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(η^5-Cyclopentadienyl)[η^2-bis(*tert*-butylsulfonyl)acetylene]-(carbonyl)cobalt
An electrophilic reagent to yield CpCo-stabilized cyclobutadiene derivatives

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Dedicated to Professor Adolf Krebs on the occasion of his 70th birthday

Abstract

Various substituted (R = H, CH_3, $SiMe_3$, CO_2Me, $COCH_3$, $EtMe_4$) (R-η^5-cyclopentadienyl)[η^2-bis(*tert*-butylsulfonyl)acetylene](carbonyl)cobalt complexes (**8**–**13**) proved to be very reactive towards alkynes under rather mild conditions. Dithiaacetylenes reacted at room temperature, dialkyl- and diarylalkynes had to be heated to 80–90 °C to yield the corresponding R-CpCo-stabilized cyclobutadiene complexes **18**–**37** and **39**–**42**. X-ray investigations on **24**–**26**, **30**, **36** and **39**–**41** showed almost equal C–C bond lengths in the cyclobutadiene rings. © 2002 Published by Elsevier Science B.V.

Keywords: Cyclobutadiene complexes; Alkynes; Cobalt complexes; Cyclization

1. Introduction

Since the first synthesis of dicarbonyl(η^5-cyclopentadienyl)cobalt [$CpCo(CO)_2$] in 1955 [1,2], this compound has played a major role in organocobalt chemistry [3]. Among others, the reactions of $CpCo(CO)_2$ with alkynes have been investigated intensively [3], because a number of useful molecules can be prepared in a straight forward fashion. By this way CpCo-complexes of cyclobutadienes [4], cyclopentadienones [5] and benzoquinones have been prepared; the trimerization of alkynes [6] has also been achieved. The disadvantage of the metal supported oligomerization of alkynes is that, for unsymmetrical substituted alkynes always isomers are produced. This obstacle might overcome if oligomerization could be carried out in stepwise fashion.

The first evidence for a stepwise mechanism was reported by Lee and Brintzinger [7], who were able to demonstrate by means of IR spectroscopy that on irradiation of $CpCo(CO)_2$ in presence of diphenylacetylene, a complex with only one CO group must be present.

Complex **1** was the first CpCo-complex with one CO and one alkyne unit to be isolated. It was prepared by Jessel and Krebs by reacting the highly strained alkyne 3,3,6,6-tetramethyl-1-thiacycloheptyne with $CpCo(CO)_2$ [8]. Reactions of **1** with various alkynes (Scheme 1) demonstrated that the remaining CO unit in **1** could be replaced thermally or photochemically. With few exceptions the product of these reactions was always the corresponding cyclobutadiene complex as indicated in Scheme 1.

In our studies, on the reactivity of electron poor alkynes, we were able to isolate stable monoalkyne complexes by reaction of $CpCo(CO)_2$ and bis(*tert*-butylsulfonyl)acetylene (BTSA) [9] in methylene chlo-

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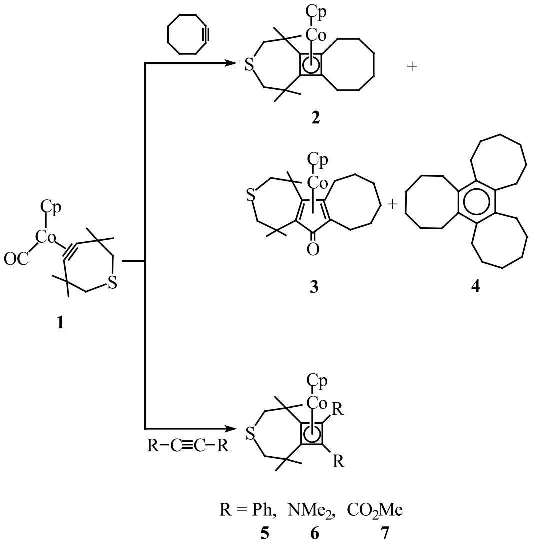
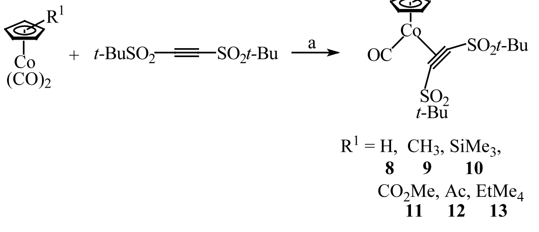
ride at room temperature (Scheme 2) [10]. This reaction could also be extended to substituted R–CpCo(CO)$_2$ complexes as shown in Scheme 2. A comparison of the results obtained by spectroscopic studies of **1** and **8** (Table 1) [8,10] indicates a stronger bonding of the alkyne unit and a weaker bonding of the CO group in **8** as compared to **1**. This suggested a higher reactivity towards alkynes, especially electron rich ones, in the case of **8** as compared to **1**. Because **8**–**13** are easily available and the *tert*-butylsulfonyl groups of resulting 1,2-bis(*tert*-butylsulfonyl)cyclobutadiene derivatives are prone to further replacement reactions, we undertook studies with various alkynes to explore the scope and limitations of a replacement of CO in **8**–**13** by triple bonds.



Scheme 1.

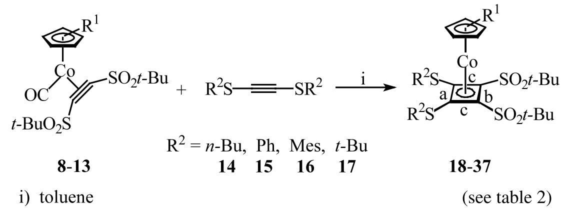


a) CH$_2$Cl$_2$, room temp.

Scheme 2.

Table 1
Comparison of the spectroscopic data of **1** and **8**

	1	**8**
^{13}C δ (C≡C)	77.92	93.72
ν(C≡C) (cm^{-1})	1880	1772
ν(CO) (cm^{-1})	1975	2017



Scheme 3.

Table 2
Yields (% in italics) of the push-pull-cyclobutadiene complexes **18**–**37**

R^2	R^1					
	H	Me	SiMe$_3$	CO$_2$Me	Ac	EtMe$_4$
n-Bu	**18**	**19**	**20**	**21**	**22**	**23**
	73	*69*	*78*	*49*	*53*	*37*
Ph	**24**	**25**	**26**	**27**	**28**	**29**
	56	*65*	*62*	*42*	*46*	*26*
Mes	**30**	–	**31**	–	**32**	–
	65	–	*13*	–	*41*	*0*
t-Bu	**33**	**34**	**35**	**36**	**37**	–
	10	*31*	*13*	*15*	*17*	*0*

Obtained from the reactions of **8**–**13** with the dithiaalkynes **14**–**17**. (For the meaning of R^1 and R^2, see Schemes 2 and 3).

2. Results

2.1. Acetylenedithioethers

As starting materials for electron rich alkynes we used acetylene dithioethers because these substances are stable, and readily available [11–13]. The reactions of **8**–**13** with an excess of the acetylene dithioethers **14**–**17** were carried out in toluene, mostly at room temperature (Scheme 3). In the case of **17**, the reaction was carried out at 90 °C. The yields of the resulting donor–acceptor cyclobutadiene complexes are summarized in Table 2. The yellow colored substances are remarkably stable. They are inert towards moisture and air. The tolerance towards steric repulsion in the CpCo-stabilized cyclobutadiene complexes is relatively high, only in the cases in which reaction was attempted between **13** and **16** or **17**, no reaction products could be detected.

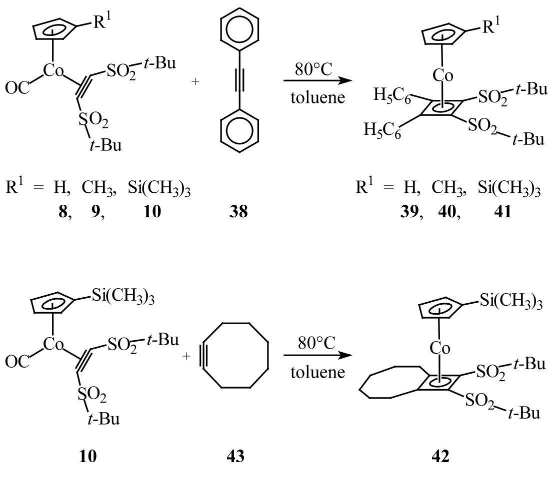
The investigations of the ^{13}C-NMR spectra reveal chemical shifts of the carbon signals of the cyclobutadiene ring adjacent to the SO$_2$-groups between $\delta = 76.1$ and 82.3. For the corresponding carbon atoms adjacent to the sulfur atoms we encounter signals between $\delta = 78.1$ and 87.0.

2.2. Further alkynes

To probe which kind of alkynes can replace the CO groups, further we studied reactions of **8**–**10** with tolane (**38**) and in part with cyclooctyne (**43**) (Scheme 4) to afford the corresponding cyclobutadiene products **39**–**42** in yields between 36 (**41**) and 60–75% as orange colored solids. The reaction had to be carried out at 80 °C in toluene, indicating less reactivity for **38** and **43** as compared to **14**–**16**.

3. Structural investigations

Of the 24 products (**18**–**37** and **39**–**42**) obtained from the reactions of **8**–**13**, **38** and **43** with the dithialkynes **14**–**17**, the products **24**–**26**, **30**, **36** and **39**–**41** yielded single crystals which could be investigated by X-ray diffraction. As examples, we show in Fig. 1, the molecular structures of **24**, **26**, **36** and **39**. The conformations of **24** and **25** in the solid state are similar. In both structures one phenyl group directs away from the metal, whereas the other phenyl–thio substituent is situated approximately in the plane of the cyclobutadiene ring. Both *tert*-butyl groups point away from the metal. In **26** both phenyl groups are directed away from the metal probably due to the bulky $SiMe_3$ group. Since in **26** both *tert*-butyl groups also point in the same direction as the phenyl groups, we expect considerable steric interactions in the space below the cyclobutadiene ring (see below). In the case of **36** (Fig. 1) two diagonally situated *tert*-butyl groups point below the plane of the cyclobutadiene ring, one above the plane, whereas the fourth is situated approximately in the plane of the cyclobutadiene ring. In **30** one mesityl group is directed towards the Cp ring, whereas the other three bulky groups point away from the metal. In **39**–**41** the *tert*-butylsulfonyl groups are pointing away from the metal, and the phenyl rings are twisted around



Scheme 4.

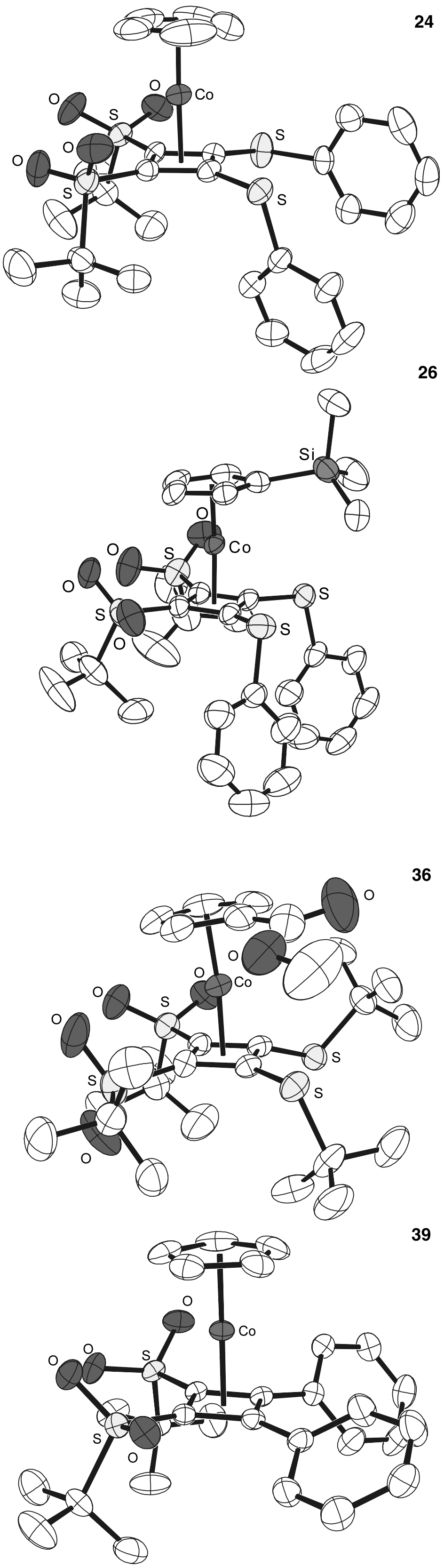


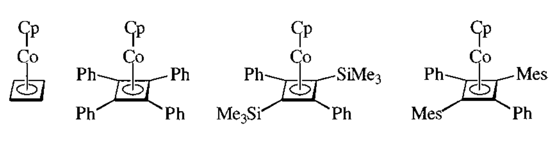
Fig. 1. ORTEP drawing of **24**, **26**, **36** and **39**. The heteroatoms are labeled, the H atoms have been omitted for the sake of clarity. Ellipsoids are at the 50% probability level.

Table 3
Selected distances (pm) and interplanar angles (°) of **24**–**26**, **30**, **36** and **39**–**41**

Compound	d(Co–Cp) [a]	d(Co–Cbd) [a]	∢(Cp–Cbd)	**a** [b]	**b** [b]	**c** [b]	
24	166	166	1.2	146	148	146	147
25	166	167	2.9	144	147	146	147
26	166	167	5.5	146	148	147	147
30	166	167	2.9	147	148	148	147
36	168	168	8.4	148	147	148	146
39	166	167	1.3	146	149	147	147
40	166	168	3.5	146	149	147	147
41	167	168	2.1	145	149	147	148

[a] Distances from the metal to the center of the corresponding rings.
[b] For the definition of **a**, **b**, **c** see Scheme 3.

the connecting C–C bonds. The relatively small methyl group of the methyl-cyclopentadienyl ligand is found to point in **40** towards the SO_2-groups, whereas in **41** the bulky $Si(CH_3)_3$ substituent points towards the phenyl groups. In comparison to **40** this reduces the strain energy within **41**, which allows both planes of the Cp- and Cbd-rings to be almost parallel in **41** as shown in Table 3. In Table 3 we have compared the most relevant bond lengths and angles of **24**–**26**, **30**, **36** and **39**–**41**. An examination of the cyclobutadiene rings in the molecules **24**–**26**, **30** and **36** shows very similar bond lengths on all four sides. There is no indication of bond alternation in the four-membered ring due to a donor–acceptor interaction. We notice that the bond lengths **b** between the *tert*-butylsulfonyl groups are slightly longer (147–148 pm) than **a** and **c** (Scheme 3). This lengthening we ascribe to repulsions between the adjacent bulky *tert*-butylsulfonyl groups. An indication of steric repulsion is also encountered if we consider the angle between the planes of the cyclopentadienyl and the cyclobutadiene rings. Both planes are almost parallel in **24**, whereas in all other structures there is a deviation by 3–8°. The most pronounced deviation occurs in **26** and **36**, for which relatively large substituents on the Cp ring interfere with bulky groups on the cyclobutadiene moiety of the molecule. A comparison with the structural data of other CpCo–cyclobutadiene complexes, such as **44**–**47** [14–17] reveals very similar bond lengths for the Cp–Co and Cbd–Co distance and for the distances within the cyclobutadiene rings (Table 4) as found in our cases. This supports our statement that there is no indication of a donor–acceptor influence in our samples.



44 **45** **46** **47**

Formula 1

4. Conclusion

We have shown that the CO group in complexes **8**–**13** can be replaced by electron rich as well as alkyl and phenyl substituted alkynes to yield the corresponding CpCo-stabilized cyclobutadiene complexes. This reaction opens a convenient and simple route to a new class of formally donor–acceptor substituted cyclobutadiene complexes, which are stable at room temperature and resistant to water and oxygen. The X-ray studies reveal almost equal C–C-distances within the cyclobutadiene rings.

5. Experimental

5.1. General methods

Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under Argon. Toluene was dried with sodium-benzophenone and distilled under Ar before use; petroleum ether and Et_2O were distilled before use. M.p. are uncorrected. Materials

Table 4
Selected distances (pm) of **44**–**47**

Compound	d(Co–Cp) [a] (pm)	d(Co–Cbd) [a] (pm)	d(C–C)(Cbd) [b] (pm)
44 [14]	166	168	144
45 [15]	167	169	145
46 [16]	167	169	147 146 147 147
47 [17]	169	170	146 147 146 146

[a] Distances from the metal to the center of the corresponding rings.
[b] Average C–C bond lengths of the cyclobutadiene rings.

used for column chromatography: silica gel 60 (Machery–Nagel). ^{1}H- and ^{13}C-NMR: Bruker AS 200 (^{1}H at 200 MHz and ^{13}C at 50.33 MHz), Bruker Avance 300 (^{1}H at 300 MHz and ^{13}C at 75.47 MHz), Bruker Avance 500 (^{1}H at 500 MHz and ^{13}C at 125.77 MHz) using the solvent as internal standard. IR: Bruker Vector 22 FT–IR. MS: low resolution: ZAB-2F; high resolution: JEOL JMS-700. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. The complexes **8**–**13** and the bis(arylthio)-–bis(alkylthio)acetylenes **14**–**17** were prepared according to literature methods. Tolane (**38**) was purchased from Acros and recrystallized from EtOH before use. Cyclooctyne was prepared according to literature procedure [18].

*5.2. General procedure for the preparation of the cyclobutadiene complexes **18**–**37** and **39**–**42***

The appropriate monoalkynecobalt complex is dissolved in 60 ml of $C_6H_5CH_3$ and the alkyne is added in one portion. The reaction mixture is stirred at room temperature (**18**–**32**), at 90 °C (**33**–**37**) or at 80 °C (**39**–**42**). After completion of the reaction, the solvent is removed by rotary evaporation and the crude product is purified by column chromatography (SiO_2, petroleum ether–Et_2O 1:1).

*5.2.1. (η^5-Cyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(n-butylthio)cyclobutadiene]cobalt(I) (**18**)*

Starting material: 252 mg (0.60 mmol) of CpCo(CO)(BTSA) (**8**) and 121 mg (0.60 mmol) of bis(*n*-butylthio)acetylene (**14**). Yield: 261 mg (73%) of **18** as a yellow solid, m.p. 70 °C. — ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.94$ (t, 6H, $\mathrm{CH_2C}\mathit{H}_3$, $^3J = 7.3$ Hz), 1.44 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.45 (s, 18H, $\mathrm{C(CH_3)_3}$), 1.62 (m, 4H, $\mathrm{SCH_2C}\mathit{H}_2$), 3.02 (m, 4H, $\mathrm{SC}\mathit{H}_2$), 5.37 (s, 5H, Cp–H). — ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 14.4$ ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.7 ($\mathit{C}\mathrm{H_2CH_3}$), 25.1 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 31.9 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$), 37.5 ($\mathrm{SCH_2}$), 62.0 ($\mathit{C}\mathrm{(CH_3)_3}$), 77.5 ($\mathit{C}$(CBD)–$SO_2$*t*Bu), 85.7 ($\mathit{C}$(CBD)–S*n*Bu), 85.9 (Cp–C). — IR (KBr): $\tilde{\nu} = 2959$, 2929, 2868, 1420, 1309 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.24), 314 (4.02), 356 nm (3.53). — HRMS (FAB+) $C_{25}H_{41}CoO_4S_4$: Calc.: 592.1220; Found: 592.1232%.

*5.2.2. (η^5-Methylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(n-butylthio)cyclobutadiene]-cobalt(I) (**19**)*

Starting material: 260 mg (0.60 mmol) of MeCpCo(CO)(BTSA) (**9**) and 121 mg (0.06 mmol) of bis(*n*-butylthio)acetylene (**14**). Yield: 251 mg (69%) of **19** as a orange oil. — ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 0.94$ (t, 6H, $\mathrm{CH_2C}\mathit{H}_3$, $^3J = 7.3$ Hz), 1.42 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.44 (s, 18H, $\mathrm{C(CH_3)_3}$), 163 (m, 4H, $\mathrm{SCH_2C}\mathit{H}_2$), 2.09 (s, 3H, Cp–$CH_3$), 2.98 (m, 4H, $\mathrm{SC}\mathit{H}_2$), 5.16/5.29 (pt, 4H, Cp–H). — ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 12.77$ (Cp–CH_3), 14.4 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.7 ($\mathit{C}\mathrm{H_2CH_3}$), 25.2 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 32.0 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$), 37.0 ($\mathrm{SCH_2}$), 62.0 ($\mathit{C}\mathrm{(CH_3)_3}$), 76.9 ($\mathit{C}$(CBD)–$SO_2$*t*Bu), 84.5 ($\mathit{C}$(CBD)–S*n*Bu), 84.9/86.5 (CpC–H), 100.6 (CpC–CH_3). — IR (film): $\tilde{\nu} = 2961$, 2872, 1461, 1352, 1310 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 252 (4.26), 316 (4.11), 354 nm (3.45). — MS (EI+): 606 [M$^+$], 485, 352, 259. — HRMS (FAB+) $C_{26}H_{43}CoO_4S_4$: Calc.: 606.1376; Found: 606.1384%.

*5.2.3. (η^5-Trimethylsilylcyclopentadienyl)[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(n-butylthio)cyclobutadiene]cobalt(I) (**20**)*

Starting material: 245 mg (0.50 mmol) of $Me_3SiCpCo(CO)$(BTSA) (**10**) and 121 mg (0.60 mmol) of bis(*n*-butylthio)acetylene (**14**). Yield: 259 mg (78%) of **20** as a orange oil. — ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.33$ (s, 9H, $\mathrm{Si(CH_3)_3}$), 0.91 (t, 6H, $\mathrm{CH_2C}\mathit{H}_3$, $^3J = 7.3$ Hz), 1.45 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.46 (s, 18H $\mathrm{C(CH_3)_3}$), 1.60 (m, 4H, $\mathrm{SCH_2C}\mathit{H}_2$), 2.95 (m, 4H, $\mathrm{SC}\mathit{H}_2$), 5.24/5.73 (pt, 4H, Cp–H). — ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 0.3$ ($\mathrm{Si(CH_3)_3}$), 14.4 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.7 ($\mathit{C}\mathrm{H_2CH_3}$), 25.3 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 32.0 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$), 37.5 ($\mathrm{SCH_2}$), 62.2 ($\mathit{C}\mathrm{(CH_3)_3}$), 76.6 ($\mathit{C}$(CBD)–$SO_2$*t*Bu), 85.6 ($\mathit{C}$(CBD)–S*n*Bu), 88.8/90.0 (CpC–H), 94.2 (CpC–$SiMe_3$). — IR (film): $\tilde{\nu} = 2959$, 2931, 2873, 1463, 1314, 1121, 841, 704, 544 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 258 (4.17), 320 (4.08), 366 nm (3.42). — HRMS (FAB+) [M$^+$] $C_{28}H_{49}CoO_4S_4Si$: Calc.: 664.1615; Found: 664.1588%.

*5.2.4. (η^5-Methoxycarbonylcyclopentadienyl)[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(n-butylthio)cyclobutadiene]cobalt(I) (**21**)*

Starting material: 238 mg (0.50 mmol) of $CpCO_2MeCo(CO)$(BTSA) (**11**) and 101 mg (0.50 mmol) of bis(*n*-butylthio)acetylene (**14**). Yield: 160 mg (49%) of **21** as a orange oil. — ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 0.95$ (t, 6H, $\mathrm{CH_2C}\mathit{H}_3$, $^3J = 7.3$ Hz), 1.44 (m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.45 (s, 18H, $\mathrm{C(CH_3)_3}$), 1.60 (m, 4H, $\mathrm{SCH_2C}\mathit{H}_2$), 3.06 (m, 4H, $\mathrm{SC}\mathit{H}_2$), 3.87 (s, 3H, CO_2CH_3), 5.63/5.78 (pt, 4H, Cp–H). — ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 14.4$ ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.7 ($\mathit{C}\mathrm{H_2CH_3}$), 25.1 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 32.0 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$), 36.0 ($\mathrm{SCH_2}$), 52.7 ($\mathrm{CO_2}\mathit{C}\mathrm{H_3}$), 62.4 ($\mathit{C}\mathrm{(CH_3)_3}$), 77.8 ($\mathit{C}$(CBD)–$SO_2$*t*Bu), 87.0 ($\mathit{C}$(CBD)–S*n*Bu), 86.9/88.7 (CpC–H), 90.7 (CpC–CO_2Me), 166.1 ($\mathit{C}\mathrm{O_2CH_3}$). — IR (film): $\tilde{\nu} =$ 2960, 1725, 1470, 1312, 1194 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.45), 322 (4.15), 366 nm (3.69). — MS (FAB+): 650 [M$^+$], 577. — HRMS (FAB+) [M$^+$] $C_{27}H_{43}CoO_6S_4$: Calc.: 650.1275; Found: 650.1280%.

5.2.5. *(η^5-Acetylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(n-butylthio)cyclobutadiene]-cobalt(I)* (**22**)

Starting material: 240 mg (0.52 mmol) of AcCp-Co(CO)(BTSA) (**12**) and 105 mg (0.52 mmol) of bis(*n*-butylthio)acetylene (**14**). Yield: 174 mg (53%) of **22** as a orange oil. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 0.94$ (t, 6H, CH$_2$C*H*$_3$, $^3J = 7.3$ Hz), 1.43 (s, 18H, C(CH$_3$)$_3$), 1.44 (m, 4H, C*H*$_2$CH$_3$), 1.60 (m, 4H, SCH$_2$C*H*$_2$), 2.50 (s, 3H, C(O)CH$_3$), 3.03 (m, 4H, SC*H*$_2$), 5.64/5.85 (pt, 4H, Cp–H). — ^{13}C-NMR (50 MHz, CDCl$_3$): $\delta = 14.4$ (CH$_2$*C*H$_3$) 22.7 (*C*H$_2$CH$_3$), 25.1 (C(*C*H$_3$)$_3$), 29.4 (C(O)*C*H$_3$), 32.0 (SCH$_2$*C*H$_2$), 36.1 (SCH$_2$), 62.4 (*C*(CH$_3$)$_3$), 78.1 (*C*(CBD)–SO$_2$*t*Bu), 86.9 (*C*(CBD)–S*n*Bu), 86.3/88.7 (CpC–H), 97.0 (Cp*C*–CO$_2$Me), 197.7 (*C*(O)CH$_3$). — IR (film): $\tilde{\nu} = 2962$, 2932, 1682, 1460, 1312 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (log ε) = 246 (4.38), 326 (4.12), 366 nm (3.60). — MS (FAB +): 635 [M + H$^+$], 561. — HRMS (FAB +) [M$^+$] C$_{27}$H$_{43}$CoO$_5$S$_4$: Calc.: 634.1325; Found: 634.2152%.

5.2.6. *(η^5-1-Ethyl-2,3,4,5-tetramethylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(n-butylthio)-cyclobutadiene]cobalt(I)* (**23**)

Starting material: 251 mg (0.50 mmol) of EtMe$_4$CpCo(CO)(BTSA) (**13**) and 121 mg (0.60 mmol) of bis(*n*-butylthio)acetylene (**14**). Yield: 125 mg (37%) of **23** as a yellow solid, m.p. 84 °C. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 0.92$ (t, 6H, CH$_2$C*H*$_3$, $^3J = 7.3$ Hz), 1.40 (s, 18H, C(CH$_3$)$_3$), 1.40 (m, 4H, CH$_2$C*H*$_2$CH$_3$), 1.60 (m, 4H, SCH$_2$C*H*$_2$), 1.91/1.93 (s, 12H, Cp–CH$_3$), 2.50 (q, 2H, Cp–C*H*$_2$CH$_3$), 2.78 (m, 4H, SC*H*$_2$). — ^{13}C-NMR (75 MHz, CDCl$_3$): $\delta = 10.0/10.2$ (Cp–CH$_3$), 14.4 (CH$_2$*C*H$_3$), 18.4 (Cp–*C*H$_2$CH$_3$), 22.9 (*C*H$_2$CH$_3$), 25.7 (C(*C*H$_3$)$_3$), 32.1 (SCH$_2$*C*H$_2$), 36.8 (SCH$_2$), 62.3 (*C*(CH$_3$)$_3$), 76.1 (*C*(CBD)–SO$_2$*t*Bu), 79.4 (*C*(CBD)–S*n*Bu), 95.4/96.4 (Cp*C*–CH$_3$), 100.7 (Cp*C*–CH$_2$-CH$_3$). — IR (film): $\tilde{\nu} = 2960$, 2929, 1458, 1360 cm^{-1}. — UV–vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (log ε) = 266 (4.01), 322 (4.04), 360 nm (3.20). — HRMS (EI +): [M$^+$] C$_{31}$H$_{53}$CoO$_4$S$_4$: Calc.: 676.2159; Found: 676.2152%.

5.2.7. *(η^5-Cyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(phenylthio)cyclobutadiene]cobalt(I)* (**24**)

Starting material: 230 mg (0.55 mmol) of Cp-Co(CO)(BTSA) (**8**) and 160 mg (0.66 mmol) of bis(phenylthio)acetylene (**15**). Yield: 196 mg (56%) of **24** as a orange solid, m.p. 186 °C. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 1.47$ (s, 18H, C(CH$_3$)$_3$), 5.28 (s, 5H, Cp–H), 7.30 (m, 10H, Ph–H). — ^{13}C-NMR (75 MHz, CDCl$_3$): $\delta = 25.1$ (C(*C*H$_3$)$_3$), 62.1 (*C*(CH$_3$)$_3$), 80.9 (*C*(CBD)–SO$_2$*t*Bu), 82.5 (*C*(CBD)–SPh), 87.0 (Cp–C), 128.2 (Ph–C$_{para}$), 129.4/131.1 (Ph–C$_{ortho/meta}$), 135.7 (Ph–C–S). — IR (KBr): $\tilde{\nu} = 2982$, 1478, 1308, 1121, 827, 718, 692, 554 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (log ε) = 248 (4.44), 296 nm (4.04). — HRMS (EI +) C$_{29}$H$_{33}$CoO$_4$S$_4$: Calc.: 632.0594; Found: 632.0589%. — C$_{29}$H$_{33}$CoO$_4$S$_4$ (632.1): Calc.: C, 55.05; H, 5.26; S, 20.27. Found: C, 54.98; H, 5.35; S, 20.00%.

5.2.8. *(η^5-Methylcyclobutadienyl)-(η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(phenylthio)cyclobutadiene]cobalt(I)* (**25**)

Starting material: 238 mg (0.55 mmol) of CpMe-Co(CO)(BTSA) (**9**) and 160 mg (0.66 mmol) of bis(phenylthio)acetylene (**15**). Yield: 231 mg (65%) of **25** as a orange solid, m.p. 180 °C. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 1.41$ (s, 18H, C(CH$_3$)$_3$), 2.14 (s, 3H, Cp–CH$_3$), 5.02/5.25 (pt, 4H, Cp–H), 7.21 (m, 10H, Ph–H). — ^{13}C-NMR (75 MHz, CDCl$_3$): $\delta = 12.9$ (Cp–CH$_3$), 25.2 (C(*C*H$_3$)$_3$), 62.1 (*C*(CH$_3$)$_3$), 80.4 (*C*(CBD)–SO$_2$*t*Bu), 81.0 (*C*(CBD)–SPh), 86.2/87.3 (Cp–C–H), 101.8 (Cp–*C*–CH$_3$), 127.9 (Ph–C$_{para}$), 129.3/130.9 (Ph–C$_{ortho/meta}$), 135.4 (Ph–C–S). — IR (KBr): $\tilde{\nu} = 3050$, 2988, 2929, 1579, 1477, 1355, 1304 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (log ε) = 250 (4.37), 300 nm (4.01). — HRMS (EI +): [M$^+$] C$_{30}$H$_{35}$CoO$_4$S$_4$: Calc.: 646.0750; Found: 646.0766%. C$_{30}$H$_{35}$CoO$_4$S$_4$ (646.1): Calc.: C, 55.71; H, 5.45; S, 19.83. Found: C, 55.67; H, 5.52; S, 19.63%.

5.2.9. *(η^5-Trimethylsilylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(phenylthio)-cyclobutadiene]cobalt(I)* (**26**)

Starting material: 245 mg (0.50 mmol) of CpSiMe$_3$Co(CO)(BTSA) (**10**) and 145 mg (0.60 mmol) of bis(phenylthio)acetylene (**15**). Yield. 217 mg (62%) of **26** as a orange solid, m.p. 137 °C. — ^{1}H-NMR (500 MHz, CDCl$_3$): $\delta = 0.35$ (s, 9H, Si(CH$_3$)$_3$), 1.38 (s, 18H, C$_8$CH$_3$)$_3$), 4.96/5.77 (pt, 4H, Cp–H), 7.15 (m, 10H, Ph–H). — ^{13}C-NMR (125 MHz, CDCl$_3$): $\delta = 0.4$ (Si(CH$_3$)$_3$), 25.2 (C(*C*H$_3$)$_3$), 62.3 (*C*(CH$_3$)$_3$), 80.5 (*C*(CBD)–SO$_2$*t*Bu), 82.1 (*C*(CBD)–SPh), 89.7/91.5 (Cp–C–H), 95.2 (Cp–*C*–SiMe$_3$), 127.9 (Ph–C$_{para}$), 129/130.9 (Ph–C$_{ortho/meta}$), 135.9 (Ph–C–S). — IR (KBr): $\tilde{\nu} = 2955$, 1581, 1477, 1310 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ (log ε) = 248 (4.30), 300 nm (4.01). — HRMS (FAB +) C$_{32}$H$_{41}$CoO$_4$S$_4$Si: Calc.: 704.0989; Found: 704.0982%. C$_{32}$H$_{41}$CoO$_4$S$_4$Si (704.1): Calc.: C, 54.52; H, 5.86; S, 18.19. Found: C, 54.51; H, 6.02; S, 18.04%.

5.2.10. *(η^5-Methoxycarbonylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(phenylthio)cyclobutadiene]cobalt(I)* (**27**)

Starting material: 238 mg (0.50 mmol) of CpCO$_2$MeCo(CO)(BTSA) (**11**) and 145 mg (0.60 mmol) of bis(phenylthio)acetylene (**15**). Yield: 161 mg (42%) of **27** as a yellow solid, m.p. 125 °C. — ^{1}H-NMR (500 MHz, CDCl$_3$): $\delta = 1.41$ (s, 18H, C(CH$_3$)$_3$), 3.93 (s, 3H, CO$_2$CH$_3$), 5.63/5.72 (pt, 4H, Cp–H), 7.10 (m, 10H, Ph–H). — ^{13}C-NMR (125 MHz, CDCl$_3$): $\delta = 25.0$ (C(*C*H$_3$)$_3$), 52.9 (CO$_2$*C*H$_3$), 62.5 (*C*(CH$_3$)$_3$), 80.7 (*C*(CBD)–SO$_2$*t*Bu), 83.3 (*C*(CBD)–SPh), 88.4/89.4 (Cp–C–H), 91.1 (Cp–*C*–CO$_2$Me), 128.2 (Ph–C$_{para}$), 129.3/131.1 (Ph–C$_{ortho/meta}$), 133.4 (Ph–C–S), 165.5 (*C*O$_2$Me). — IR (KBr): $\tilde{\nu} = 2949$, 1726, 1474, 1308, 1285 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 246 (4.45), 306 nm (4.03). — HRMS (FAB+) C$_{31}$H$_{35}$CoO$_6$S$_4$: Calc.: 690.0649; Found: 690.0690%. — C$_{31}$H$_{35}$CoO$_6$S$_4$ (690.0): Calc.: C, 53.90; H, 5.11; S, 18.57. Found: C, 53.98; H, 5.20; S, 18.56%.

5.2.11. (η^5-Acetylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(phenylthio)cyclobutadiene]cobalt(I) (**28**)

Starting material: 230 mg (0.50 mmol) of AcCp-Co(CO)(BTSA) (**12**) and 145 mg (0.60 mmol) of bis(phenylthio)acetylene (**15**). Yield: 157 mg (46%) of **28** as a orange solid, m.p. 138 °C. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 1.39$ (s, 18H, C(CH$_3$)$_3$), 2.57 (s, 3H, C(O)CH$_3$), 5.62/5.71 (pt, 4H, Cp–H), 7.11 (m, 10H, Ph–H). — ^{13}C-NMR (75 MHz, CDCl$_3$): $\delta = 25.1$ (C(*C*H$_3$)$_3$), 29.5 (C(O)*C*H$_3$), 62.5 (*C*(CH$_3$)$_3$), 80.9 (*C*(CBD)–SO$_2$*t*Bu), 83.1 (*C*(CBD)–SPh), 87.5/89.6 (Cp–C–H), 97.2 (Cp–*C*–Ac), 128.3 (Ph–C$_{para}$), 129.3/131.3 (Ph–C$_{ortho/meta}$), 133.1 (Ph–C–S), 197.0 (C(O)Me). — IR (KBr): $\tilde{\nu} = 2971$, 1681, 1309 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 246 (4.42), 308 nm (4.04). — HRMS (FAB+) [M$^+$] C$_{31}$H$_{35}$CoO$_5$S$_4$: Calc.: 674.0699; Found: 674.0711%. — C$_{31}$H$_{35}$CoO$_5$S$_4$ (674.8): Calc.: C, 55.18; H, 5.23; S, 19.01. Found: C, 55.04; H, 5.20; S, 18.95%.

5.2.12. (η^5-1-Ethyl-2,3,4,5-tetramethylcyclopentadienyl)[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(phenylthio)-cyclobutadiene]cobalt(I) (**29**)

Starting material: 231 mg (0.46 mmol) of EtMe$_4$CpCo(CO)(BTSA) (**13**) and 134 mg (0.55 mmol) of bis(phenylthio)acetylene (**15**). Yield: 85 mg (26%) of **29** as a yellow solid, m.p. 161 °C. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 1.04$ (t, 3H, CH$_2$C*H*$_3$, $^3J = 7.6$ Hz), 1.29 (s, 18H, C(CH$_3$)$_3$), 2.03/2.04 (s, 12H, Cp–CH$_3$), 2.63 (q, 2H, C*H*$_2$CH$_3$, $^3J = 7.6$ Hz), 6.95 (m, 10H, Ph–H). — ^{13}C-NMR (75 MHz, CDCl$_3$): $\delta = 10.0/10.3$ (Cp–CH$_3$), 14.3 (CH$_2$*C*H$_3$), 18.3 (*C*H$_2$CH$_3$), 25.5 (C(*C*H$_3$)$_3$), 62.4 (*C*(CH$_3$)$_3$), 76.1 (*C*(CBD)–SO$_2$*t*Bu), 78.1 (*C*(CBD)–SPh), 96.1/97.2 (Cp*C*–CH$_3$), 101.2 (Cp*C*–CH$_2$CH$_3$), 127.5 (Ph–C$_{para}$), 128.9/131.1 (Ph–C$_{ortho/meta}$), 134.6 (Ph–C–S). — IR (KBr): $\tilde{\nu} =$ 2966, 2928, 1476, 1307 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 256 (4.47), 316 (4.36), 362 nm (3.70). — HRMS (FAB+) [M+H$^+$] C$_{35}$H$_{46}$CoO$_4$S$_4$: Calc.: 717.1611; Found: 717.1580%. C$_{35}$H$_{45}$CoO$_4$S$_4$ (717.2): Calc.: C, 58.64; H, 6.33. Found: C, 58.42; H, 6.25%.

5.2.13. (η^5-Cyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(mesitylthio)cyclobutadiene]cobalt(I) (**30**)

Starting material: 230 mg (0.55 mmol) of Cp-Co(CO)(BTSA) (**8**) and 180 mg (0.55 mmol) of bis(mesitylthio)acetylene (**16**). Yield: 258 mg (65%) of **30** as a yellow solid, m.p. 218 °C. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 1.28$ (s, 18H, C(CH$_3$)$_3$), 2.28 (s, 6H, Ph–CH$_3$), 2.64 (12H, Ph–CH$_3$), 4.99 (s, 5H, Cp–H), 6.91 (s, 4H, Ph–H). — ^{13}C-NMR (125 MHz, CDCl$_3$): $\delta = 21.4$ (Ph–CH$_{3(para)}$), 23.4 Ph–CH$_{3(ortho)}$), 25.0 (C(*C*H$_3$)$_3$), 62.3 (*C*(CH$_3$)$_3$), 81.1 (*C*(CBD)–SO$_2$*t*Bu), 85.3 (*C*(CBD)–SMes), 86.5 (Cp–C), 129.5 (Ph–C$_{meta}$), 131.5 (PhC–S), 139.5 (Ph–C$_{para}$), 143.4 (Ph–C$_{ortho}$). — IR (KBr): $\tilde{\nu} = 3124$, 2967, 2922, 1460 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 252 (4.29), 300 (3.93), 324 nm (3.82). — HRMS (FAB+): C$_{35}$H$_{45}$CoO$_4$S$_4$: Calc.: 716.1533; Found: 716.1531%.

5.2.14. (η^5-Trimethylsilylcyclopentadienyl)-[η^4-1,2-bis-(tert-butylsulfonyl)-3,4-bis(mesitylthio)cyclobutadiene]-cobalt(I) (**31**)

Starting material: 245 mg (0.50 mmol) of CpSiMe$_3$Co(CO)(BTSA) (**10**) and 163 mg (0.50 mmol) of bis(mesitylthio)acetylene (**16**). Yield: 50 mg (13%) of **31** as a yellow solid, m.p. 195 °C. — ^{1}H-NMR (500 MHz, CDCl$_3$): $\delta = 0.23$ (s, 9H, Si(CH$_3$)$_3$), 1.22 (s, 18H, C(CH$_3$)$_3$), 2.27 (s, 6H, Ph–CH$_3$), 2.67 12H, Ph–CH$_3$), 4.59/5.45 (pt, 4H, Cp–H), 6.91 (s, 4H, Ph–H). — ^{13}C-NMR (50 MHz, CDCl$_3$): $\delta = -0.03$ (Si(CH$_3$)$_3$), 21.6 (Ph–CH$_{3(para)}$), 24.3 (Ph–CH$_{3(ortho)}$), 25.4 (C(*C*H$_3$)$_3$), 62.8 (*C*(CH$_3$)$_3$), 81.8 (*C*(CBD)–SO$_2$*t*Bu), 85.2 (*C*(CBD)–SMes), 88.6/91.3 (CpC–H), 95.7 (CpC–SiMe$_3$), 129.9 (PhC$_{meta}$), 132.7 (PhC–S), 139.8 (PhC$_{para}$), 144.0 (PhC$_{ortho}$). — IR (KBr): $\tilde{\nu} =$ 2955, 1462, 1309 cm^{-1}. — UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 264 (4.20), 314 (3.81), 366 nm (3.27). — HRMS (FAB+) [M+H$^+$] C$_{38}$H$_{54}$CoO$_4$S$_4$Si: Calc.: 789.2006; Found: 789.2021%.

5.2.15. (η^5-Acetylcyclopentadienyl)-[η^4-1,2-bis-(tert-butylsulfonyl)-3,4-bis(mesitylthio)cyclobutadiene]-cobalt(I) (**32**)

Starting material: 85 mg (0.18 mmol) of AcCp-Co(CO)(BTSA) (**12**) and 60 mg (0.18 mmol) of bis(mesitylthio)acetylene (**16**). Yield: 56 mg (41%) of **32** as a yellow solid, m.p. 219 °C. — ^{1}H-NMR (300 MHz, CDCl$_3$): $\delta = 1.26$ (s, 18H, C(CH$_3$)$_3$), 2.26 (s, 6H, Ph–CH$_3$), 2.55 (s, 3H, C(O)CH$_3$), 2.58 (12H, Ph–CH$_3$), 5.17/5.35 (pt, 4H, Cp–H), 6.92 (s, 4H, Ph–H). — ^{13}C-NMR (75 MHz, CDCl$_3$): $\delta = 21.6$ (Ph–CH$_{3(para)}$), 23.7 (Ph–CH$_{3(ortho)}$), 25.3 (C(*C*H$_3$)$_3$), 29.6 (C(O)CH$_3$), 62.9 (*C*(CH$_3$)$_3$), 82.5 (*C*(CBD)–SO$_2$*t*Bu), 86.9 (*C*(CBD)–SMes), 87.9/88.6 (CpC–H), 96.6 (Cp*C*–Ac), 129.9 (PhC$_{meta}$), 131.0 (PhC–S), 140.1 (PhC$_{para}$), 144.1 (PhC$_{ortho}$), 197.1 (*C*(O)CH$_3$). — IR (KBr): $\tilde{\nu} =$

2926, 1685, 1461, 1309 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 258 (4.42), 318 (3.95), 378 nm (3.51). — HRMS (FAB+) [M+H$^+$] $C_{37}H_{48}CoO_5S_4$: Calc.: 759.1716; Found: 759.1755%. $C_{37}H_{47}CoO_5S_4$ (759.2): Calc.: C, 58.55; H, 6.24; S, 16.90. Found: C, 58.67; H, 6.30; S, 15.80%.

5.2.16. *(η^5-Cyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(tert-butylthio)cyclobutadiene]-cobalt(I)* (***33***)

Starting material: 230 mg (0.55 mmol) of CpCo(CO)(BTSA) (**8**) and 222 mg (1.10 mmol) of bis(*tert*-butylthio)acetylene (**17**). Yield: 99 mg (30%) of **33** as a yellow solid, m.p. 204 °C (dec.). — ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.48/1.50 (s, 36H, $C(CH_3)_3$), 5.38 (s, 5H, Cp–H). — ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 25.7 ($SO_2C(\mathit{C}H_3)_3$), 32.8 ($SC(\mathit{C}H_3)_3$), 50.8 ($S\mathit{C}(CH_3)_3$), 62.5 ($SO_2\mathit{C}(CH_3)_3$), 82.3 (*C*(CBD)–SO$_2$*t*Bu), 84.0 (*C*(CBD)–S*t*Bu), 87.8 (CpC). — IR (KBr): $\tilde{\nu}$ = 2965, 1632, 1460, 1307 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 260 (4.44), 314 (4.07), 352 (3.57), 366 nm (3.47). — HRMS (FAB+) [M+H$^+$] $C_{25}H_{42}CoO_4S_4$: Calc.: 593.1298; Found: 593.1332%. $C_{25}H_{41}CoO_4S_4$ (592.1): Calc.: C, 50.65; H, 6.97. Found: C, 50.61; H, 7.04%.

5.2.17. *(η^5-Methylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(tert-butylthio)cyclobutadiene]-cobalt(I)* (***34***)

Starting material: 239 mg (0.53 mmol) of CpMeCo(CO)(BTSA) (**9**) and 215 mg (1.06 mmol) of bis(*tert*-butylthio)acetylene (**17**). Yield: 101 mg (31%) of **34** as a orange solid, m.p. 138 °C (dec.). — ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.48/1.50 (s, 36H, $C(CH_3)_3$), 2.07 (s, 3H, Cp–CH_3), 5.15/5.34 (pt, 4H, Cp–H). — ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 12.7 (Cp–CH_3), 25.7 ($SO_2C(\mathit{C}H_3)_3$), 32.9 ($SC(\mathit{C}H_3)_3$), 50.4 ($S\mathit{C}(CH_3)_3$), 62.6 ($SO_2\mathit{C}(CH_3)_3$), 81.6 (*C*(CBD)–SO$_2$*t*Bu), 82.6 (*C*(CBD)–S*t*Bu), 86.4/88.9 (CpC–H), 101.4 (Cp*C*–Me). — IR (KBr): $\tilde{\nu}$ = 2966, 2922, 1472, 1305 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 262 (4.31), 316 nm (3.98). — HRMS (FAB+) [M+H$^+$] $C_{26}H_{44}CoO_4S_4$: Calc.: 607.1454; Found: 607.1413%. $C_{26}H_{43}CoO_4S_4$ (606.1): Calc.: C, 51.46; H, 7.14; S, 21.14. Found: C, 51.22; H, 7.14; S, 20.91%.

5.2.18. *(η^5-Trimethylsilylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(tert-butylthio)-cyclobutadiene]cobalt(I)* (***35***)

Starting material: 245 mg (0.50 mmol) of $CpSiMe_3Co(CO)(BTSA)$ (**10**) and 202 mg (1.00 mmol) of bis(*tert*-butylthio)acetylene (**17**). Yield: 42 mg (13%) of **35** as a orange solid, m.p. 84 °C (dec.). — ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.31 (s, 9H, $Si(CH_3)_3$), 1.48/1.49 (s, 36H, $C(CH_3)_3$), 5.30/5.76 (pt, 4H, Cp–H). — ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 0.3 ($Si(CH_3)_3$), 25.8 ($SO_2C(\mathit{C}H_3)_3$), 32.9 ($SC(\mathit{C}H_3)_3$), 50.9 ($S\mathit{C}(CH_3)_3$), 62.8 ($SO_2\mathit{C}(CH_3)_3$), 81.1 (*C*(CBD)–SO$_2$*t*Bu), 88.9 (*C*(CBD)–S*t*Bu), 93.7/94.6 (CpC–H), 95.1 (Cp*C*–SiMe$_3$). — IR (KBr): $\tilde{\nu}$ = 2961, 1314 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 264 (4.21), 320 nm (3.89). — HRMS (El+) $C_{28}H_{49}CoO_4S_4Si$: Calc.: 664.1615; Found: 664.1617%.

5.2.19. *(η^5-Methoxycarbonylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(tert-butylthio)-cyclobutadiene]cobalt(I)* (***36***)

Starting material: 238 mg (0.50 mmol) of $CpCo_2MeCo(CO)(BTSA)$ (**11**) and 202 mg (1.00 mmol) of bis(*tert*-butylthio)acetylene (**17**). Yield: 50 mg (15%) of **36** as a yellow solid, m.p. 150 °C (dec.). — ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.50/1.52 (s, 36H, $C(CH_3)_3$), 3.87 (s, 3H, CO_2CH_3), 5.65/5.81 (pt, 4H, Cp–H). — ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 24.9 ($SO_2C(\mathit{C}H_3)_3$), 32.2 ($SC(\mathit{C}H_3)_3$), 50.6 ($S\mathit{C}(CH_3)_3$), 52.0 ($CO_2\mathit{C}H_3$), 62.4 ($SO_2\mathit{C}(CH_3)_3$), 82.0 (*C*(CBD)–SO$_2$*t*Bu), 84.4 (*C*(CBD)–S*t*Bu), 88.3/89.4 (CpC–H), 90.5 (Cp*C*–CO$_2$Me), 165.2 ($\mathit{C}O_2CH_3$). — IR (KBr): $\tilde{\nu}$ = 2960, 1724, 1473 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 248 (4.75), 310 nm (4.40). — HRMS (FAB+): [M+H$^+$] $C_{27}H_{44}CoO_6S_4$: Calc.: 651.1353; Found: 651.1385%. $C_{27}H_{43}CoO_6S_4$ (651.1): Calc.: C, 49.83; H, 6.66; S, 19.71. Found: C, 49.62; H, 6.66; S, 19.68%.

5.2.20. *(η^5-Acetylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-bis(tert-butylthio)-cyclobutadiene]cobalt(I)* (***37***)

Starting material: 230 mg (0.50 mmol) of AcCpCo(CO)(BTSA) (**12**) and 202 mg (1.00 mmol) of bis(-*tert*-butylthio)acetylene (**17**). Yield: 54 mg (17%) of **37** as a yellow solid, m.p. 177 °C (dec.). — ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.48/1.50 (s, 36H, $C(CH_3)_3$), 2.49 (s, 3H, $C(O)CH_3$), 5.71/5.86 (pt, 4H, Cp–H). — ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 25.7 ($SO_2C(\mathit{C}H_3)_3$), 29.3 ($C(O)\mathit{C}H_3$), 32.8 ($SC(\mathit{C}H_3)_3$), 51.5 ($S\mathit{C}(CH_3)_3$), 62.9 ($SO_2\mathit{C}(CH_3)_3$), 83.0 (*C*(CBD)–SO$_2$*t*Bu), 85.1 (*C*(CBD)–S*t*Bu), 89.5/89.7 (CpC–H), 97.0 (Cp*C*–Ac), 196.7 ($\mathit{C}(O)CH_3$). — IR (KBr): $\tilde{\nu}$ = 2964, 1683, 1461, 1368 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 260 (4.56), 310 nm (4.20). — HRMS (FAB+) [M+H$^+$] $C_{27}H_{44}CoO_5S_4$: Calc.: 635.1404; Found: 635.1431%. $C_{27}H_{43}CoO_5S_4$ (634.1): Calc.: C, 51.08; H, 6.83; S, 20.20. Found: C, 50.86; H, 6.83; S, 20.21%.

5.2.21. *(η^5-Cyclopentadienyl)-[η^4-1,2-bis-(tert-butylsulfonyl)-3,4-diphenylcyclobutadiene]cobalt(I)* (***39***)

Starting material: 209 mg (0.50 mmol) of CpCo(CO)(BTSA) (**8**) and 89 mg (3.34 mmol) of tolane (**38**). Yield: 209 mg (62%) of **39** as a orange solid. —

^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.33$ (s, 18H, C(CH$_3$)$_3$), 5.27 (s, 5H, Cp–H), 7.26 (m, 6H, Ph–H), 7.60 (m, 4H, Ph–H). — ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta =$ 24.9 (C(*C*H$_3$)$_3$), 61.8 (*C*(CH$_3$)$_3$), 76.5 (*C*(CBD)–Ph), 82.5 (*C*(CBD)–SO$_2$*t*Bu), 86.0 (Cp–C), 128.2/130.6 (Ph–C$_{ortho/meta}$), 128.3 (Ph–C$_{para}$), 131.7 (Ph*C*–CBD). — IR (KBr): $\tilde{\nu} = 2971$, 2931, 1631, 1443, 1307, 1117 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.30), 264 (4.22), 302 (3.98), 350 (3.27), 396 nm (2.92). — HRMS (FAB+) $C_{29}H_{33}CoO_4S_2$: Calc.: 568.1152; Found: 568.1169%.

5.2.22. *(η^5-Methylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-diphenylcyclobutadiene]cobalt(I) (**40**)*

Starting material: 50 mg (0.12 mmol) of MeCpCo(CO)(BTSA) (**9**) and 21 mg (0.12 mmol) of tolane (**38**). Yield: 44 mg (66%) of **40** as a orange solid. — ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.31$ (s, 18H, C(CH$_3$)$_3$), 1.57(s, 3H, Cp–CH$_3$), 5.07 (pt, 2H, Cp–H), 5.26 (pt, 2H, Cp–H), 7.26 (m, 6H, Ph–H), 7.60 (m, 4H, Ph–H). — ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 11.4$ (Cp–CH$_3$), 25.0 (C(*C*H$_3$)$_3$), 61.9 (*C*(CH$_3$)$_3$), 77.2 (*C*(CBD)–Ph), 81.7 (*C*(CBD)–SO$_2$*t*Bu), 85.0/86.6 (Cp–C), 99.7 (Cp*C*–Me), 128.1 (Ph–C$_{para}$), 128.2/130.4 (Ph–C$_{ortho/meta}$), 131.8 (Ph*C*–CBD). — IR (KBr): $\tilde{\nu} =$ 2973, 2930, 1475, 1443, 1308, 1116 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 248 (4.42), 274 (4.38), 310 (4.15), 358 nm (3.61). — HRMS (FAB+) $C_{30}H_{35}CoO_4S_2$: Calc.: 582.1309; Found: 582.1356%.

5.2.23. *(η^5-Trimethylsilylcyclopentadienyl)-[η^4-1,2-bis(tert-butylsulfonyl)-3,4-diphenylcyclobutadiene]cobalt(I) (**41**)*

Starting material: 172 mg (0.35 mmol) of Me$_3$SiCpCo(CO)(BTSA) (**10**) and 62 mg (0.35 mmol) of tolane (**38**). Yield: 80 mg (36%) of **41** as a orange solid. — ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = -0.22$ (s, 9H, Si(CH$_3$)$_3$), 1.28 (s, 18H, C(CH$_3$)$_3$), 5.23 (pt, 2H, Cp–H), 5.91 (pt, 2H, Cp–H), 7.29 (m, 6H, Ph–H), 7.72 (m, 4H, Ph–H). — ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta =$ −0.7 (Si(CH$_3$)$_3$), 24.3 (C(*C*H$_3$)$_3$), 61.3 (*C*(CH$_3$)$_3$), 76.7 (*C*(CBD)–Ph), 81.8 (*C*(CBD)–SO$_2$*t*Bu), 87.5/89.6 (Cp–C), 92.4 (Cp*C*–SiMe$_3$), 127.4/130.3 (Ph–C$_{ortho/meta}$), 127.7 (Ph–C$_{para}$), 131.3 (Ph*C*–CBD). — HRMS (FAB+) $C_{32}H_{41}CoO_4S_2Si$: Calc.: 640.1548; Found: 640.1552%.

5.2.24. *(η^5-Trimethylsilylcyclopentadienyl)-{1,8,9,10-η^4-9,10-bis(tert-butylsulfonyl)-bicyclo-[6.2.0]-deca-1,9-diene}cobalt(I) (**42**)*

Starting material: 172 mg (0.35 mmol) of Me$_3$SiCpCo(CO)(BTSA) (**10**) and 38 mg (0.35 mmol) of cyclooctyne (**43**). Yield: 151 mg (75%) of **42** as a orange–red oil. — ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta =$ 0.24 (s, 9H, Si(CH$_3$)$_3$), 1.38 (s, 18H, C(CH$_3$)$_3$), 1.48–1.75 (m, 12H, CH$_2$), 4.94 (pt, 2H, Cp–H), 5.12 (pt, 2H, Cp–H). — ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = -0.2$ (Si(CH$_3$)$_3$), 24.0 (C(*C*H$_3$)$_3$), 24.7/24.9/26.3 (CH$_2$), 60.1 (*C*(CH$_3$)$_3$), 72.4 (*C*(CBD)–CH$_2$), 86.2 (*C*(CBD)–SO$_2$*t*Bu), 88.1/89.1 (Cp–C), 93.7 (Cp*C*–SiMe$_3$). — IR (KBr): $\tilde{\nu} = 2929$, 2860, 1631, 1290 cm^{-1}. — UV–vis (CH_2Cl_2): λ_{max} (log ε) = 290 (4.15), 340 nm (3.14). — HRMS (FAB+) $C_{26}H_{43}CoO_4S_2Si$: Calc.: 570.1704; Found: 570.1721%.

6. X-ray crystallography and structure solutions

Data were collected on a Syntex-R3-diffractometer (**24**, **25** at 293 K), a Siemens-Stoe AED2 diffractometer (**36** at 295 K), a Nonius-CAD4 diffractometer (**26** at 293 K) and a Bruker-Smart CCD-diffractometer (**30** and **39**–**41** at 200 K) using graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Intensities of all data-sets were corrected for Lorentz and polarization effects. An empirical absorption correction was performed for **24**–**26**, **30** and **39**–**41**. The structures were solved by direct methods (SHELXS-97 [19]). The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were considered at calculated positions using an appropriate riding model. In some cases disorder of parts of the structure was found: the *tert*-butyl groups of **26** are disordered, each at two positions with 50% multiplicity, one *tert*-butyl group of **40** (at S2) is disordered at two positions with ca. 50% multiplicity, the SiMe$_3$-group in **41** is disordered at two positions (63/37% occupation). The refinement was carried out with SHELXL-97 [20] (Table 5).

7. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC — 162686 (**24**), — 162687 (**25**), — 162688 (**26**), — 162689 (**30**), — 162690 (**36**), — 162691 (**39**), — 162692 (**40**), — 162693 (**41**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 5
Crystallographic data of **24**–**26**, **30**, **36**, **39**–**41**

Compound	**24**	**25**	**26**	**30**	**36**	**39**	**40**	**41**
Empirical formula	$C_{29}H_{33}CoO_4S_4$	$C_{30}H_{35}CoO_4S_4$	$C_{32}H_{41}CoO_4S_4Si$	$C_{35}H_{45}CoO_4S_4$	$C_{27}H_{43}CoO_6S_4$	$C_{29}H_{33}CoO_4S_2$	$C_{30}H_{35}CoO_4S_2$	$C_{32}H_{41}CoO_4S_2Si$
Molecular mass (g mol^{-1})	632.8	646.8	705.0	716.935	650.830	568.60	582.63	640.79
Temperature (K)	293	293	293	200(2)	295(2)	200(2)	200(2)	200(2)
Crystal color	Red	Orange	Orange	Yellow	Orange	Yellow	Orange	Orange
Crystal shape	Polyhedron	Polyhedron	Needle	Polyhedron	Polyhedron	Polyhedron	Polyhedron	Polyhedron
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca*	*Pbca*	$P2_1/n$	$P2_1/n$	$P2_1/c$	*Pbca*	*Pbca*	$P2_1/n$
a (Å)	17.865(5)	17.704(5)	11.744(4)	9.6829(2)	18.455(2)	10.5333(1)	14.0195(1)	10.3384(2)
b (Å)	18.126(5)	18.372(6)	12.511(9)	28.2080(5)	9.221(7)	17.8048(2)	14.5048(2)	18.3567(3)
c (Å)	18.297(5)	18.604(5)	24.58(2)	13.1599(3)	18.49(1)	28.8910(3)	27.1778(4)	16.9720(3)
α (°)	90	90	90	90	90	90	90	90
β (°)	90	90	102.15(3)	103.6930(10)	91.90(5)	90	90	94.518(1)
γ (°)	90	90	90	90	90	90	90	90
V (Å^3)	5925(3)	6051(3)	3530(4)	3492.27(12)	3145(4)	5418.3(1)	5526.6(1)	3210.9(1)
Z	8	8	4	4	4	8	8	4
D_{calc} (mg m^{-3})	1.42	1.42	1.33	1.36	1.37	1.39	1.40	1.33
μ (mm^{-1})	0.89	0.88	0.79	0.767	0.848	0.821	0.806	0.736
$F(000)$	2640	2704	1480	1512	1376	2384	2448	1352
Crystal size (mm)	0.40 × 0.60 × 0.75	0.50 × 0.80 × 0.95	0.50 × 0.30 × 0.30	0.22 × 0.22 × 0.12	0.45 × 0.30 × 0.25	0.50 × 0.16 × 0.11	0.22 × 0.20 × 0.18	0.23 × 0.18 × 0.18
H_{min}/h_{max}	0/23	0/23	0/15	−11/11	−21/20	−13/13	−18/18	−13/12
K_{min}/k_{max}	0/23	0/23	0/16	−34/32	0/10	−23/23	−18/18	−23/23
l_{min}/l_{max}	0/23	0/24	−32/31	−16/15	0/21	−37/37	−35/35	−21/22
Reflections collected	6588	6714	8892	26 045	4928	53 053	54 281	21 165
Reflections unique	5977	6093	8493	6087	4928	6209	6317	7349
Reflections observed	3937	4085	6212	4590	3000	4745	4418	4853
Variables	344	352	436	409	358	331	366	404
$R(F)$	0.058	0.064	0.032	0.037	0.0534	0.034	0.040	0.043
$R_w(F^2)$	0.109	0.131	0.080	0.074	0.1198	0.073	0.092	0.089
S (Goodness-of-fit) and F^2	1.06	2.61	1.04	1.04	1.011	1.05	1.00	1.01
$(\Delta\rho)_{max}$ (e A^{-3})	0.57	0.46	0.25	0.30	0.404	0.34	0.46	0.35
$(\Delta\rho)_{min}$ (e A^{-3})	−0.28	−0.48	−0.34	−0.32	−0.35	−0.32	−0.37	−0.32

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