0480. Found: 1025.0490.

*5.2.9. Cyclobutadieno superphane **21***

Starting materials: 287 mg (1.20 mmol) of CpECo$(CO)_2$ (**2b**) and 414 mg (1.20 mmol) of 1,4,11,14-tetrathiacycloeicosa-2,12-diene (**7**) in 50 ml of decaline. The mixture is stirred for 2 d at 160–170 °C. Yield: 74 mg (12%). Yellow solid; m.p. 221 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.36 (b, 16H, SCH_2CH_2 CH_2), 1.62 (b, 16H, SCH_2CH_2), 2.71 (b, 16H, SCH_2), 3.80 (b, 6H, OCH_3), 4.92 (b, 4H, Cp*H*), 5.34 (b, 4H, Cp*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.1 ($SCH_2CH_2CH_2$), 30.1 (SCH_2CH_2), 35.8 (SCH_2), 51.7 (OCH_3), 82.4 (*C*(Cbd)), 84.0 (*C*(Cp)H), 85.9 (d, *C*(Cp)H), 87.6 (s, *C*(Cp)), 166.6 (s, *C*O). IR (KBr): 2926, 1718, 1628, 1469, 1366, 1284. UV–vis (CH_2 Cl_2, 0.035 mg ml^{-1}) λ [nm] (log ε): 238 (4.64), 342 (4.62), 314 (3.34), 356 (3.61). HRMS (FAB^+) $C_{46}H_{62}O_4S_8Co_2$: Calc.: 1052.1078. Found: 1052.1099.

*5.2.10. Cyclobutadieno superphane (1,2)-**22***

Starting materials: 239 mg (1.0 mmol) of CpECo$(CO)_2$ (**2b**) and 281 mg (1.0 mmol) of 1,7-dithiacyclooctadeca-8,17-diene (**11**) in 60 ml of decaline. The mixture is stirred for 2 d at 200 °C. Yield: 231 mg (25%). Yellow solid; m.p. 203 °C (recrystallized from toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80–1.81 (m, 32H, CH_2), 2.14–2.18 (m, 4H, CH_2), 2.22–2.25 (m, 4H, CH_2), 2.34–2.44 (m, 4H, CH_2), 2.45–2.54 (m, 4H, CH_2), 3.79

(s, 6H, OCH_3), 4.78 (s, 4H, Cp*H*), 5.15 (s, 4H, Cp*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.1 (*C*H_2), 29.5 (*C*H_2), 29.6 (*C*H_2), 30.5 (*C*H_2), 30.9 (*C*H_2), 31.2 (*C*H_2), 34.8 (*C*H_2), 51.4 (O*C*H_3), 75.4 (*C*(Cbd)), 83.6 (*C*(Cp)H), 85.9 (*C*(Cbd)), 86.3 (*C*(Cp)H), 87.6 (*C*(Cp)), 167.3 (*C*O). IR (KBr): 2927, 2854, 1712, 1637, 1466, 1284, 1143, 775. UV–vis (CH_2Cl_2, 0.038 mg ml^{-1}) λ [nm] (log ε): 380 (3.16), 328 (3.61), 296 (4.42), 260 (4.29). HRMS (FAB$^+$) $C_{46}H_{62}S_4O_4Co_2$: Calc.: 924.2195. Found: 924.2172. Elemental Anal. Calc. $C_{46}H_{62}S_4O_4Co_2 \cdot 0.5C_7H_8$: C, 61.22; H, 6.85; S, 13.21. Found: C, 61.26; H, 6.91; S, 13.13%.

*5.2.11. Cyclobutadieno superphane (1,2)-**23** and cyclobutadieno cyclopentadienono superphane **24***

Starting materials: 175 mg (0.73 mmol) of CpECo(CO)$_2$ (**2b**) and 225 mg (1.20 mmol) of 1,8-dithiacycloeicosa-9,19-diene (**12**) in 60 ml of decaline. The mixture is stirred for 2 d at 200 °C. Yield: 40 mg (6%) of (1,2)-**23** and 23 mg (3%) of **24**. Analytical data of (1,2)-**23**: Yellow solid; m.p. 162 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (m, 24H, C H_2), 1.45 (m, 8H, CH_2), 1.52 (m, 8H, CH_2), 1.93 (m, 4H, CH_2), 2.03 (m, 4H, CH_2), 2.52 (m, 8H, CH_2), 3.78 (s, 6H, OCH_3), 4.83 (s, 4H, Cp*H*), 5.20 (s, 4H, Cp*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.5 (*C*H_2), 25.8 (*C*H_2), 28.6 (*C*H_2), 28.8 (*C*H_2), 29.3 (*C*H_2), 29.6 (*C*H_2), 30.7 (*C*H_2), 36.4 (*C*H_2), 51.4 (O*C*H_3), 77.8 (*C*(Cbd)), 82.9 (*C*(Cp)H), 84.9 (*C*(Cp)H), 85.6 (*C*(Cbd)), 87.7 (*C*(Cp)), 167.5 (*C*O). IR (KBr): 2927 (s), 2853 (m), 1716 (s), 1637 (m), 1466 (s), 1281 (s), 1142 (s), 773 (w). UV–vis (CH_2Cl_2, 0.098 mg ml^{-1}) λ [nm] (log ε): 376 (3.40), 332 (3.72), 290 (4.56), 266 (4.44). HRMS (FAB$^+$) $C_{50}H_{70}S_4O_4Co_2$: Calc.: 980.2821. Found: 980.2756. Elemental Anal. Calc.: C, 61.20; H, 7.19; S, 13.07. Found: C, 61.03; H, 7.14; S, 13.00%. Analytical data of **24**: Orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20–1.65 (m, 40H, CH_2), 1.85 (m, 4H, CH_2), 1.92 (m, 4H, CH_2), 2.29 (m, 4H, CH_2), 2.45 (m, 4H, CH_2), 3.79 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 4.81 (s, 2H, Cp*H*), 5.08 (m, 4H, Cp*H*), 5.21 (s, 2H, Cp*H*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.4 (*C*H_2), 27.1 (*C*H_2), 27.5 (*C*H_2), 27.6 (*C*H_2), 28.2 (*C*H_2), 28.4 (*C*H_2), 28.6 (*C*H_2), 29.1 (*C*H_2), 29.2 (*C*H_2), 29.4 (*C*H_2), 29.5 (*C*H_2), 35.8 (*C*H_2), 51.1 (O*C*H_3), 51.7 (O*C*H_3), 66.2 (*C*), 66.4 (*C*), 75.9 (*C*), 76.2 (*C*), 76.4 (*C*), 82.5 (*C*(Cp)H), 84.5 (*C*(Cp)H), 85.3 (*C*), 86.9 (*C*(Cp)H), 89.2 (*C*), 130.0 (*C*), 165.0 (*C*O), 167.3 (*C*O). IR (KBr): 2935, 2867, 1685, 1617, 1460, 1290, 753. UV–vis (CH_2Cl_2, 0.172 mg ml^{-1}) λ [nm] (log ε): 418 (3.46), 382 (3.63), 338 (4.15), 288 (4.37),

Table 3
Crystallographic data and details of the refinement procedure for **13**–**15** and **17b**

	13	**14**	**15**	**17b**
Empirical formula	$C_{15}H_{19}O_2S_4Co$	$C_{12}H_{18}S_6$	$C_{17}H_{19}O_2S_4Co$	$C_{19}H_{23}CoO_2S_2$
Formula mass (g/mol)	418.50	354.66	442.53	406.42
Crystal size (mm)	$0.29 \times 0.26 \times 0.12$	$0.20 \times 0.20 \times 0.12$	$0.30 \times 0.06 \times 0.02$	$0.40 \times 0.19 \times 0.18$
Crystal colour	Yellow	Yellow	Yellow	Yellow
Crystal shape	Polyhedron	Polyhedron	Needle	Polyhedron
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$C2/c$
a (Å)	29.7408(2)	6.0451(2)	29.4947(13)	29.3702(4)
b (Å)	8.2700(1)	8.3623(3)	9.8251(5)	9.6702(2)
c (Å)	14.7878(2)	9.3457(2)	13.1586(6)	13.3178(2)
α (°)	90	114.959(1)	90	90
β (°)	94.715(1)	103.484(1)	104.758(1)	105.353(1)
γ (°)	90	91.557(1)	90	90
V (Å^3)	3624.85(7)	418.42(2)	3687.4(3)	3647.48(11)
d_{calc} (g/cm^3)	1.534	1.407	1.594	1.480
Z	8	1	8	8
h_{min}/h_{max}	−38/38	−7/7	−33/33	−38/38
k_{min}/k_{max}	−10/10	−10/10	−11/11	−12/12
l_{min}/l_{max}	−19/19	−12/12	−15/15	−17/17
μ (mm^{-1})	1.410	0.799	1.391	1.178
T_{max}/T_{min}	0.85/0.69	0.91/0.86	0.98/0.72	0.82/0.65
Refl. collected	36,385	4332	14,151	18,531
Refl. unique	8270	1896	2925	4193
Refl. observed	6723	1611	1833	3328
Parameter	407	85	218	231
$R(F)$	0.029	0.037	0.043	0.033
$R_w(F^2)$	0.067	0.098	0.068	0.079
S (Gof) on F^2	1.06	1.05	0.96	1.05
$(\Delta\rho)_{max}$ (e Å^{-3})	0.28	0.41	0.37	0.57
$(\Delta\rho)_{min}$ (e Å^{-3})	−0.44	−0.38	−0.31	−0.31

Table 4
Crystallographic data and details of the refinement procedure for **19**, **21**, (1,2)-**22** and (1,2)-**23**

	19	**21**	(1,2)-**22**	(1,2)-**23**
Empirical formula	$C_{45}H_{57}O_4S_8Cl_9Co_2$	$C_{46}H_{62}O_4S_8Co_2$	$C_{53}H_{70}Co_2O_4S_4$	$C_{50}H_{70}Co_2O_4S_4$
Formula mass (g/mol)	1355.30	1053.37	1017.19	981.16
Crystal size (mm)	$0.16 \times 0.12 \times 0.06$	$0.40 \times 0.26 \times 0.02$	$0.40 \times 0.28 \times 0.24$	$0.30 \times 0.18 \times 0.13$
Crystal colour	Yellow	Yellow	Yellow	Yellow
Crystal shape	Polyhedron	Plate	Polyhedron	Polyhedron
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pnma*	$P\bar{1}$
a (Å)	14.3662(3)	9.8456(2)	14.1328(2)	9.9815(1)
b (Å)	14.9954(1)	10.3022(1)	24.4816(1)	10.0150(2)
c (Å)	16.7845(3)	12.2588(2)	14.8173(2)	13.2283(2)
α (°)	115.819(1)	105.498(1)	90	75.588(1)
β (°)	111.504(1)	94.444(1)	90	86.656(1)
γ (°)	92.278(1)	95.393(1)	90	70.014(1)
V (Å^3)	2941.23(8)	1186.07(3)	5126.69(10)	1203.10(3)
d_{calc} (g/cm^3)	1.530	1.475	1.318	1.354
Z	2	1	4	1
h_{min}/h_{max}	−15/15	−12/12	−18/18	−12/12
k_{min}/k_{max}	−17/17	−13/13	−31/31	−12/12
l_{min}/l_{max}	−17/17	−15/15	−19/19	−16/16
μ (mm^{-1})	1.296	1.094	0.853	0.906
$T_{max.}/T_{min.}$	0.93/0.92	0.98/0.67	0.82/0.73	0.89/0.77
Refl. collected	19,353	12,285	51,340	11,415
Refl. unique	7189	5391	6014	4886
Refl. observed	4043	4176	4696	3841
Parameter	642	272	314	308
$R(F)$	0.057	0.034	0.035	0.041
$R_w(F^2)$	0.107	0.074	0.091	0.098
S (Gof) on F^2	1.01	1.01	1.16	1.02
$(\Delta\rho)_{max}$ (e Å^{-3})	0.52	0.41	0.67	0.70
$(\Delta\rho)_{min}$ (e Å^{-3})	−0.46	−0.27	−0.38	−0.41

264 (4.28). HRMS (FAB$^+$) $C_{51}H_{70}S_4O_5Co_2$: Calc.: 1009.2848. Found: 1009.2828.

5.3. X-ray crystallography and structure solution

The crystallographic data were recorded with a Bruker Smart CCD diffractometer at 200(2) K at a wavelength λ of 0.71073 Å. Relevant crystal and data collection parameters are given in Tables 3 and 4. Structure solution and refinement were carried out using SHELXTL [27]. An empirical absorption correction was carried out using SADABS [27] based on the Laue symmetry of the reciprocal space. Hydrogen atoms were included at calculated positions. ORTEP drawings were obtained by using ORTEP-3 for Windows program by Farrugia [28]. In **17b** and (1,2)-**23** we found disorder between S and CH_2 moieties (4:1 and 3:1, respectively).

5.4. Cyclic voltammetry

The electrochemical measurements were performed with the potentiostat system PGSTAT20 (METROHM). A traditional three-electrode, three-compartment cell geometry was employed for voltammetry experiments with a Ag/AgCl reference electrode in dichloromethane separated from the test solution by a Haber–Luggin capillary. The E values reported for chemically reversible systems were an average of the observed anodic and cathodic peak potentials. A supporting electrolyte concentration of 0.1 M of [n-Bu_4N][PF_6] was employed. The working electrode for cyclic voltammetry was a GC disk of 3 mm diameter. All measurements were recorded with a scan rate of 100 and 200 mV s^{-1}. Samples were measured at a concentration of 1 mmol l^{-1} in dichloromethane at room temperature. Oxygen was removed by purging argon through the cell. All potentials refer to the ferrocene/ferrocenium couple as internal standard (0.0 mV), as recommended by IUPAC [29]. Referred to a saturated calomel electrode (SCE) 460 mV have to be added for a solution of dichloromethane [30].

6. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 231117–231124 for compound **13**–**15**, **17b**, **19**, **21**, (1,2)-**22** and (1,2)-**23**. Copies of this information may be obtained free of charge from:

The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax.(int code) +44(1223)336-033 or e-mail: data_request@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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