Mono(alkyne)cobalt Complexes and Electron-Rich Alkynes − The Formation of an Alkyne-Bridged Dinuclear Cobalt Complex by a One-Pot Procedure

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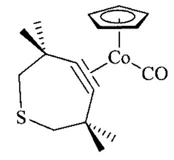
[η^2-Bis(*tert*-butylsulfonyl)acetylene](carbonyl)(η^5-trimethylsilylcyclopentadienyl)cobalt (**2c**) proved to be reactive towards bis(telluro)- and bis(seleno)-substituted alkynes **3** and **4**, respectively, to yield *push-pull*-substituted CpCo-stabilized cyclobutadiene complexes. By utilizing the unsymmetrical diyne **6** and the symmetrical bis(thio)-substituted triyne **7** it was shown that only the most electron-rich triple bond was attacked by the electrophilic compound **2c**. In the case of **7** a dinuclear CpCo-stabilized cyclobutadiene complex **14** bridged by one acetylene moiety was obtained. All the reactions could be carried out at room temperature under rather mild conditions. X-ray investigations of **8**, **12**, **14a**, and **15** show almost equal C–C bond lengths in the cyclobutadiene moieties.

Introduction

Nearly 50 years ago dicarbonyl(η^5-cyclopentadienyl)cobalt [CpCo(CO)$_2$] was synthesized for the first time.[1,2] Since that time this compound has proved to be a very convenient and efficient reagent for the di- and trimerization of alkynes.[3] Several useful and theoretically attractive molecules like cyclobutadienes,[4] cyclopentadienones,[5,6] and benzene derivatives[7] have been synthesized by this reagent. As one possible mechanism, the subsequent replacement of the CO units by acetylene fragments was proposed yielding first a monoacetylene, then a diacetylene complex that is converted by a metal-mediated cycloaddition process into a 16-electron metallacycle.[7,8] The latter species has the ability to react with a further acetylene fragment or to form the cyclobutadiene[4] by a reductive elimination process. To obtain more insight into the mechanism, several intermediates were isolated and characterized crystallographically. Krebs and Jessel succeeded in the isolation of a mono(alkyne)cobalt complex **1** by using the highly strained 3,3,6,6-tetramethyl-1-thiacycloheptyne.[9] Our group was able to synthesize a variety of mono(alkyne)cobalt complexes[10] **2a−f** with the very electron-deficient compound bis(*tert*-butylsulfonylacetylene) (BTSA).[11]

In the course of our in-depth study of electron-rich alkynes[12−14] and their reactions with electrophilic metal fragments, we elucidated the reaction of our mono(alkyne)cobalt complexes **2a−f** with several electron-rich alkynes under mild conditions.[15] Until now we have treated only thio- or carbon-substituted symmetrical acetylene fragments with the mono(alkyne) cobalt complexes.[15] The more electron-rich thio-substituted acetylenes reacted faster and with greater ease than the carbon-substituted compounds, for which heating was needed to initiate the reaction.[15] Therefore, we raised the question whether other elements such as selenium or tellurium are also able to act in the same way as sulfur. Furthermore, we are interested in the reaction of polyacetylene systems in which the mono(alkyne) complex has the choice to discriminate between acetylene units with slightly different electron densities, or even to react twice with the polyalkyne molecule. As model compounds we chose bis(methylseleno)acetylene (**3**),[16] bis(methyltelluro)acetylene (**4**),[17] bis(methylthio)butadiyne (**5**),[14b] (methylthio)(trimethylsilyl)butadiyne (**6**),[14b] and bis(methylthio)hexatriyne (**7**).[14b]



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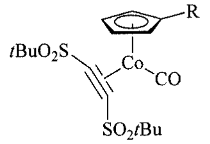
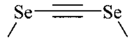


2a–2f
(R = H, CH$_3$, SiMe$_3$, CO$_2$Me, Ac, Et$_4$Me)



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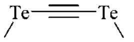

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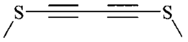

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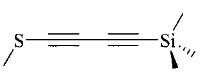

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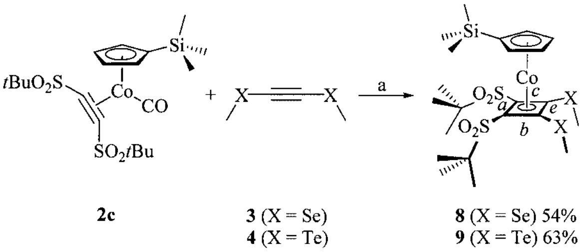
Results and Discussion

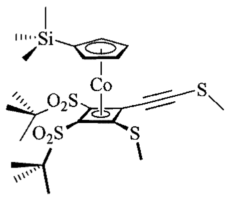
To ensure reasonable solubilities of the products, we chose **2c** because the $Si(CH_3)_3$ substituent at the Cp ring enhances the solubility in toluene.[10] The reaction between the mono(alkyne)cobalt complex **2c** and alkynes **3**−**7** were carried out in toluene at room temperature and in the dark since the electron-rich alkynes are light-sensitive. The two monoacetylenic substrates **3** and **4** afforded the selenium- and tellurium-substituted cyclobutadiene complexes **8** and **9**, respectively, in 54−63% yield (Scheme 1). Due to the high-lying HOMO of **3** and **4**, the activation energy of this reaction is low.



a) toluene, r.t.

Scheme 1

The reaction of **2c** with the two butadiynes **5** and **6** yielded cyclobutadiene complexes **10** and **12**, respectively. Even by using a high excess of mono(alkyne)cobalt complex, a second attack to the still unchanged triple bond did not take place. Complex **12** was obtained as the only product in the reaction of **2c** with **6**. The subtle differences in the electron density between the two triple bonds in **6** should therefore be important in determining the regioselectivity of the electrophilic attack by the mono(alkyne) complex. Furthermore, in the reaction of **2c** with **5**, a decomposition process of the mono(alkyne)cobalt species took place: the highly electron-deficient BTSA reacted in a Diels−Alder reaction with the CpH(TMS) moiety to afford the norbornadiene derivative **11** in 40% yield.



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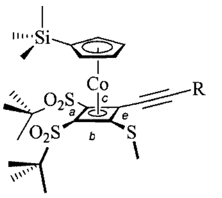
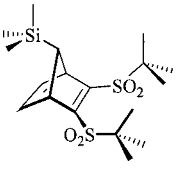


12 (R = SiMe$_3$)
15 (R = H)



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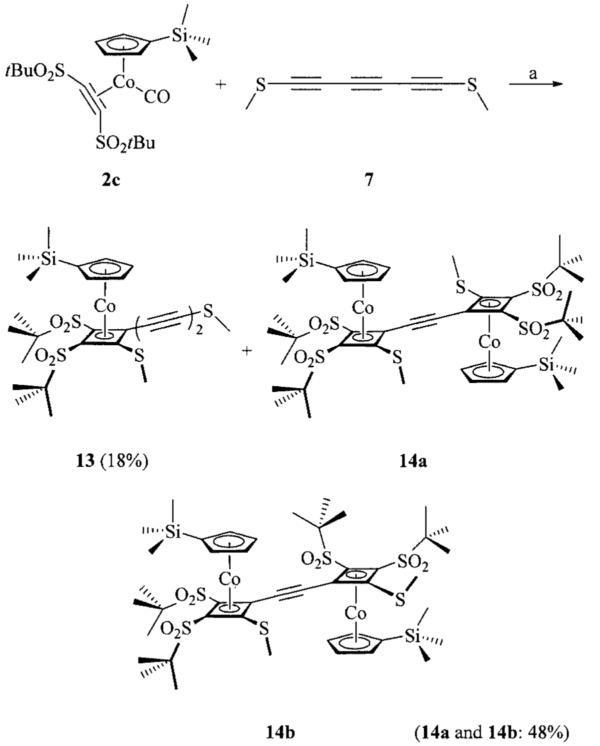
We ascribe the observation that the second triple bond in **5** did not react to steric repulsion between the two adjacent cobalt fragments. Thus, the reaction of the electron-rich hexatriyne **7** with excess **2c** was now even more interesting. The analysis of the reaction products showed that only the terminal triple bonds with the higher electron density (relative to the central one) were attacked. Two compounds resulted, the mono- and the disubstituted products **13** and **14**.



a) toluene, r.t.

Scheme 2

For the dinuclear compound, three stereoisomers **14a** and **14b** are possible. NMR spectroscopic investigations revealed their ratio to be approximately 1:1. Separation by column chromatography proved to be unsuccessful, and therefore recrystallization experiments were carried out instead. From a mixture of dichloromethane and diethyl ether the C_i-symmetrical stereoisomer **14a** was obtained as a pure compound.

This reaction reveals an interesting alternative route to bridged dinuclear cyclobutadiene complexes;[18] this is important especially because the introduction of only one acetylene fragment between two metal-stabilized cyclobutadiene fragments is still a difficult goal to reach. The usual method by Bunz et al. is a multi-step sequence starting with the lithiation of metal-capped cyclobutadiene complexes to afford, after treatment with iodine, the corresponding iodides. According to this, with a Stille-type reaction, coupling with the acetylene fragment takes place.[18,19] Even tri- and tetranuclear complexes have been achieved in combination with Glaser-type reactions in this manner.[18,19] Efforts to synthesize dinuclear complexes with bridging butadiyne moieties by a deprotection reaction of **12** (yielding **15**) and a subsequent Glaser coupling of the deprotected cobalt complex **15** failed. We ascribe this behavior to the divalent sulfur atom in the starting material that may hinder the catalytic activity of the copper species.

All the cyclobutadiene complexes were yellow to red in color, and were remarkably stable as they are inert towards moisture and air. The characteristic features of the ^{13}C NMR spectra are the chemical shifts of the cyclobutadiene ring atoms that show values between δ = 75 and 85 ppm. Only in the case of the tellurium-substituted cyclobutadiene complex **9** do we encounter signals at δ = 53.6 ppm for the carbon atoms adjacent to the tellurium atoms. Such a "heavy-atom effect" that influences this relatively low-frequency resonance has been reported before.[14a,20]

Four cyclobutadiene complexes **8**, **12**, **14a**, and **15** yielded single crystals which could be investigated by X-ray crystal-

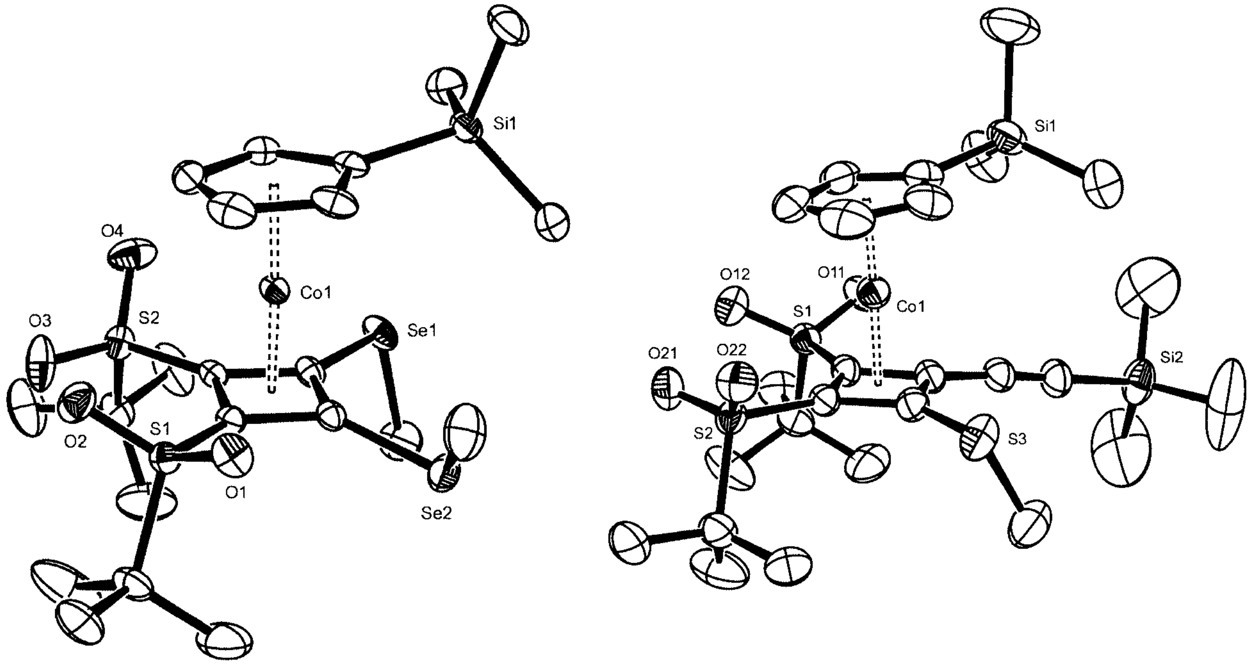


Figure 1. ORTEP plots (50% ellipsoid probability) of the molecular structures of **8** (left) and **12** (right)

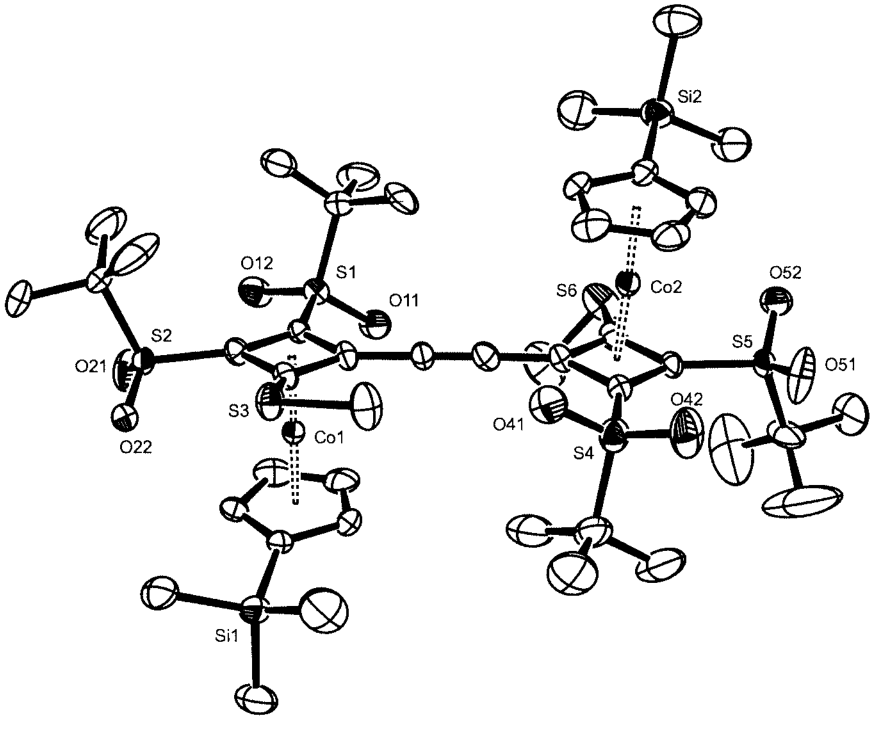


Figure 2. ORTEP plot (50% ellipsoid probability) of the molecular structure of **14a**

Table 1. Selected distances [pm] and interplanar angles φ [°] of **8**, **12**, **14a**, and **15**; for the definition see Scheme 1

Compound	*d*(Co−Cp)	*d*(Co−Cbd)	φ(Cp−Cbd)	*a*	*b*	*c*	*e*
8	167.5	168.1	4.8	149.1	147.9	147.4	146.2
12[a]	166.7	168.3	6.1	148.6	146.5	147.3	146.1
	166.0	167.2	5.5	148.3	148.2	147.1	145.7
14a	166.1	167.3	5.0	150.0	144.3	146.6	147.5
	167.1	167.8	8.1	148.2	146.0	146.6	144.3
15[b]	165.9	167.0	4.5	148.6	146.3	146.9	144.7

[a] Two independent molecules exist in the asymmetric unit. [b] Disorder between the SMe and the C_2H moieties, the values should be considered imprecise.

lography. As examples, we show the molecular structures of the mononuclear complexes **8** and **12** in Figure 1 and the dinuclear cobalt complex **14a** in Figure 2.

All the conformations in the solid state are highly influenced by the rather bulky *tert*-butylsulfonyl groups. In all cases they point away from the metal center, and to avoid steric interactions with the rather voluminous $Si(CH_3)_3$ substituent at the Cp ring, the latter points in the opposite direction. This behavior allows an almost parallel orientation of the Cp and the Cbd rings. In Table 1, we have compared the interplanar angles of the π-systems as well as the most relevant distances.

The mean distance between the cobalt atom and the four-membered cycle is slightly larger than the distance between the cobalt atom and the five-membered cycle. An examination of the CpCo-stabilized cyclobutadiene systems shows only weak variations. Due to steric repulsions, the longest bond is found to be between the two adjacent *tert*-butylsulfonyl groups (*a*). Any indication of bond alternation in the four-membered ring was not found as can be seen in Table 1. Relative to the unsubstituted $CpCo(C_4H_4)$[21] ($a = b = c = e = 144$ pm), the cyclobutadiene moiety in our systems is slightly enlarged due to the repulsion described above.

Conclusions

We have shown that the CO group in mono(alkyne)cobalt complexes can be replaced by seleno- and telluro-substituted alkynes to yield seleno- and telluro-substituted cyclobutadiene complexes. An important parameter that affects this substitution reaction under mild conditions is the HOMO energy of the alkyne and not the type of heteroatom attached to it. Furthermore, our studies reveal that mono(alkyne)cobalt complexes are able to differentiate between triple bonds with slightly different electron densities in a polyalkyne system, where the attack always takes place at the most electron-rich triple bond. In the case of a hexatriyne system, the attack of two mono(alkyne)cobalt complexes affords a dinuclear complex bridged by one triple bond. Our X-ray investigations reveal that the various substitution patterns do not strongly influence the C−C bond lengths within the metal-capped π-system.

Experimental Section

General Methods: Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under argon using dried solvents. Materials used for column chromatography: Neutral alumina (Merck), Celite (Fluka). Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. All melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker WH 300 (^{1}H at 300 MHz and ^{13}C at 75.47 MHz) and Bruker Avance 500 (^{1}H at 500 MHz and ^{13}C at 125.77 MHz) using the solvent as internal standard. IR spectra were recorded with a Bruker Vector 22 FT-IR. UV light absorption data were recorded with a Hewlett Packard 8452A spectrometer. High resolution mass spectra were recorded using a JEOL JMS-700. The starting materials **3**−**7** were prepared according to literature methods.[10][14b,16,17]

General Procedure for the Preparation of the Cyclobutadiene Complexes from Mono(alkyne)cobalt Complex 2c and Electron-Rich Alkynes: To a solution of the mono(alkyne)cobalt complex **2c** in toluene (50 mL) was added the corresponding electron-rich polyalkyne in one portion. To avoid any light, the reaction flask was wrapped with aluminum foil. The reaction mixture was stirred at room temperature for 7−14 d. After completion of the reaction (shown by thin-layer chromatography), the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-3,4-bis(methylseleno)cyclobutadiene](η^5-trimethylsilylcyclopentadienyl)cobalt(I) (8): Starting materials: $CpSiMe_3Co(CO)(BTSA)$ (**2c**) (100 mg, 0.20 mmol) and 2,5-diselenahex-3-yne (**3**) (47 mg, 0.20 mmol). Column chromatography with light petroleum/diethyl ether (2:1) as eluent afforded 73 mg (54%) of **8** as a yellow solid. M.p. 135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.32 (s, 9 H, CH_3), 1.45 (s, 18 H, CH_3), 2.31 (s, 6 H, CH_3), 5.20 (ps, 2 H, CpH), 5.74 (ps, 2 H, CpH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.2 (CH_3), 10.5 (CH_3), 24.8 (CH_3), 61.6 (C), 77.0 (C), 78.1 (C), 88.5 (CH), 89.5 (CH), 94.1 (C) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 248 (4.17), 288 (4.00), 322 (3.96), 372 (3.37) nm. IR (KBr) $\tilde{\nu}$ = 2930, 1628, 1458 cm^{-1}. HRMS (FAB+): calcd. for $C_{22}H_{37}CoO_4S_2{}^{80}Se_2Si$ 675.9565 [M$^+$]; found 675.9593. $C_{22}H_{37}CoO_4S_2Se_2Si$ (675.9): calcd. C 39.17, H 5.53; found C 39.35, H 5.59.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-3,4-bis(methyltelluro)-cyclobutadiene](η^5-trimethylsilylcyclopentadienyl)cobalt(I) (9): Starting materials: $CpSiMe_3Co(CO)(BTSA)$ (**2c**) (60 mg, 0.12 mmol) and 2,5-ditellurahex-3-yne (**4**) (38 mg, 0.12 mmol). Column chromatography with light petroleum/diethyl ether (2:1) as eluent afforded 58 mg (63%) of **9** as an orange solid. M.p. 18 °C.

^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.32 (s, 9 H, CH$_3$), 1.40 (s, 18 H, CH$_3$), 2.10 (s, 6 H, CH$_3$), 5.07 (ps, 2 H, CpH), 5.64 (ps, 2 H, CpH) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = −12.9 (CH$_3$), 0.3 (CH$_3$), 25.1 (CH$_3$), 53.6 (C), 61.5 (C), 82.7 (C), 88.5 (CH), 89.9 (CH), 94.5 (C) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 262 (4.14), 290 (4.02), 324 (3.69), 356 (3.41), 584 (3.21) nm. IR (KBr): ṽ = 2929, 1628, 1459 cm^{-1}. HRMS (FAB+): calcd. for $C_{22}H_{37}CoO_4S_2Si^{128}Te_2$ 771.9324 [M$^+$]; found 771.9326. $C_{22}H_{37}CoO_4S_2SiTe_2$ (771.9): calcd. C 34.23, H 4.83; found C 34.69, H 4.91.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-3-(methylthio)-4-(methylthioethynyl)-cyclobutadiene](η^5-trimethylsilylcyclopentadienyl)cobalt(I) (10) and the Norbornadiene Derivative 11: Starting materials: CpSiMe$_3$Co-(CO)(BTSA) (**2c**) (100 mg, 0.20 mmol) and 2,7-dithiaocta-3,5-diyne (**5**) (14 mg, 0.10 mmol). Column chromatography with hexane/diethyl ether (1:1) as eluent afforded 30 mg (49%) of **10** as a yellow highly viscous oil and 32 mg (40%) of **11** as a colorless solid.

10: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.33 (s, 9 H, CH$_3$), 1.42 (s, 18 H, CH$_3$), 2.40 (s, 3 H, CH$_3$), 2.46 (s, 3 H, CH$_3$), 5.16 (ps, 1 H, CpH), 5.39 (ps, 1 H, CpH), 5.70 (ps, 1 H, CpH), 5.80 (ps, 1 H, CpH) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = −0.5 (CH$_3$), 18.4 (CH$_3$), 18.7 (CH$_3$), 24.5 (CH$_3$), 24.7 (CH$_3$), 61.3 (C), 61.8 (C), 76.3 (C), 76.5 (C), 77.4 (C), 85.2 (C), 85.4 (C), 87.9 (CH), 88.4 (CH), 89.3 (CH), 90.2 (C), 90.9 (CH), 92.8 (C) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 262 (4.47), 324 (4.20), 358 (3.68), 364 (3.82), 404 (3.73) nm. IR (film): ṽ = 2930, 2145, 1475, 1432, 1315 cm^{-1}. HRMS (FAB+): calcd. for $C_{24}H_{37}CoO_4S_4Si$ 604.0676 [M$^+$]; found 604.0693.

11: M.p. 173 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = −0.1 (s, 9 H, CH$_3$), 1.41 (s, 18 H, CH$_3$), 2.58 (s, 1 H, CH), 4.20 (s, 2 H, CH), 6.97 (s, 2 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): *δ* = −0.8 (CH$_3$), 24.1 (CH$_3$), 61.9 (CH), 62.4 (CH), 84.5 (CH), 142.5 (CH), 166.3 (C) ppm. UV/Vis (CH$_2$Cl$_2$), λ_{max} (log ε) = 262 (3.47) nm. IR (KBr) ṽ = 2954, 1629, 1476, 1317 cm^{-1}. HRMS (FAB+): calcd. for $C_{18}H_{32}O_4S_2Si$ 405.1589 [M$^+$]; found 405.1558. $C_{18}H_{32}O_4S_2Si$ (405.2): calcd. C 53.43, H 7.97, S 15.85; found C 53.44, H 8.04, S 15.94.

[η^4−1,2-Bis(*tert*-butylsulfonyl)-3-(methylthio)-4-(trimethylsilylethynyl)cyclobutadiene](η^5-trimethylsilylcyclopentadienyl)cobalt(I) (12): Starting materials: CpSiMe$_3$Co(CO)(BTSA) (**2c**) (80 mg, 0.16 mmol) and (methylthio)(trimethylsilyl)butadiyne (**6**) (33 mg, 0.20 mmol). Column chromatography with hexane/diethyl ether (2:1) as eluent afforded 46 mg (45%) of **12** as a yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.17 (s, 9 H, CH$_3$), 0.33 (s, 9 H, CH$_3$), 1.41 (s, 9 H, CH$_3$), 1.42 (s, 9 H, CH$_3$), 2.47 (s, 3 H, CH$_3$), 5.13 (ps, 1 H, CpH), 5.39 (ps, 1 H, CpH), 5.70 (ps, 1 H, CpH), 5.82 (ps, 1 H, CpH) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = −0.5 (CH$_3$), −0.4 (CH$_3$), 17.7 (CH$_3$), 24.4 (CH$_3$), 24.8 (CH$_3$), 61.2 (C), 62.0 (C), 62.8 (C), 76.2 (C), 76.9 (C), 85.5 (C), 88.0 (CH), 88.5 (CH), 89.5 (CH), 90.9 (CH), 93.1 (C) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 262 (4.22), 322 (4.01), 370 (3.44) nm. IR (KBr) ṽ = 2958, 2145, 1631, 1426, 1312, 1249 cm^{-1}. HRMS (FAB+): calcd. for $C_{26}H_{34}CoO_4S_3Si_2$ 630.1194 [M$^+$]; found 630.1152.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-3-(methylthio)-4-(methylthiobutadiynyl)cyclobutadiene](η^5-trimethylsilylcyclopentadienyl)cobalt(I) (13) and the Dinuclear Cyclobutadiene Cobalt(I) Complex 14: Starting materials: CpSiMe$_3$Co(CO)(BTSA) (**2c**) (155 mg, 0.32 mmol) and 2,9-dithiadeca-3,5,7-triyne (**7**) (24 mg, 0.14 mmol). Column chromatography with *n*-hexane/diethyl ether (1:1) as eluent afforded 16 mg (18%) of **13** as an orange oil and 76 mg (48%) of a mixture of **14a** and **14b** as an orange solid.

13: ^{1}H NMR (500 MHz, CDCl$_3$: δ = 0.33 (s, 9 H, CH$_3$), 1.42 (s, 18 H, CH$_3$), 2.45 (s, 3 H, CH$_3$), 2.47 (s, 3 H, CH$_3$), 5.18 (ps, 1 H, CpH), 5.42 (ps, 1 H, CpH), 5.70 (ps, 1 H, CpH), 5.81 (ps, 1 H, CpH) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = −1.0 (CH$_3$), 18.4 (CH$_3$), 19.0 (CH$_3$), 24.2 (CH$_3$), 24.4 (CH$_3$), 61.3 (C), 61.6 (C), 62.5 (C), 72.9 (C), 77.4 (C), 77.4 (C), 78.3 (C), 79.0 (C), 82.0 (C), 86.7 (C), 87.7 (CH), 88.8 (CH), 89.0 (CH), 90.8 (CH), 93.3 (C) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 236 (4.58), 252 (4.59), 270 (4.49), 324 (4.11), 378 (3.73) nm. IR (KBr) ṽ = 2967, 2931, 2174, 2097, 1628, 1458, 1314, 1250 cm^{-1}. HRMS (FAB+): calcd. for $C_{26}H_{38}CoO_4S_4Si$ 629.0755 [M$^+$ + H]; found 629.0751.

14a: ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.33 (s, 18 H, CH$_3$), 1.46 (ps, 36 H, CH$_3$), 2.47 (s, 6 H, CH$_3$), 5.21 (ps, 2 H, CpH), 5.33 (ps, 2 H, CpH), 5.71 (ps, 4 H, CpH) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = −0.3 (CH$_3$), 19.1 (CH$_3$), 24.7 (CH$_3$), 24.9 (CH$_3$), 61.5 (C), 61.5 (C), 63.5 (C), 76.0 (C), 78.4 (C), 84.3 (C), 88.3 (CH), 88.8 (C), 88.8 (CH), 89.9 (CH), 90.0 (CH), 94.6 (C) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 264 (4.48), 318 (4.34), 404 (3.85) nm. IR (KBr) ṽ = 2969, 1631, 1461, 1313, 1249 cm^{-1}. HRMS (FAB+): calcd. for $C_{44}H_{69}Co_2O_6S_6Si_2$ 1091.1520 [M$^+$ + H]; found 1091.1492.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-3-(methylthio)-4-(ethynyl)cyclobutadiene](η^5-trimethylsilylcyclopentadienyl)cobalt(I) (15): Starting materials: **12** (59 mg, 0.09 mmol) and a solution of sodium hydroxide (0.3 mL, 0.30 mmol of 1.0 N) in methanol (30 mL). The mixture was stirred for 3 h and extracted with diethyl ether. Column chromatography with hexane → hexane/diethyl ether (1:1) as eluent afforded 31 mg (59%) of **15** as a yellow solid. M.p. 130 °C (dec.). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.33 (s, 9 H, CH$_3$), 1.43 (s, 9 H, CH$_3$), 1.43 (s, 9 H, CH$_3$), 2.47 (s, 3 H, CH$_3$), 3.39 (s, 1 H, CH), 5.20 (ps, 1 H, CpH), 5.35 (ps, 1 H, CpH), 5.74 (ps, 1 H, CpH), 5.83 (ps, 1 H, CpH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = −0.5 (CH$_3$), −18.4 (CH$_3$), 24.5 (CH$_3$), 24.7 (CH$_3$), 61.4 (C), 61.7 (C), 63.1 (C), 76.6 (C), 77.0 (C), 77.6 (C), 85.1 (C), 85.8 (CH), 88.3 (CH), 88.7 (CH), 89.2 (CH), 90.9 (CH), 93.7 (C) ppm. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 258 (4.48), 282 (4.27), 320 (4.31), 376 (3.55) nm. IR (KBr): ṽ = 2969, 1628, 1461, 1416, 1312, 1249, 1164 cm^{-1}. HRMS (FAB+): calcd. for $C_{23}H_{35}CoO_4S_3Si$ 558.0735 [M$^+$]; found 558.759. $C_{23}H_{35}CoO_4S_3Si$ (558.1): calcd. C 49.44, H 6.31, S, 17.22; found C 49.10, H 6.32, S 16.80.

X-ray Diffraction Analyses: The reflections were collected at 200(2) K with a Bruker Smart CCD diffractometer (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[22] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. 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 calculated according to stereochemical aspects. In the case of **12**, two independent molecules were found in the asymmetric unit. In **15**, the ethynyl moiety and the methylthio unit were disordered (2:1). Structure solution and refinement were carried out with the SHELXTL (5.10) software package.[22] ORTEP drawings were obtained using the ORTEP-3 for Windows program by L. Farrugia.[23] Table 2 contains the crystallographic information and details of the refinement procedure. CCDC-225694 to -225698 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: data_request@ccdc.cam.ac.uk].

Table 2. Crystallographic data and details of the refinement procedure for **8**, **11**, **12**, **14a**, and **15**

	8	**11**	**12**	**14a**	**15**
Empirical formula	$C_{22}H_{37}CoO_4S_2Se_2Si$	$C_{18}H_{32}O_4S_2Si$	$C_{26}H_{43}CoO_4S_3Si_2$	$C_{44}H_{68}Co_2O_8S_6Si_2$	$C_{23}H_{35}CoO_4S_3Si$
Formula mass [g/mol]	674.60	404.66	630.92	1091.43	558.74
Crystal size [mm]	0.40 × 0.20 × 0.09	0.40 × 0.32 × 0.06	0.32 × 0.30 × 0.30	0.32 × 0.20 × 0.16	0.36 × 0.05 × 0.03
Crystal color	yellow	colorless	yellow	red	yellow
Crystal shape	polyhedron	polyhedron	polyhedron	polyhedron	needle
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Cc*	$P2_1/n$	$P2_1/c$	*Cc*	$P2_1/c$
a [Å]	10.5834(1)	10.1921(1)	29.0406(2)	23.4650(1)	14.8676(2)
b [Å]	16.2163(2)	12.1916(1)	19.3468(1)	20.0117(3)	10.1951(2)
c [Å]	16.3188(2)	17.4848(2)	11.6699(2)	12.2655(2)	13.1370(2)
β [°]	98.579(1)	98.633(1)	92.854(1)	112.077(1)	94.627(1)
V [Å^3]	2769.35(5)	2148.50(4)	6548.52(13)	5337.27(12)	2740.19(7)
$D_{calcd.}$ [g/cm^3]	1.618	1.251	1.280	1.358	1.354
Z	4	4	8	4	4
h_{min}/h_{max}	−13/13	−13/13	−37/37	−30/30	−18/18
k_{min}/k_{max}	−20/20	−15/15	−25/25	−25/25	−12/12
l_{min}/l_{max}	−20/21	−22/22	−15/15	−15/15	−22/21
μ [mm^{-1}]	3.47	0.32	0.82	0.95	0.92
$T_{max.}/T_{min.}$	1.00/0.77	1.00/0.93	0.82/0.71	0.89/0.71	0.97/0.73
Refl. collected	12188	21643	67395	27315	23966
Refl. unique	6144	4907	15014	12125	5210
Refl. observed	5605	3882	9708	9548	3184
Parameter	300	235	675	580	307
$R(F)$	0.022	0.035	0.047	0.043	0.065
$R_w(F^2)$	0.048	0.083	0.110	0.101	0.151
S (Gof) on F^2	0.83	1.04	1.02	1.01	1.03
$(\Delta\rho)_{max}$ [e·Å^{-3}]	0.25	0.39	0.96	1.38	0.74
$(\Delta\rho)_{min}$ [e·Å^{-3}]	−0.33	−0.30	−0.42	−0.44	−0.63

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