Structural Properties of Bis(hexacarbonyldicobalt) Complexes with Heteroatoms Next to the Former Triple Bonds − A Contribution to the Mechanism of the Pauson−Khand Reaction

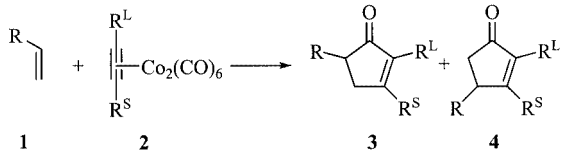
Daniel B. Werz,[a] J. Hilko Schulte,[a] Bernhard J. Rausch,[a] Rolf Gleiter,*[a] and Frank Rominger[a]

Keywords: Alkynes / Chalcogens / Cobalt / Pauson−Khand reaction

The bis(hexacarbonyldicobalt) complexes of cyclic diynes with sila-, thia- and selena-substituted acetylene units have been isolated. The structural features of these complexes have been elucidated by means of X-ray diffraction analyses on single crystals. In three cases (**24′**, **25′** and **29′**) the X-ray investigations show bis(pentacarbonyldicobalt) complexes instead of bis(hexacarbonyldicobalt) ones. Their empty coordination sites are each occupied by divalent chalcogen moieties from the opposite side of the molecule affording distorted C_2Co_2 cores. These results corroborate the possibility of intramolecular activation in Pauson–Khand reactions of chalcogen-containing substrates.

Introduction

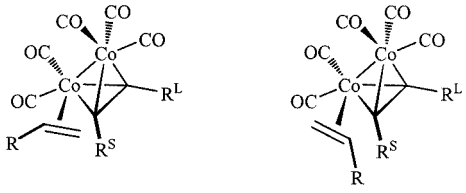
The reaction of hexacarbonyldicobalt complexes of alkynes with olefins to yield cyclopentenones, first described by Pauson et al.,[1,2] has emerged as a frequently used procedure in chemistry.[3−6] Although this reaction has been known for more than 30 years, the mechanistic elucidation is still in progress. Some points which have been looked at more closely are the structural details of hexacarbonyldicobalt complexes[7,8] of various alkynes, and substituent[9] and solvent effects.[10] The energetics of reasonable intermediates along the possible pathway have also been calculated by computational chemistry.[11] One of the major questions in this field of chemistry is (besides the formation of stereoisomers)[12] the understanding of the formation of regioisomers and their control. The reaction of unsymmetrical alkynes with terminal olefins yields regioisomeric mixtures of cyclopentenones as shown in Scheme 1.



1 2 3 4

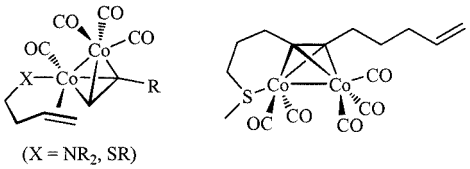
Scheme 1

Usually, the larger substituent (R^L) at the alkyne adopts the α-position to the CO group, whereas the substituent (R) at the olefin gives rise to the 1:1 mixture shown. To rationalize these results, an equilibrium between **5** and **6** was assumed before the insertion step.[3−6]



5 6

This assumption was further corroborated by a study in which heteroatoms were tethered to the olefin by a carbon chain. This led to the postulation that an intermediate such as **7** was involved,[13a] which would lead to a preference for **3**. Experiments with externally added sulfides confirmed this view.[13b]



(X = NR_2, SR)

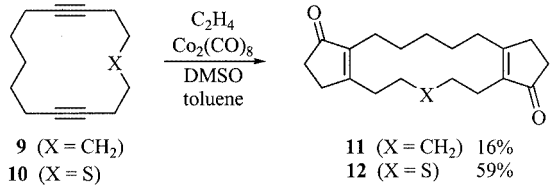
7 8

With respect to the role of heteroatom participation it is also of interest that the amine oxide promoted Pauson−Khand reaction is accelerated in the presence of heteroatoms such as sulfur, nitrogen and even oxygen in

[a] Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
E-mail: rolf.gleiter@urz.uni-heidelberg.de

the homopropargylic position.[14] During these studies even intermediates such as **8** could be detected.[14]

Our interest in the effect of heteroatoms in the Pauson–Khand reaction, especially sulfur, arose when we studied the twofold Pauson–Khand reaction of cyclic diynes **9** and **10** with ethylene (Scheme 2).[9a,10c] We found a strong increase in the yield when **10** was used. Here the sulfur atom takes the homopropargylic position. To learn more about the effects of chalcogen atoms, even in other positions, we have synthesized a series of bis(hexacarbonyldicobalt) complexes of cyclic diynes with heteroatoms next to the $[C_2Co_2(CO)_6]$ core. In this paper we report on the syntheses and the structural investigations of these species. These studies allowed us to isolate three species in which a CO ligand is replaced by an intramolecular thio(seleno) ether ligand and to characterize them crystallographically.



9 (X = CH_2)
10 (X = S)

11 (X = CH_2) 16%
12 (X = S) 59%

Scheme 2

Results and Discussion

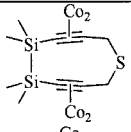
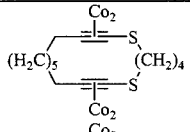
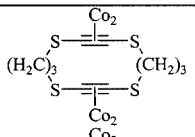
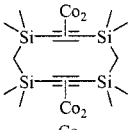
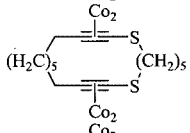
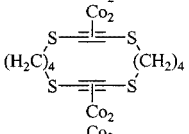
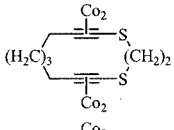
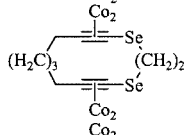
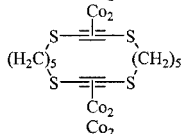
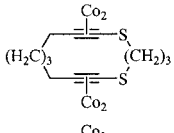
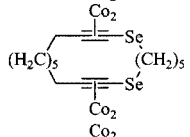
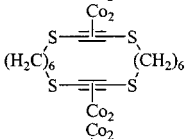
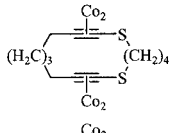
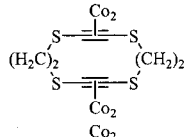
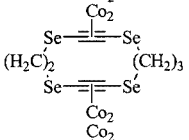
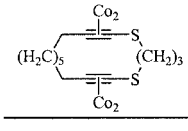
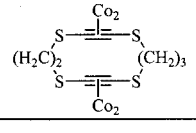
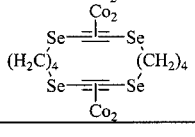
We used the recently synthesized cyclic sila-, thia- and selenadiynes as starting materials. They were treated with octacarbonyldicobalt in dichloromethane to afford the corresponding complexes after crystallization or column chromatography. The resulting products, which could be obtained in 33–85% yield, are red to black solids, and several of them are sensitive to light. All new bis(hexacarbonyldicobalt) complexes and the isolated yields obtained for the syntheses of **13**–**30** are given in Table 1.

Most of the bis(hexacarbonyldicobalt) complexes show three characteristic absorptions in the IR spectrum in the range between 2000 and 2100 cm^{-1}. Group-theory considerations reveal that a $C_2Co_2(CO)_6$ core with a local C_{2v} symmetry should show five different IR-active vibrations in this range. The smaller number can be explained easily by the relatively low resolution of the spectrometer.

To study the structural data of these complexes, efforts were made to obtain single crystals suitable for X-ray crystallography. This was possible except for **17** and **18**. The crystallisation was performed either by solvent evaporation at room temperature or by crystallizing the complexes from the crude reaction mixture at −78 °C.

All the complexes are dominated by the bulky $C_2Co_2(CO)_6$ units (Figures 1 and 2). The tethers between

Table 1. Cyclic heterosubstituted $Co_2(CO)_6$ complexes **13**–**30** [Co_2 = $Co_2(CO)_6$]

Compound		Yield (%)	Compound		Yield (%)	Compound		Yield (%)
	**13**	83		**19**	82		**25**	46
	**14**	85		**20**	79		**26**	56
	**15**	75		**21**	62		**27**	46
	**16**	77		**22**	62		**28**	52
	**17**	69		**23**	56		**29**	0[a]
	**18**	62		**24**	35		**30**	33

[a] Only the bis(pentacarbonyldicobalt) complex **29′** was isolated.

these moieties often tend to adopt a zig-zag arrangement. However, the longer the tethers become, the more gauche conformations can be observed. Such conformations minimize the empty space between the coordinated triple bonds, as shown in Figure 2.

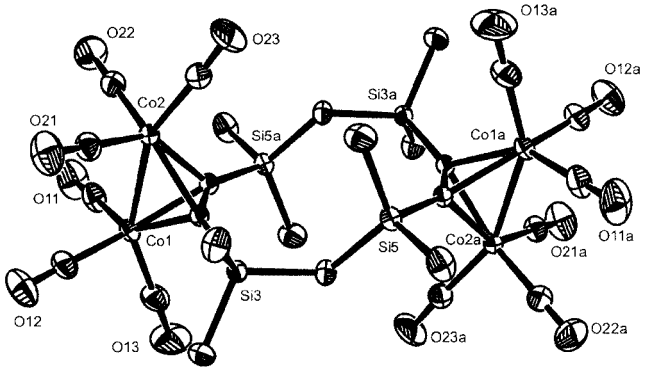


Figure 1. ORTEP plot (50% ellipsoid probability) of the molecular structure of **14**

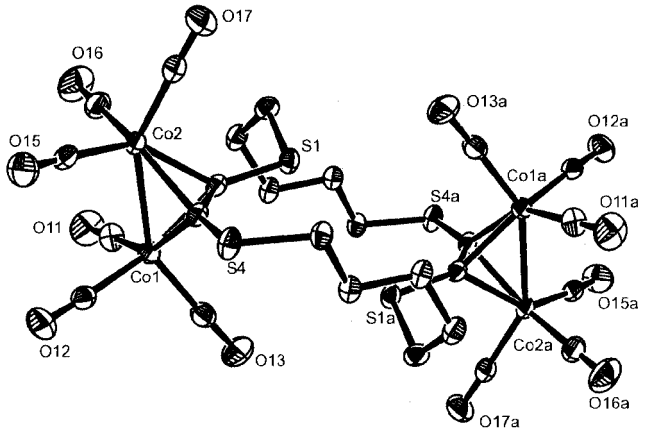


Figure 2. ORTEP plot (50% ellipsoid probability) of the molecular structure of **27**

Typical structural features of the heterosubstituted pseudo-tetrahedral Co_2C_2 cores are the planarity of the Co-coordinated fragments (the former triple bond and the adjacent heteroatoms or methylene groups lie in one plane), the elongation of the former triple bond due to its coordination (132−135 pm) and the bent geometry of the coordinated alkyne moieties (134−150°). The metal−carbonyl bond lengths vary between 177 and 185 pm. The longer distances are found *trans* to the acetylenic group, whereas the shorter ones are found in the *cis* position. These differences can be rationalized in terms of metal−ligand d → π* back-donation.[11a] The six CO ligands do not participate equally in the redistribution of electron density from the coordinated triple bond. As a result, different bond lengths are observed. Further structural data (except for **15**, which shows strong disorder) are given in Table 2; for the definition of the parameters see Figure 3.

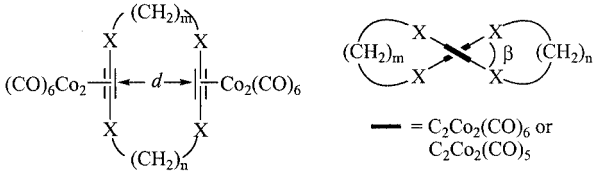


Figure 3. Definition of the transannular distance *d* and the torsion angle *β* in heterosubstituted cyclic bis(hexacarbonyldicobalt) and bis(pentacarbonyldicobalt) complexes

It is interesting to note that the bond lengths of the coordinated triple bonds in the chalcogen-substituted diyne complexes are somewhat larger than the values found in CH_2-substituted diyne complexes.[8l] This observation shows that the assumption of stronger bonding between the electron-rich triple bond of chalcogen-substituted acetylenes and the electron-poor $Co_2(CO)_6$ moiety is reasonable. Furthermore, a comparison of the Co−CC distances of the sila-substituted complexes **13** and **14** with the distances found in the chalcogen-substituted complexes reveals much

Table 2. Selected transannular distances between the former triple bonds, bond lengths and bond angles of the compounds **13**, **14**, **16**, **19**−**23**, **26**−**28** and **30**

Compd.	Distance *d* [a] Co_2C_2 [pm]	Torsion angle *β* [a] Co_2C_2 [°]	Bond lengths [pm]				Angles [°] X−C≡$C_{coord.}$ [b]
			C≡$C_{coord.}$	Co−CO	CoC≡O	Co−CC	
13	421.0	60.2	133.1−134.1	178.7−182.7	113.3−114.1	197.6−202.6	143.9−150.3
14	517.8	0	134.1	179.1−182.3	113.1−113.8	200.3−201.8	145.1−145.3
16	603.8	82.9	132.7−134.0	179.0−183.3	112.6−113.9	195.1−198.0	143.7−146.4
19	673.6	29.9	133.8−134.4	179.2−183.3	112.4−114.0	195.4−199.6	135.2−145.0
20	727.8	28.1	134.7−135.2	177.7−183.5	112.5−115.4	195.3−197.5	138.2−145.2
21	600.2	56.2	133.3−133.6	178.5−182.5	112.8−114.0	195.0−197.7	139.3−146.3
22	731.4	29.1	131.9	177.1−184.8	109.9−116.0	193.5−199.0	137.7−146.8
23	528.6	0	135.3	179.7−183.4	112.8−113.3	194.3−196.9	144.0−145.5
26	673.4	0	134.6	178.7−182.3	111.0−114.5	194.1−195.7	136.4−143.5
27	690.4	0	134.9	179.4−183.1	112.5−113.3	195.0−199.2	133.7−141.5
28	826.0	0	135.1	179.8−183.4	112.5−113.8	195.3−198.0	137.6−143.7
30	695.3	0	133.8	179.0−183.1	112.3−113.6	194.6−196.7	135.6−142.5

[a] See Figure 3 for definition of distance *d* and torsion angle *β*. [b] X = $Si(CH_3)_2$, S, Se or CH_2.

longer distances for the slightly electron-poor sila-substituted alkyne, indicating a weaker coordination..

Crystallization experiments with **24**, **25** and **29** afforded crystals in which the molecules have lost two CO ligands (**24′**, **25′** and **29′**). The empty coordination sites are occupied by chalcogen donors placed at the opposite side of the molecule. A top and side view of structure **25′** is shown in Figure 4. Due to the C_1 symmetry of **24′**, and **29′**, and their low solubility in the usual solvents, it was not possible to get reliable NMR spectroscopic data for these compounds. The IR data show no significant differences to the corresponding bis(hexacarbonyldicobalt) complexes. Therefore, only the X-ray data of **24′**, **25′** and **29′** are discussed.

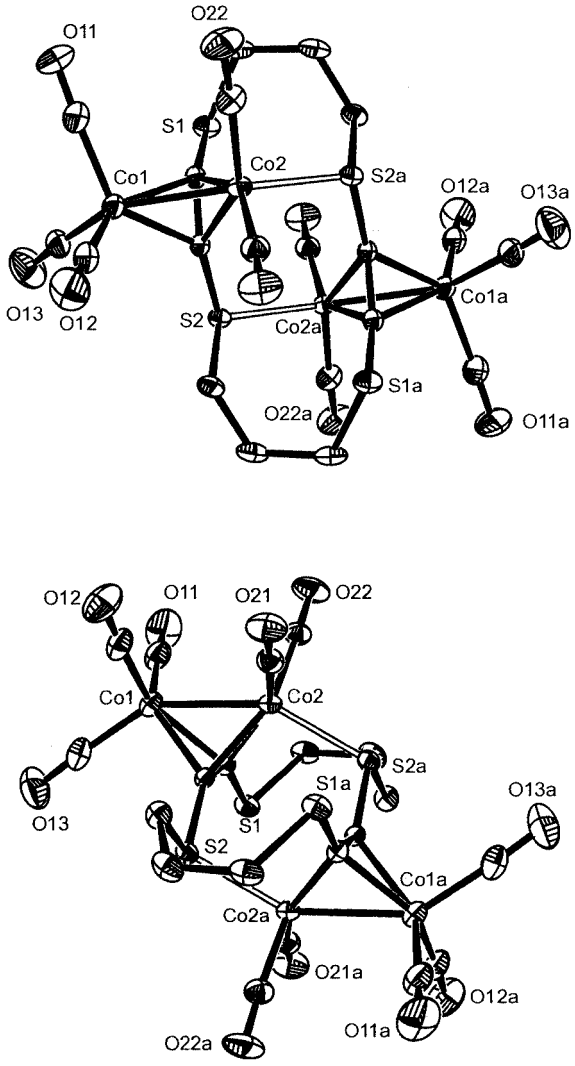
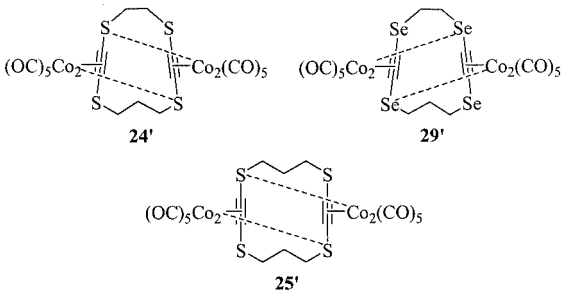


Figure 4. ORTEP plots (50% ellipsoid probability) of the bis(pentacarbonyldicobalt) complexe **25′** (top view and side view)

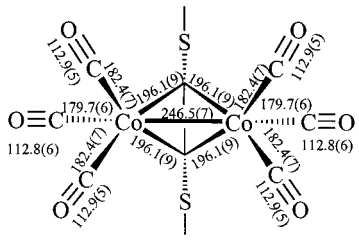


In Table 3 we present their most important structural features. From **24′** we obtained two different modifications (α and β). As Table 3 demonstrates, the C_2Co_2 core is much more distorted due to the chalcogen ligand — the Co−CC distances vary between 191 and 199 pm. The smaller $X-C{\equiv}C_{coord.}$ angles might be caused by the formation of a chelate complex. In Figure 5 the averaged structural parameters of a dithia-substituted $C_2Co_2(CO)_6$ core (type **A**) are compared with a dithia-substituted $C_2Co_2(CO)_5$ core with a further (pseudoaxial) sulfur ligand (type **B**). The averaged parameters are based on data of the four systems of type **A** and five systems of type **B**. Whereas the Co−CC distance in type **A** shows a value of 196 pm, the coordinating sulfur ligand strongly disfavors the former C_{2v} symmetry. As a result the Co−CC bond lengths vary between 192 and 198 pm. The changed electron density is also responsible for the different lengths of the OC−Co bonds indicating a significant change in metal−ligand d → π* backbonding. To the best of our knowledge, there is only one crystallographically characterized example in the literature showing a pentacarbonyldicobalt complex coordinated by a divalent sulfur atom in an intramolecular manner.[15] Selenium as a coordinating moiety and a doubly bridged bis(pentacarbonyldicobalt) complex were, until now, unknown.

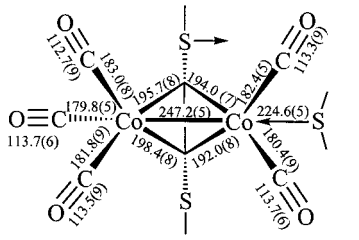
Table 3. Selected transannular distances between the former triple bonds, bond lengths and bond angles of the compounds **24′α**, **24′β**, **25′** and **29′**

Compd.	Distance d [a] Co_2C_2 [pm]	Torsion angle β [a] Co_2C_2 [°]	Bond lengths [pm]					Angles [°] $X-C{\equiv}C_{coord.}$ [b]
			$C{\equiv}C_{coord.}$	Co−CO	CoC≡O	Co−CC	X−Co	
24′α [c]	361.1	0	135.8	180.0−182.6	113.3−114.7	190.9−199.2	224.6	135.2−139.6
	361.5	0.8	133.7−134.7	178.2−184.2	110.8−114.9	191.4−198.3	224.3−224.8	133.0−139.2
24′β	357.7	0	136.3	179.7−182.9	112.2−113.7	192.2−197.8	224.8	134.4−139.3
25′	365.4	0	135.7	178.9−183.3	112.6−113.4	192.9−199.2	225.1	135.4−139.9
29′	374.8	0	135.1	179.4−182.2	113.1−113.7	192.7−198.0	236.4	134.4−139.3

[a] See Figure 3 for definition of distance d and torsion angle β. [b] X = S or Se. [c] 1.5 independent molecules in the asymmetric unit.



A



B

Figure 5. Comparison of the bond lengths (with standard deviation) in dithia-substituted hexacarbonyldicobalt complexes (type **A**) and pentacarbonyldicobalt complexes (type **B**); the averaged values refer to data of four systems of type **A** and five systems of type **B**

Conclusions

Our in-depth study of the structural features of sila-, thia- and selena-substituted bis(hexacarbonyldicobalt) complexes has revealed that the molecular solid-state structures of these complexes are the result of an interplay between the bulky $C_2Co_2(CO)_6$ moieties and the conformational needs of the tethers. In many cases the tethers adopt conformations that minimize the empty space between the bulky units. Our search to find evidence for cobalt−chalcogen interactions proved to be successful. Cobalt−heteroatom interactions, especially cobalt−sulfur interactions, are thought to play an important role in Pauson−Khand reactions. Two tetrathia- as well as one tetraselenacyclodiyne afforded bis(pentacarbonyldicobalt) complexes with coordinating divalent chalcogen atoms occupying the sixth coordination site of the C_2Co_2 core.

Experimental Section

General Methods: Moisture- and oxygen-sensitive reactions were conducted in oven-dried glassware under argon using dried solvents. Melting points are uncorrected. Due to the black color of several compounds some of the melting points (**23**−**25** and **28**) were determined by differential scanning calorimetry (DSC). Materials used for column chromatography: Neutral alumina (Merck), Celite (Fluka). ^{1}H NMR and ^{13}C NMR: 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 residual solvent as internal standard. IR: Bruker Vector 22 FT-IR. UV/Vis: Hewlett Packard 8452 A spectrometer. MS (FAB+, EI+): High resolution: Jeol JMS-700. FD mass spectra refer to data from a Jeol JMS-700 instrument and were measured from dichloromethane solutions (c = 3−5 mg·mL^{-1}) of the corresponding complexes. For FD mass spectra no high resolution is possible. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. The starting materials were prepared according to literature methods.[16−19]

General Procedure for the Preparation of the Bis(hexacarbonyldicobalt) Complexes from Cyclic Diynes: The cyclic diyne was dissolved in 30−50 mL of dichloromethane and the octacarbonyldicobalt was added in one portion. The reaction flask was wrapped with aluminium foil to exclude daylight. The resulting dark mixture was stirred at room temperature in the dark for 1−2 h. The crude mixture was filtered and stored at −78 °C overnight. In many cases crystals of the pure product could be obtained. In other cases, the crude product was absorbed on Celite and purified by column chromatography on neutral alumina (grade III), eluting with mixtures of light petroleum/diethyl ether.

(μ:μ-5,5,6,6-Tetramethyl-5,6-disila-1-thiacyclonona-3,7-diyne)bis(hexacarbonyldicobalt) (13): Starting materials: 5,5,6,6-tetramethyl-5,6-disila-1-thiacyclonona-3,7-diyne (250 mg, 1.10 mmol) and octacarbonyldicobalt (840 mg, 2.40 mmol). Yield: 727 mg (83%). Red solid, m.p. 104 °C (dec). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.43 (br., 12 H, CH_3), 3.87 (br., 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 1.4 (CH_3), 40.1 (CH_2), 78.9 (C), 110.4 (C), 200.9 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2085, 2052, 2023, 1577, 1405 cm^{-1}. HRMS (FAB+): calcd. ($C_{22}H_{17}Co_4O_{12}SSi_2$) 796.7307; found 796.7300.

(μ:μ-1,1,3,3,6,6,8,8-Octamethyl-1,3,6,8-tetrasilacyclodeca-4,9-diyne)bis(hexacarbonyldicobalt) (14): Starting materials: 1,1,3,3,6,6,8,8-octamethyl-1,3,6,8-tetrasilacyclodeca-4,9-diyne (50 mg, 0.16 mmol) and octacarbonyldicobalt (220 mg, 0.65 mmol). Yield: 120 mg (85%). Dark red solid, m.p. 124 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.38 (br., 28 H, CH_3/CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 3.7 (CH_3), 5.8 (CH_2), 93.9 (C), 200.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2957, 2083, 2045, 2017, 1629, 1534, 1408 cm^{-1}. MS (FD+): m/z = 860 [M$^+$]. $C_{26}H_{28}Co_4O_{12}Si_4$ (880.6): calcd. C 35.46, H 3.21; found C 35.58, H 3.50.

(μ:μ-1,4-Dithiacyclotrideca-5,12-diyne)bis(hexacarbonyldicobalt) (15): Starting materials: 1,4-dithiacyclotrideca-5,12-diyne (210 mg, 1.00 mmol) and octacarbonyldicobalt (752 mg, 2.20 mmol). Yield: 590 mg (75%). Red solid, m.p. > 200 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72 (m, 4 H, CH_2), 3.10 (m, 10 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.1 (CH_2), 30.2 (CH_2), 33.9 (CH_2), 36.1 (CH_2), 91.6 (C), 100.4 (C), 199.0 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2936, 2089, 2050, 2023, 1625, 1432 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 nm (4.55), 292 (4.41), 314 (4.29), 360 (3.68), 374 (3.61), 408 (3.41). MS (FD+): m/z = 782 [M$^+$]. $C_{23}H_{14}Co_4O_{12}S_2$ (782.2): calcd. C 35.32, H 1.80, S 8.20; found C 35.20, H 1.95, S 8.08.

(μ:μ-1,5-Dithiacyclotetradeca-6,13-diyne)bis(hexacarbonyldicobalt) (16): Starting materials: 1,5-dithiacyclotetradeca-6,13-diyne (224 mg, 1.00 mmol) and octacarbonyldicobalt (752 mg, 2.20 mmol). Yield: 610 mg (77%). Red solid, m.p. 125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (m, 8 H, CH_2), 1.92 (m, 4 H, CH_2), 3.21 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.8 (CH_2), 32.0 (CH_2), 35.6 (CH_2), 35.8 (CH_2), 36.9 (CH_2), 94.2 (C), 102.3 (C), 199.2 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2936, 2088, 2050, 2022, 1625, 1432 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 nm (4.35), 318 (4.10), 352 (4.69). MS (FD+): m/z = 796 [M$^+$]. $C_{24}H_{16}Co_4O_{12}S_2 \cdot 0.5CH_2Cl_2$ (838.7): calcd. C 35.84, H 2.09; found C 35.68, H 2.14.

(μ:μ-1,6-Dithiacyclopentadeca-7,14-diyne)bis(hexacarbonyldicobalt) (17): Starting materials: 1,6-dithiacyclopentadeca-7,14-diyne

(238 mg, 1.00 mmol) and octacarbonyldicobalt (752 mg, 2.20 mmol). Yield: 560 mg (69%). Red solid, m.p. 77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (m, 10 H, CH_2), 1.92 (m, 4 H, CH_2), 3.14 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 (CH_2), 28.8 (CH_2), 31.2 (CH_2), 33.2 (CH_2), 35.2 (CH_2), 94.7 (C), 101.7 (C), 199.4 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2929, 2086, 2047, 2019, 1628 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 294 nm (4.14), 324 (3.99). HRMS (EI+, 70 eV): calcd. ($C_{25}H_{18}Co_4O_{12}S_2$) 809.7568; found 809.7505.

(μ:μ-1,5-Dithiacyclohexadeca-6,15-diyne)bis(hexacarbonyldicobalt) (18): Starting materials: 1,5-dithiacyclohexadeca-6,15-diyne (190 mg, 0.75 mmol) and octacarbonyldicobalt (567 mg, 1.66 mmol). Yield: 380 mg (62%). Red solid, m.p. 87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (m, 12 H, CH_2), 2.10 (m, 4 H, CH_2), 3.14 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.7 (CH_2), 28.7 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 35.8 (CH_2), 96.2 (C), 103.1 (C), 199.4 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2927, 2087, 2048, 2020, 1628 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 258 nm (4.53), 294 (4.37), 320 (4.24). HRMS (EI+, 70 eV): calcd. ($C_{26}H_{20}Co_4O_{12}S_2$) 823.7724; found 823.7687.

(μ:μ-1,6-Dithiacycloheptadeca-7,16-diyne)bis(hexacarbonyldicobalt) (19): Starting materials: 1,6-dithiacycloheptadeca-7,16-diyne (266 mg, 1.00 mmol) and octacarbonyldicobalt (752 mg, 2.20 mmol). Yield: 590 mg (82%). Red solid, m.p. 94 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (m, 6 H, CH_2), 1.90 (m, 8 H, CH_2), 3.00 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.8 (CH_2), 29.0 (CH_2), 31.6 (CH_2), 31.8 (CH_2), 35.0 (CH_2), 37.6 (CH_2), 97.4 (C), 103.3 (C), 199.4 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2931, 2086, 2048, 2017, 1631 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 262 nm (4.36), 288 (4.24), 318 (4.12), 406 (3.30). HRMS (EI+, 70 eV): calcd. ($C_{27}H_{23}Co_4O_{12}S_2$) 838.7959; found 838.7913.

(μ:μ-1,7-Dithiacyclooctadeca-8,17-diyne)bis(hexacarbonyldicobalt) (20): Starting materials: 1,7-dithiacyclooctadeca-8,17-diyne (281 mg, 1.00 mmol) and octacarbonyldicobalt (752 mg, 2.20 mmol). Yield: 670 mg (79%). Red solid, m.p. 115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (m, 8 H, CH_2), 1.93 (m, 8 H, CH_2), 2.05 (m, 4 H, CH_2), 2.91 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.4 (CH_2), 27.3 (CH_2), 29.2 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.3 (CH_2), 37.2 (CH_2), 99.0 (C), 103.7 (C), 200.2 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2932, 2086, 2046, 2018, 1628, 1338 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 262 nm (4.27), 294 (4.13), 324 (4.03). MS (FD+): *m*/*z* = 852 [M$^+$]. $C_{28}H_{24}Co_4O_{12}S_2$ (852.4): calcd. C 39.46, H 2.84, S 7.52; found C 39.53, H 3.00, S 7.55.

(μ:μ-1,4-Diselenacyclotrideca-5,12-diyne)bis(hexacarbonyldicobalt) (21): Starting materials: 1,4-diselenacyclotrideca-5,12-diyne (306 mg, 1.00 mmol) and octacarbonyldicobalt (752 mg, 2.20 mmol). Yield: 540 mg (62%). Red solid, m.p. > 230 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80 (m, 6 H, CH_2), 3.12 (m, 4 H, CH_2), 3.44 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.3 (CH_2), 28.5 (CH_2), 30.4 (CH_2), 34.2 (CH_2), 80.1 (C), 102.2 (C), 199.1 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2936, 2088, 2050, 2018, 1625, 1154 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 270 nm (4.49), 316 (4.26), 366 (3.52), 424 (3.16). MS (FD+): *m*/*z* = 876 [M$^+$]. $C_{23}H_{14}Co_4O_{12}Se_2$ (876.0): calcd. C 31.53, H 1.61; found C 31.64, H 1.74.

(μ:μ-1,7-Diselenacyclooctadeca-8,17-diyne)bis(hexacarbonyldicobalt) (22): Starting materials: 1,7-diselenacyclooctadeca-8,17-diyne (374 mg, 1.00 mmol) and octacarbonyldicobalt (752 mg, 2.20 mmol). Yield: 590 mg (62%). Red solid, m.p. 105 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.80 (m, 16 H, CH_2), 3.00 (m, 8 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.9 (CH_2), 28.3 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 31.4 (CH_2), 32.0 (CH_2), 35.7 (CH_2), 86.5 (C), 104.6 (C), 199.8 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2932, 2086, 2047, 2019, 1628, 1430 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 260 nm (4.47), 302 (4.27), 324 (4.23). HRMS (EI+, 70 eV): calcd. ($C_{28}H_{24}Co_4O_{12}Se_2$) 946.6857; found 946.6910.

(μ:μ-1,4,7,10-Tetrathiacyclododeca-2,8-diyne)bis(hexacarbonyldicobalt) (23): Starting materials: 1,4,7,10-tetrathiacyclododeca-2,8-diyne (150 mg, 0.64 mmol) and octacarbonyldicobalt (438 mg, 1.28 mmol). Yield: 293 mg (56%). Black solid, m.p. 173 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.26 (s, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.3 (CH_2), 96.3 (C), 198.0 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2092, 2058, 2026, 1627, 1258, 875 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε): = 264 nm (4.57), 426 (3.48). MS (FD+): *m*/*z* = 804 [M$^+$]. $C_{20}H_8Co_4O_{12}S_4$ (804.3): calcd. C 29.87, H 1.00, S 15.95; found C 29.82, H 1.15, S 15.68.

(μ:μ-1,4,7,10-Tetrathiacyclotrideca-2,8-diyne)bis(hexacarbonyldicobalt) (24): Starting materials: 1,4,7,10-tetrathiacyclotrideca-2,8-diyne (138 mg, 0.61 mmol) and octacarbonyldicobalt (400 mg, 1.17 mmol). Yield: 173 mg (35%). Black solid, m.p. 172 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (br., 2 H, CH_2), 3.17 (s, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.3 (CH_2), 35.5 (CH_2), 36.6 (CH_2), 94.5 (C), 97.2 (C), 198.3 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2926, 2091, 2057, 2027, 1699, 1627, 1409, 874 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 nm (4.60), 318 (4.29), 436 (3.60). MS (FD+): *m*/*z* = 818 [M$^+$]. $C_{21}H_{10}Co_4O_{12}S_4$ (818.3): calcd. C 30.82, H 1.23; found C 30.41, H 1.54.

(μ:μ-1,4,8,11-Tetrathiacyclotetradeca-2,9-diyne)bis(hexacarbonyldicobalt) (25): Starting materials: 1,4,8,11-tetrathiacyclotetradeca-2,9-diyne (150 mg, 0.58 mmol) and octacarbonyldicobalt (400 mg, 1.16 mmol). Yield: 221 mg (46%). Black solid, m.p. 165 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (br., 4 H, CH_2), 3.15 (s, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.1 (CH_2), 36.1 (CH_2), 97.2 (C), 198.5 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2920, 2091, 2054, 2027, 1628, 1437, 876 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 276 nm (4.48), 320 (4.30), 422 (3.62). MS (FD+): *m*/*z* = 832 [M$^+$], 804 (M$^+$ − CO), 776 [M$^+$ − 2CO]. $C_{22}H_{12}Co_4O_{12}S_4$ (832.3): calcd. C 31.75, H 1.45; found C 31.37, H 1.80.

(μ:μ-1,4,9,12-Tetrathiacyclohexadeca-2,10-diyne)bis(hexacarbonyldicobalt) (26): Starting materials: 1,4,9,12-tetrathiacyclohexadeca-2,10-diyne (180 mg, 0.62 mmol) and octacarbonyldicobalt (430 mg, 1.26 mmol). Yield: 299 mg (56%). Black solid, m.p. 153 °C (dec). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.98 (br., 8 H, CH_2), 2.92 (br., 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 30.3 (CH_2), 37.6 (CH_2), 98.7 (C), 206.1 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2934, 2093, 2040, 2013, 1636, 1416, 876 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 274 nm (4.43), 314 (4.30), 326 (4.25), 474 (3.73). MS (FD+): *m*/*z* = 860 [M$^+$]. $C_{24}H_{16}Co_4O_{12}S_4$ (860.4): calcd. C 33.50, H 1.87, S 14.91; found C 33.26, H 2.05, S 14.81.

(μ:μ-1,4,10,13-Tetrathiacyclooctadeca-2,11-diyne)bis(hexacarbonyldicobalt) (27): Starting materials: 1,4,10,13-tetrathiacyclooctadeca-2,11-diyne (180 mg, 0.57 mmol) and octacarbonyldicobalt (430 mg, 1.26 mmol). Yield: 235 mg (46%). Dark red solid, m.p. 168 °C (dec). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.67 (m, 4 H, CH_2), 1.89 (m, 8 H, CH_2), 2.97 (m, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 27.7 (CH_2), 29.7 (CH_2), 37.8 (CH_2), 98.9 (C), 199.2 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2089, 2051, 2028, 1636, 1434, 869 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 278 nm (4.48), 322 (4.33), 474 (3.52). MS (FD+): *m*/*z* = 888 [M$^+$]. $C_{26}H_{20}Co_4O_{12}S_4$ (888.4): calcd. C 35.15, H 2.27, S 14.44; found C 34.84, H 2.52, S 14.44.

Table 4. Crystallographic data and details of the refinement procedure for **13**−**16** and **19**−**20**

	13	**14**	**15**	**16**	**19**	**20**
Empirical formula	$C_{22}H_{16}Co_4O_{12}SSi_2$	$C_{26}H_{28}Co_4O_{12}Si_4$	$C_{23}H_{14}Co_4O_{12}S_2$	$C_{24}H_{16}Co_4O_{12}S_2$	$C_{27}H_{22}Co_4O_{12}S_2$	$C_{28}H_{24}Co_4O_{12}S_2$
Formula mass [g/mol]	796.31	880.56	782.18	796.21	838.29	852.31
Crystal size [mm]	0.36 × 0.18 × 0.04	0.36 × 0.24 × 0.18	0.33 × 0.18 × 0.10	0.34 × 0.18 × 0.05	0.26 × 0.24 × 0.24	0.37 × 0.30 × 0.11
Crystal colour	red	red	red	red	red	red
Crystal shape	polyhedron	polyhedron	polyhedron	polyhedron	polyhedron	irregular
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	*C*2/*c*	$P2_1/n$	*C*2/*c*	*P*bca	*P*bca	$P2_1/c$
a [Å]	24.6657(4)	10.0976(1)	15.5282(3)	15.9396(1)	23.2823(2)	12.3900(2)
b [Å]	8.1164(1)	17.7572(2)	14.5913(1)	13.6356(2)	10.3609(1)	10.5220(1)
c [Å]	31.8073(5)	10.4170(1)	14.9780(2)	27.6465(4)	27.3080(1)	26.7455(3)
α [°]	90	90	90	90	90	90
β [°]	102.97(1)	96.821(1)	118.154(1)	90	90	101.023(1)
γ [°]	90	90	90	90	90	90
V [Å^3]	6205.36(16)	1854.60(3)	2992.13(7)	6008.86(13)	6587.39(9)	3422.42(7)
$D_{calcd.}$ [g/cm^3]	1.71	1.58	1.74	1.76	1.69	1.65
Z	8	2	4	8	8	4
h_{min}/h_{max}	−29/29	−13/13	−20/20	−20/20	−30/29	−15/16
k_{min}/k_{max}	−9/9	−23/23	−18/18	−17/17	−13/13	−13/13
l_{min}/l_{max}	−36/38	−13/13	−19/19	−35/35	−35/35	−34/34
μ [mm^{-1}]	2.30	1.94	2.38	2.37	2.16	2.08
$T_{min.}/T_{max.}$	0.73/0.92	0.59/0.75	0.51/0.80	0.50/0.89	0.60/0.62	0.51/0.80
Refl. collected	22172	18838	15393	59728	64315	33775
Refl. unique	5371	4221	3431	6885	7552	7785
Refl. observed	4333	3822	2331	4101	5594	5871
Parameter	374	212	226	398	406	415
R(*F*)	0.028	0.021	0.039	0.037	0.027	0.090
$R_w(F^2)$	0.062	0.053	0.087	0.057	0.055	0.231
S (Gof) on F^2	1.16	1.06	1.03	0.99	1.04	1.20
$(\Delta\rho)_{max}$ [e·Å^{-3}]	0.41	0.35	0.59	0.47	0.34	1.91
$(\Delta\rho)_{min}$ [e·Å^{-3}]	−0.34	−0.39	−0.39	−0.53	−0.33	−1.02

Table 5. Crystallographic data and details of the refinement procedure for **21**−**25′**

	21	**22**	**23**	**24′α**	**24′β**	**25′**
Empirical formula	$C_{23}H_{14}O_{12}Se_2Co_4$	$C_{28.5}H_{25}O_{12}Se_2Co_4Cl$	$C_{20}H_8O_{12}S_4Co_4$	$C_{19}H_{10}O_{10}S_4Co_4$	$C_{19}H_{10}O_{10}S_4Co_4$	$C_{20}H_{12}O_{10}S_4Co_4$
Formula mass [g/mol]	875.98	988.57	804.26	762.27	762.27	776.30
Crystal size [mm]	0.37 × 0.34 × 0.29	0.24 × 0.13 × 0.02	0.11 × 0.10 × 0.04	0.08 × 0.07 × 0.05	0.24 × 0.06 × 0.02	0.40 × 0.22 × 0.01
Crystal colour	red	red	black	black	brown	black
Crystal shape	irregular	irregular	plate	irregular	plate	irregular
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1/c$	*C*2/*c*	$P2_1/c$	*Pbca*	$P2_1/n$	*P*bca
a [Å]	14.9883(2)	57.887(8)	14.023(2)	13.3108(11)	7.485(1)	13.1604(3)
b [Å]	13.9693(2)	7.713(1)	7.8014(9)	12.9832(11)	14.779(2)	13.1567(3)
c [Å]	15.6865(1)	16.260(2)	13.218(2)	14.6488(13)	34.588(5)	15.1823(3)
α [°]	90	90	90	90	90	90
β [°]	111.454(1)	105.369(3)	105.006(2)	90	91.293(3)	90
γ [°]	90	90	90	90	90	90
V [Å^3]	3056.81(6)	7000(2)	1396.7(3)	2531.6(4)	3825.2(9)	2628.78(10)
$D_{calcd.}$ [g/cm^3]	1.90	1.88	1.91	2.00	1.99	1.96
Z	4	8	2	4	6	4
h_{min}/h_{max}	−19/19	−52/49	−17/18	−10/17	−9/9	−15/15
k_{min}/k_{max}	−18/18	−7/7	−7/10	−17/17	−19/11	−15/15
l_{min}/l_{max}	−20/20	−9/14	−17/17	−19/19	−46/42	−17/17
μ [mm^{-1}]	4.57	4.08	2.69	2.96	2.94	2.85
$T_{min.}/T_{max.}$	0.28/0.35	0.44/0.92	0.76/0.92	0.80/0.87	0.54/0.94	0.86/1.00
Refl. collected	30553	8346	9908	17625	26709	19496
Refl. unique	7008	2745	3471	3156	9468	2085
Refl. observed	5236	2202	3171	3009	4877	1545
Parameter	370	289	197	189	514	172
R(*F*)	0.032	0.057	0.034	0.054	0.054	0.026
$R_w(F^2)$	0.067	0.136	0.081	0.104	0.092	0.052
S (Gof) on F^2	1.01	1.04	1.09	1.34	0.86	1.02
$(\Delta\rho)_{max}$ [e·Å^{-3}]	1.55	0.84	1.13	0.62	1.13	0.33
$(\Delta\rho)_{min}$ [e·Å^{-3}]	−1.06	−0.73	−0.37	−0.68	−1.30	−0.31

Table 6. Crystallographic data and details of the refinement procedure for **26**−**30**

	26	**27**	**28**	**29′**	**30**
Empirical formula	$C_{24}H_{16}O_{12}S_4Co_4$	$C_{26}H_{20}O_{12}S_4Co_4$	$C_{28}H_{24}O_{12}S_4Co_4$	$C_{19}H_{10}O_{10}Se_4Co_4$	$C_{24}H_{16}O_{12}Se_4Co_4$
Formula mass [g/mol]	860.37	888.42	916.48	949.85	1047.95
Crystal size [mm]	0.15 × 0.12 × 0.07	0.35 × 0.05 × 0.04	0.40 × 0.29 × 0.03	0.22 × 0.16 × 0.02	0.09 × 0.06 × 0.03
Crystal colour	black	black	black	black	dark red
Crystal shape	plate	polyhedron	plate	polyhedron	irregular
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Pbca$	$P2_1/n$
a [Å]	14.195(3)	7.9853(2)	11.6804(4)	13.3071(1)	14.08(1)
b [Å]	7.7600(2)	14.8038(3)	10.7416(4)	13.0699(2)	7.849(6)
c [Å]	15.668(3)	14.1503(3)	15.3996(6)	15.5527(1)	16.21(1)
α [°]	90	90	90	90	90
β [°]	109.752(4)	93.360(1)	111.015(1)	90	115.44(1)
γ [°]	90	90	90	90	90
V [Å^3]	1624.3(6)	1669.87(6)	1803.62(12)	2704.96(5)	1617(2)
$D_{calcd.}$ [g/cm^3]	1.76	1.77	1.69	2.33	2.15
Z	2	2	2	4	2
h_{min}/h_{max}	−18/18	−9/9	−15/15	−17/17	−18/17
k_{min}/k_{max}	−9/10	−18/18	−13/13	−16/16	−10/7
l_{min}/l_{max}	−20/18	−17/17	−19/19	−20/20	−21/17
μ [mm^{-1}]	2.32	2.26	2.10	7.84	6.58
$T_{max.}/T_{min.}$	0.72/0.85	0.51/0.92	0.49/0.94	0.58/1.00	0.59/0.83
Refl. collected	11295	15733	18132	26329	11595
Refl. unique	4054	3395	4133	3098	4036
Refl. observed	3377	2436	3116	2339	3054
Parameter	247	208	226	181	217
$R(F)$	0.053	0.033	0.028	0.032	0.045
$R_w(F^2)$	0.128	0.062	0.057	0.056	0.089
S (Gof) on F^2	1.08	1.01	1.03	1.12	1.07
$(\Delta\rho)_{max}$ [e·Å^{-3}]	0.73	0.37	0.38	0.75	1.12
$(\Delta\rho)_{min}$ [e·Å^{-3}]	−0.32	−0.36	−0.38	−0.76	−1.95

(μ:μ-1,4,11,14-Tetrathiacycloeicosa-2,12-diyne)bis(hexacarbonyldicobalt) (28): Starting materials: 1,4,11,14-tetrathiacycloeicosa-2,12-diyne (307 mg, 0.89 mmol) and octacarbonyldicobalt (610 mg, 1.78 mmol). Yield: 421 mg (52%). Black solid, m.p. 138 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55 (br., 8 H, CH_2), 1.86 (br., 8 H, CH_2), 2.95 (br., 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.1 (CH_2), 29.2 (CH_2), 37.6 (CH_2), 99.3 (C), 198.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2931, 2857, 2087, 2049, 2026, 1637, 1458, 870 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 280 nm (4.29), 318 (4.15), 472 (3.38), 556 (3.02). MS (FD+): m/z = 916 [M$^+$]. $C_{28}H_{24}Co_4O_{12}S_4$ (916.5): calcd. C 36.70, H 2.64, S 14.00; found C 36.51, H 2.94, S 13.99.

(μ:μ-1,4,7,10-Tetraselenacyclotrideca-2,8-diyne)bis(pentacarbonyldicobalt) (29′): Starting materials: 1,4,7,10-tetraselenacyclotrideca-2,8-diyne (102 mg, 0.24 mmol) and octacarbonyldicobalt (160 mg, 0.48 mmol). Yield: 143 mg (63%). Black solid, m.p. 144 °C (dec). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.2 (CH_2), 27.3 (CH_2), 28.7 (CH_2), 31.2 (CH_2), 32.9 (CH_2), 208.1 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2056, 2016, 1621, 1404, 803 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [nm] (log ε): 304 (4.25), 348 (4.09), 448 (3.75), 490 (3.58). MS (FD+): m/z = 950 [M$^+$].

(μ:μ-1,4,9,12-Tetraselenacyclohexadeca-2,10-diyne)bis(hexacarbonyldicobalt) (30): Starting materials: 1,4,9,12-tetraselenacyclohexadeca-2,10-diyne (150 mg, 0.32 mmol) and octacarbonyldicobalt (219 mg, 0.64 mmol). Yield: 110 mg (33%). Black solid, m.p. 147 °C (dec). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.05 (br., 8 H, CH_2), 3.02 (br., 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 31.0 (CH_2), 32.4 (CH_2), 105.1 (C), 206.7 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 2929, 2090, 2053, 2037, 2011, 1637, 1413, 1200 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε): 250 nm (4.25), 276 (3.91), 306 (4.04), 482 (3.44). MS (FD+): m/z = 1047 [M$^+$]. $C_{24}H_{16}Co_4O_{12}Se_4$ (1047.9): calcd. C 27.51, H 1.54; found C 26.95, H 1.68.

X-ray Diffraction Analyses: The reflections were collected with Bruker Smart CCD and Bruker APEX diffractometers (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarization effects. Numerical (face indexing for **23**) or empirical absorption corrections were applied using SADABS.[20] The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically (except the carbon atoms of **22**) according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects. In **15** we found disorder between the sulfur atoms and the methylene units by a C_2 axis. In **24′α**, **24′β** (two different modifications of **24′**) and **29′** we found disorder between the ethane and the propane chain by an inversion center. In **16**, **26**, **28** and **30** we found some disorder in the alkane chains, and the minor positions were refined as isotropic only. Structure solution and refinement were carried out with SHELXTL software package.[20] ORTEP drawings were obtained using the ORTEP-3 for Windows program by Farrugia.[21] Tables 4, 5 and 6 contain the crystallographic data and details of the data collection and the refinement procedure. CCDC-223985 to -224001 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].

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft (SFB 623), the Fonds der Chemischen Industrie and the BASF Aktienge-

sellschaft, Ludwigshafen, for financial support. D. B. W. and J. H. S. thank Michela Doria, Mathias Basler, Markus Seitz and Fanny Caroline Liu for preparative assistance. D. B. W. is grateful to the Studienstiftung des deutschen Volkes for a graduate fellowship. We thank Prof. W. Siebert for helpful discussions.

[1] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, *J. Chem. Soc., Chem. Commun.* **1971**, 36.
[2] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, *J. Chem. Soc., Perkin Trans. 1* **1973**, 975−977.
[3] P. L. Pauson, *Tetrahedron* **1985**, *41*, 5855−5860.
[4] [4a] O. Geis, H.-G. Schmalz, *Angew. Chem.* **1998**, *110*, 955−958; *Angew. Chem. Int. Ed.* **1998**, *37*, 911−915. [4b] A. J. Fletcher, S. D. R. Christie, *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657−1668.
[5] [5a] K. M. Brummond, J. L. Kent, *Tetrahedron* **2000**, *56*, 3263−3283. [5b] T. Sugihara, M. Yamaguchi, M. Nishizawa, *Chem. Eur. J.* **2001**, *8*, 1589−1595.
[6] [6a] P. L. Pauson, in *Organometallics in Organic Synthesis* (Eds.: A. de Meijere, H. tom Dieck), Springer, Berlin **1988**, pp. 233−246. [6b] N. E. Schore, in *Comprehensive Organic Synthesis* (Ed.: B. M. Trost), Pergamon, Oxford **1991**, vol. 5, pp. 1037−1062. [6c]N. E. Schore, *Org. React.* **1991**, *40*, 1−90. [6d] N. E. Schore, in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford **1995**, vol. 12, pp. 703−739.
[7] [7a] F. A. Cotton, J. D. Jamerson, B. R. Stults, *J. Am. Chem. Soc.* **1976**, *98*, 1774−1779. [7b] F. Baert, A. Guelzim, J. M. Poblet, R. Wiest, J. Demuynck, M. Benard, *Inorg. Chem.* **1986**, *25*, 1830−1841. [7c] W. G. Sly, *J. Am. Chem. Soc.* **1959**, *81*, 18−20. [7d] N. A. Bailey, R. Mason, *J. Chem. Soc. (A)* **1968**, 1293−1299. [7e] D. Gregson, J. A. K. Howard, *Acta Crystallogr., Sect. C* **1983**, *39*, 1024−1027.
[8] [8a] M. Gruselle, B. Malezieux, J. Vaissermann, H. Amouri, *Organometallics* **1998**, *17*, 2337−2343. [8b] S. J. Doig, R. P. Hughes, R. E. Davis, S. M. Gadol, K. D. Holland, *Organometallics* **1984**, *3*, 1921−1922. [8c] M. Saha, S. Muchmore, D. van der Helm, K. M. Nicholas, *J. Org. Chem.* **1986**, *51*, 1960−1966. [8d] M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1999**, 3719−3728. [8e] M. I. Bruce, B. D. Kelly, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2000**, *604*, 150−156. [8f] X. Verdaguer, A. Moyano, M. A. Pericàs, A. Riera, A. Alvarez-Larena, J.-F. Pinella, *Organometallics* **1999**, *18*, 4275−4285. [8g] M. A. Brook, J. Urschey, M. Stradiotto, *Organometallics* **1998**, *17*, 5342−5346. [8h] A. M. Montana, K. M. Nicholas, M. A. Khan, *J. Org. Chem.* **1988**, *53*, 5193−5201. [8i] J. Ju, B. R. Reddy, M. Khan, K. M. Nicholas, *J. Org. Chem.* **1989**, *54*, 5426−5428. [8j] A. Gelling, J. C. Jefferey, D. C. Povey, M. J. Went, *J. Chem. Soc., Chem. Commun.* **1991**, 349−351. [8k] B. Happ, T. Bartik, C. Zucchi, M. C. Rossi, F. Ghelfi, G. Palyi, G. Varadi, G. Szalontai, I. T. Horvath, A. Chiesi-Villa, C. Guastini, *Organometallics* **1995**, *14*, 809−819. [8l] B. J. Rausch, R. Gleiter, F. Rominger, *J. Chem. Soc., Dalton Trans.* **2002**, 2219−2226. [8m] J. H. Schulte, R. Gleiter, F. Rominger, *Org. Lett.* **2002**, *4*, 3301−3304. [8n] C. M. Gordon, M. Kiszka, I. R. Dunkin, W. J. Kerr, J. S. Scott, J. Gebicki, *J. Organomet. Chem.* **1998**, *554*, 147−154.
[9] [9a] B. J. Rausch, R. Gleiter, *Tetrahedron Lett.* **2001**, *42*, 1651−1653. [9b] F. Antras, M. Ahmar, B. Cazes, *Tetrahedron Lett.* **2001**, *42*, 8157−8160. [9c] M. E. Krafft, R. H. Romero, I. L. Scott, *Synlett* **1995**, 577−578. [9d] X. Verdaguer, J. Vázquez, G. Fuster, V. Bernardes-Génisson, A. E. Greene, A. Moyano, M. A. Pericàs, A. Riera, *J. Org. Chem.* **1998**, *63*, 7037−7052.
[10] [10a] J. G. Donkervoort, A. R. Gordon, C. Johnstone, W. J. Kerr, U. Lange, *Tetrahedron* **1996**, *52*, 7391−7420. [10b] N. Jeong, S. H. Hwang, *Angew. Chem.* **2000**, *112*, 650−652; *Angew. Chem. Int. Ed.* **2000**, *39*, 636−638. [10c] B. J. Rausch, H. Becker, R. Gleiter, F. Rominger, *Synlett* **2002**, 723−726.
[11] [11a] F. Robert, A. Milet, Y. Gimbert, D. Konya, A. E. Greene, *J. Am. Chem. Soc.* **2001**, *123*, 5396−5400. [11b] T. J. M. de Bruin, A. Milet, F. Robert, Y. Gimbert, A. E. Greene, *J. Am. Chem. Soc.* **2001**, *123*, 7184−7185. [11c] M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2001**, *123*, 1703−1708.
[12] [12a] Y. K. Chung, *Coord. Chem. Rev.* **1999**, *188*, 297−341. [12b] K. M. Brummond, J. L. Kent, *Tetrahedron* **2000**, *56*, 3263−3283. [12c] I. Marchueta, E. Montenegro, D. Panov, M. Poch, X. Verdaguer, A. Moyano, M. A. Pericàs, A. Riera, *J. Org. Chem.* **2001**, *66*, 6400−6409. [12d] S. T. Ingate, J. Marco-Contelles, *Org. Prep. Proceed. Int.* **1998**, *30*, 121−143. [12e] M. A. Pericàs, J. Balsells, J. Castro, I. Marchueta, A. Moyano, A. Riera, J. Vázquez, X. Verdaguer, *Pure Appl. Chem.* **2002**, *74*, 167−174.
[13] [13a] M. E. Krafft, J. A. Juliano, I. L. Scott, C. Wright, M. D. McEachin, *J. Am. Chem. Soc.* **1991**, *113*, 1693−1703. [13b] T. Sugihara, M. Yamada, M. Yamaguchi, M. Nishizawa, *Synlett* **1999**, 771−773.
[14] M. E. Krafft, I. L. Scott, R. H. Romero, S. Feibelmannn, C. E. van Pelt, *J. Am. Chem. Soc.* **1993**, *115*, 7199−7207.
[15] J. E. Davies, L. J. Hope-Weeks, M. J. Mays, P. R. Raithby, *Chem. Commun.* **2000**, 1411−1412.
[16] [16a] E. Kloster-Jensen, G. Aamdal Eliassen, *Angew. Chem.* **1985**, *97*, 587−588; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 565−566. [16b] R. Gleiter, J. Classen, B. J. Rausch, T. Oeser, F. Rominger, *J. Organomet. Chem.* **2002**, *641*, 3−8.
[17] C. Benisch, S. Bethke, R. Gleiter, T. Oeser, H. Pritzkow, F. Rominger, *Eur. J. Org. Chem.* **2000**, 2479−2488.
[18] D. B. Werz, R. Gleiter, F. Rominger, *J. Org. Chem.* **2002**, *67*, 4290−4297.
[19] J. H. Schulte, D. B. Werz, F. Rominger, R. Gleiter, *Org. Biomol. Chem.* **2003**, *1*, 2788−2794.
[20] G. M. Sheldrick, Bruker Analytical X-ray Division, Madison, WI, **1997**.
[21] ORTEP-3 for Windows: A Version of ORTEP-III with a Graphical User Interface (GUI): L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Received November 24, 2003
Early View Article
Published Online April 26, 2004

